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Handbook of Waste Biorefinery

Circular Economy of Renewable Energy

Springer

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Preface

We live in a material world, where climate promises have not yet been delivered.

The way we explore raw materials and manage their waste is fundamental to the most diverse aspects of our environmental and economic future. Therefore, if we are to embrace sustainability—minimize environmental impacts and be economically competitive—paradigm changes around waste disposal must be ubiquitous and emerging. That is, actions, as usual, cannot continue. We should begin forthwith.

In fact, in the past, the creation of waste in connection with production and consumption was accepted as a necessary evil. Today, going beyond the perception of waste as a problem to waste as a resource is the main global challenge. For this purpose, it is imperative that we apply the predicted aphorism—"in nature nothing is created, nothing is lost, everything is transformed," and that we transform the residue of our ignorance into economically viable and environmentally sustainable alternatives.

However, this premise has so far been woefully underexplored. As such, new measures should project a much broader network than traditional approaches to waste prevention, reuse, and recycling. Notwithstanding, they should also represent a shift in how we think about sustainability, from a resilient and competitive perspective.

In this road ahead, industry models under biorefinery approaches have been proposed as promising technological avenues and are now becoming proactive in adopting strategies to harness residual biomass. It is through integrative and processing intensifier routes that waste biorefineries generate various products such as food, bioenergy, biochemicals, and biomaterials. However, with significant investment being made in such a transformation, it is indisputable that this transition must be knowledge-based.

Therefore, the handbook you have before you is timely once focuses on gathering and transferring detailed technical-scientific information on key fundamentals, feedstocks, conventional and advanced processing technologies, as well as policy discussions and issues associated with intellectual property and waste biorefinery. In addition, the visions, lessons, and practical experiences of sustainable waste management, through social, environmental, and economic indicators, were also included in order to provide a way of saving our resources, reducing the chances of future failures, speeding up the consolidation process and, therefore, the development of sustainable circular economies in the world.

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Part I
Fundamentals

Chapter 1
Principles, Concepts, and Recent Trends Applied to the Waste Biorefineries

Luciano Jacob Corrêa, Gilson Campani, and Vítor Badiale Furlong

Abstract The concern with global warming currently occupies a prominent place in the international context. As a result, it is necessary to change the global energy matrix to a cleaner, renewable, and sustainable one. The concept of sustainability has been in focus in recent years and is closely linked to the replacement of exhaustible sources by renewable energy sources. In this context, biorefineries play an important role, as they allow the conversion of biomass into bioenergy and bioproducts of commercial interest, in order to find a solution that combines economic viability with environmentally friendly production. Biorefineries have been the subject of study in numerous research, development, and innovation projects in most developed and developing countries. The versatility of waste biorefineries with regard to the products obtained and their different added values makes these facilities economically attractive. However, there are still numerous bottlenecks that must be overcome, which cover technical, scientific, economic, and political issues. At the moment, several studies have been carried out to define the best technologies and products from biomass. All these technological routes must be analyzed from an economic, social, and environmental perspective.

1.1 Waste Biorefineries: Context, Principles, and Importance

Over the last few centuries, humanity has been facing intense population growth and industrialization, which led to an increasing per capita consumption and waste generation. The environment has also been strongly impacted, with the accelerated sea rising and acidification, deforestation, land degradation, climate change, and

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Table 1.1 Circular economy potentials for sustainable development

Economic goals	Environmental goals	Social goals
• Reduced costs with raw materials, energy, emission control, waste management, insurance, and taxes. • Green marketing; • New market opportunities.	• Lower demand for virgin materials and energy inputs. • Reduced wastes and emissions. • Reduced carbon footprint. • Generation of nutrients used by nature.	• New employment opportunities. • Sharing economy. • Increased sense of community, cooperation, and participation.

biodiversity depletion (Souza et al. 2015). This worrisome scenario is clearly unsustainable under the economic, ecological, and social perspectives.

The concept of circular economy (CE) arises as a promising approach to achieve sustainable economic development, and has been promoted by several national governments and business organizations worldwide (Beaulieu et al. 2015; European Commission 2015; Ellen MacArthur Foundation, Deutsche Post Foundation, and McKinsey Center for Business and Environment 2015). In the CE, companies and consumers are encouraged to reuse, remanufacture, and recycle products, as well as to convert end-of-life materials into valuable goods with a minimal release of waste to the environment. Successful CE implementation contributes to the three aspects of sustainable development (economic, ecological, and social), according to the CE potentials summarized in Table 1.1 (Korhonen et al. 2018).

Green chemistry (GC), defined as the design of chemical products and processes with minimal use and generation of hazardous substances (Anastas and Lankey 2000), is also imperative to promote sustainable development. The GC principles are based on the following aims (Clark et al. 2009): (i) maximum conversion of reactants into products, (ii) minimum waste generation, (iii) use and production of non-hazardous raw materials and products, (iv) safer and more efficient processes, and (v) use of renewable feedstocks. This area has been driving promising opportunities for process innovation regarding the implementation of clean technologies, product substitution, and the use of renewable feedstocks for the production of energy, chemicals, and materials (Pfaltzgraff and Clark 2014).

The use of renewable feedstocks, such as biomass from living organisms (plants, animals, and microorganisms), is one of the cornerstones for both CE and GC approaches. Biomass is a carbon resource that can be renewed in a time interval acceptable to its consumption (up to a few decades). Fossil resources are otherwise finite and present higher net emission of CO_2 in their derived product life cycles, as the carbon is not fixated in a reasonable timescale (see Fig. 1.1). The global market for bio-based chemicals was valued at US$ 59 billion in 2018, with an expected compound annual growth rate (CAGR) of 10% during 2019–2025 (Market Research Future 2021). However, the majority of organic chemicals are still derived from fossil resources (85% fossil-based, 10% bio-based, and 5% by recycling), even though most of such products could technically be substituted by their bio-based

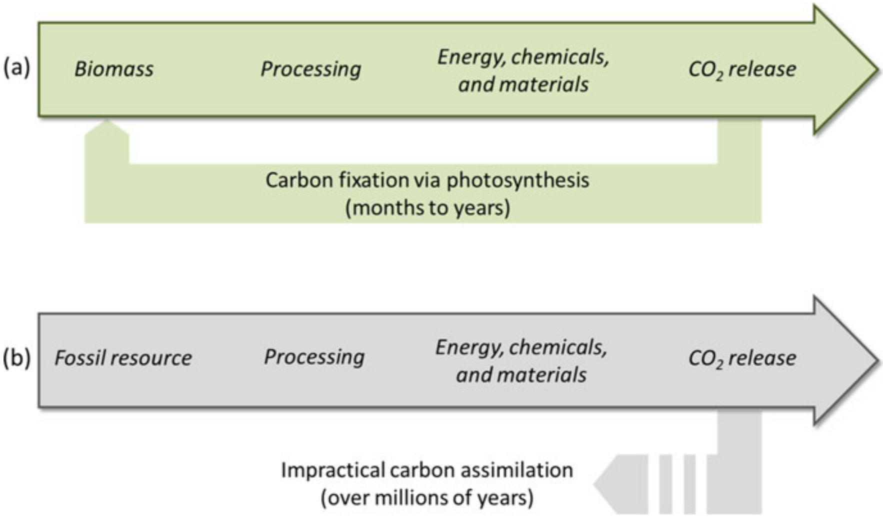

Fig. 1.1 Production cycles based on (**a**) biomass and (**b**) fossil resources

counterparts (Carus et al. 2020; Jong et al. 2020; Kähler et al. 2021). These facts reveal the increasing economic importance and the vast potential for biomass as an alternative feedstock to reduce the dependence on non-renewable resources.

Biomass feedstocks vary from wastes (industrial, agricultural, and domestic residues) to the more expensive dedicated crops (e.g., sugar, starch, and oil crops). Regarding their utilization, there is a competition to produce energy (biofuels, electricity, and heat), chemicals (amino acids, organic acids, antibiotics, vitamins, etc.), and materials (paper, cotton, fertilizers, polymers, etc.), besides food and feed (Ferreira 2017). This issue can be addressed by the integrated processing of different biomass feedstocks into products through bio-based industries, also known as biorefineries. A general definition for biorefineries has been devised by the International Energy Agency (IEA Bioenergy Task 42) (Jong et al. 2020): "biorefinery is the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat)." Therefore, analog to the oil refinery, biorefinery also produces energy and chemicals, but with a major difference: the use of renewable feedstocks, while the former is based on fossil resources (oil, gas, and coal).

Biorefineries must be designed considering the local feedstock availability, as well as sustainable technologies to ensure the maximal plant efficiency: ideally every output must have a use or value (Pfaltzgraff and Clark 2014). In this context, the use of waste-derived feedstocks is of great importance for several reasons: negative-valued biomass (savings with residues management), closed-loop approach (addressing the CE), and lower demand for fresh materials with reduced environmental impact by feedstock industries (i.e., reduced water and land usage, greenhouse gas footprint, and loss of biodiversity) (Grigg and Read 2001; Mohan et al.

2016). Waste biorefineries thus promote a sustainable bio-based circular economy (or circular bioeconomy), instead of the linear and unsustainable economy based on taking, making, and disposing (Carus and Dammer 2018; Leong et al. 2021).

Biorefineries can be classified based on the used feedstock or processing technology. For instance, there are lignocellulosic (cellulose-containing biomass and wastes), whole crop (grain and/or straw portions of a crop), and marine (marine biomass) biorefineries, as well as biochemical (aerobic/anaerobic digestion, fermentation, and enzymatic processes), chemical (esterification, hydrolysis, catalytic processes, etc.), and thermochemical (combustion, gasification, pyrolysis, among others) biorefineries (Kamm and Kamm 2004; van Ree and Annevelink 2007). In the case of multiple feedstocks and processes, the plant may be designated as an advanced biorefinery (Ferreira 2017). This generic classification is simple but presents some flaws, such as the lack of specificity (not taking into consideration the intermediates, products, and other details), ambiguity (a biorefinery may present different classifications), and the problem to define biorefineries with multiple feedstocks and/or processes.

Another classification that has been adopted relies on four features of the biorefinery concept: feedstocks (from residues to dedicated crops), platforms (core intermediates, such as C5–C6 carbohydrates, syngas, lignin, pyrolysis oil), products (biofuels, chemicals, materials, etc.), and processing technologies (chemical, biochemical, thermochemical, and mechanical processes) (Jong et al. 2020). For classification, the biorefinery is first named according to the number of platforms, marketable products, feedstocks, and, if necessary, the processes—e.g., number of platform (*platforms*) biorefinery for *products* from *feedstocks*. Then, a table is set up with the biorefinery's main features (name, platforms, products, feedstocks, and processes) (Cherubini et al. 2009). This classification procedure is preferred due to its flexibility and accuracy to identify multiple aspects of the biorefinery systems. A classification example is presented in Table 1.2 for a biorefinery that converts municipal solid waste into ethanol and methanol based on the syngas platform (Enerkem 2021).

Biorefineries may be at different phases of development according to their degree of complexity and flexibility. Particularly, they may be subdivided into biorefineries of phases I, II, and III (Kamm and Kamm 2004). Phase I biorefineries, the simplest ones, are based on single feedstock, with fixed processes and no product diversification—e.g., one-platform (oil) biorefinery for biodiesel from oil crops (soybean). Phase II biorefineries also convert one feedstock, but using flexible processes and targeting different products, depending on the demand—e.g., one-platform (C6 sugar) biorefinery for bioethanol, starch, and feed from starch crops (corn).

Table 1.2 Classification of a selected waste biorefinery (Enerkem 2021)

Name	Platforms	Products	Feedstock	Processes
One-platform (syngas) biorefinery for methanol and ethanol from municipal solid waste	Syngas	Ethanol and methanol	Municipal solid waste	Separation, gasification, and catalytic processes

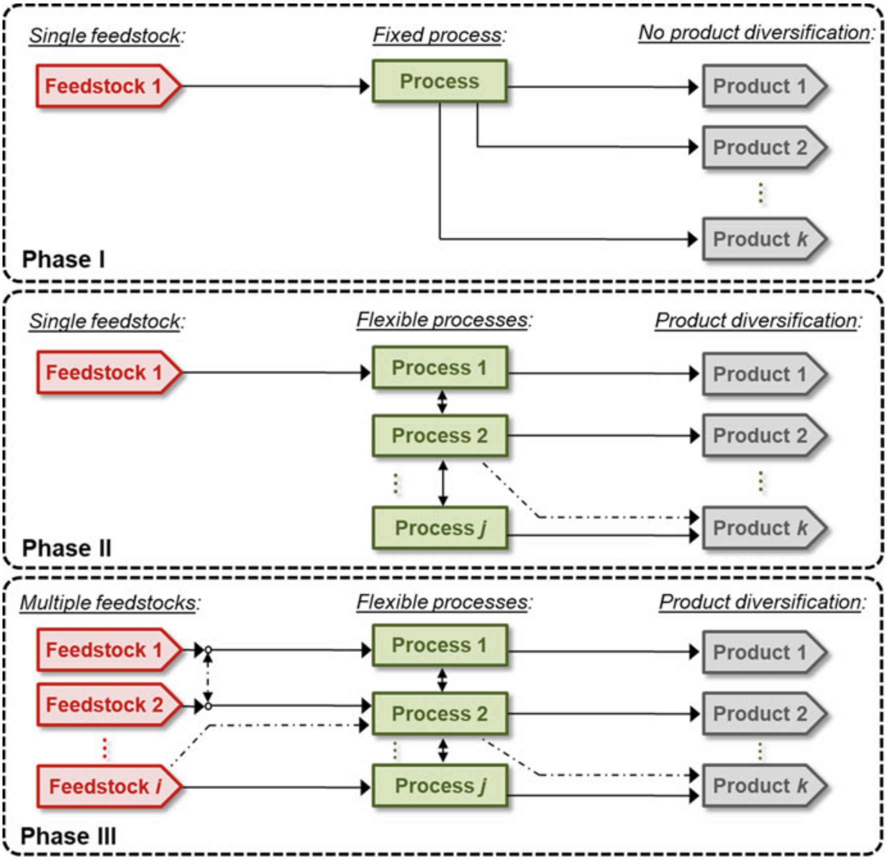

Fig. 1.2 Phases of biorefineries development

Phase III biorefineries, in turn, are product-driven, presenting highly integrated and flexible processes to convert multiple feedstocks (switching between or blending them) into a diverse portfolio of products—e.g., four-platform (C6 and C5 sugars, lignin, and syngas) for biofuels, chemicals, feed, electricity, and heat from lignocellulosic crops and residues. These industries are the most complex and advanced, in agreement on the biorefinery concept in its broadest extension. Figure 1.2 shows a schematic overview of the three biorefinery phases along with their main characteristics.

1.2 Feedstocks, Platforms, Products, and Processes

Within the International Energy Agency (IEA Bioenergy Task 42) (Jong et al. 2020) a biorefinery classification method was developed. This classification approach is based on four main characteristics, which are able to classify and describe a

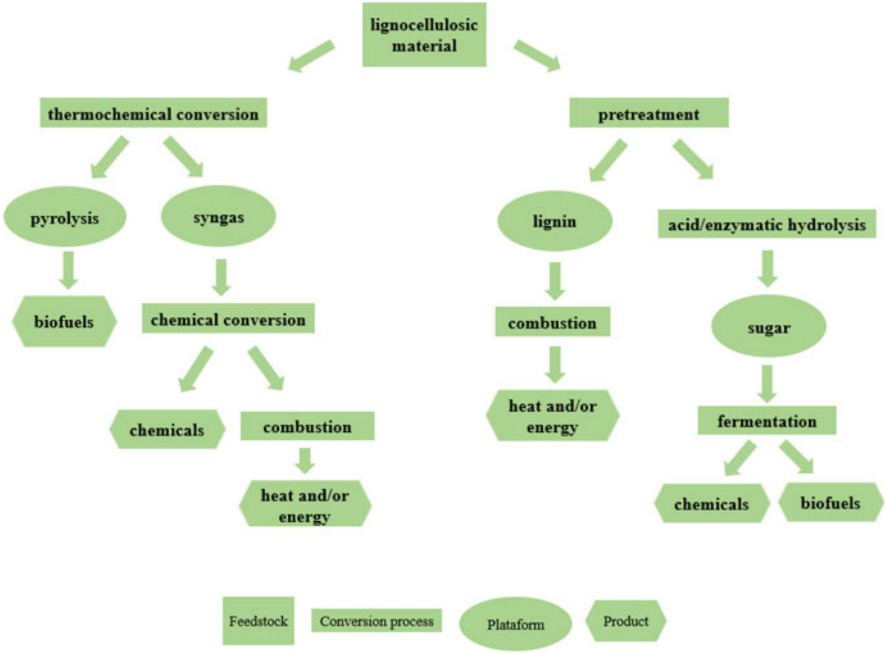

Fig. 1.3 Example of classification of biorefineries from lignocellulosic material

biorefinery system: platforms, products, raw materials, and processes. According to Cherubini et al. (2009) each biorefinery system is treated independently and classified according to their characteristics.

Figure 1.3 shows an example of this method of classifying biorefineries starting from a lignocellulosic material.

1.2.1 Feedstocks: Dedicated Feedstocks and Residues/Waste

Biorefineries are classified into two major groups: biorefineries designed to process a specific crop and biorefineries that process waste (Cherubini et al. 2009).

Dedicated/Nonwaste Feedstock Dedicated feedstock crops involve fresh carbon-based feedstock, which is currently developed for biorefinery use/purpose in the agricultural, aquaculture, and forestry sectors. This is known as primary feedstock, which is used exclusively for biorefinery purposes and is widely known as energy crops. Dedicated raw material basically involves the following types of crops (Pfaltzgraff and Clark 2014; Badgujar and Bhanage 2018).

- Cultures of lignocellulosic materials: forest hardwood, softwood, pine, and miscanthus.

- Grasses: green plant materials, grass silage, immature cereals, herbs, shrubs, and plants shoots.
- Marine biomass: marine algae, marine plants, and marine micro and macroalgae.
- Oil crops: rapeseed oil, coconut oil, soybean oil, palm oil, jatropha oil, and cottonseed oil.
- Starch crops: wheat and corn.
- Sugar crops: sugarcane, sugar beet, sorghum, potato, and rice.

Residual/Waste as a Feedstock The residual feedstock involves carbon-based raw materials in the form of waste or by-products or waste from agricultural, aquaculture, forestry, domestic, organic, and industrial waste. This is known as secondary raw material, which are by-products of the primary and necessary processing suitable for disposal or reuse (Pfaltzgraff and Clark 2014; Badgujar and Bhanage 2018).

Residual feedstock usually involves the following carbon-based residues or bioproducts:

- Residues from the treatment of lignocellulosic materials: crop residues, sawmill residues, non-edible part of the crop, and forest residues.
- Organic waste/by-products: urban and industrial organic waste, household waste, vegetable waste, and animal manure (bovine and swine).
- Oil-based waste: animal fats from food industries, tanning waste, ghee-oil waste, soap industry waste, residential, and restaurant oil waste.
- Grass residues/waste: green plant materials, grass silage, immature silage leachate cereals, and plant shoots.

1.2.2 Biorefinery Processes

In biorefinery systems, several process technologies can be applied to convert biomass feedstock into marketable products. This classification approach identifies four main subgroups of processes:

- *Biochemicals*: Biochemical processes have the potential to convert substrates into final products in one or a few steps using moderate reaction conditions (mild temperature and pressure), which can lead to a more sustainable production due to the less energy requirements and waste generation. These processes include anaerobic digestion, fermentation, and other enzymatic conversions using biological catalysts (microorganisms or their subcomponents) (Cherubini et al. 2009; Alvim et al. 2014; Sadhukhan et al. 2014).
- *Thermochemical***:** The thermochemical processing is a special case of chemical processing, involving thermal decomposition, thermal oxidation, etc. In these processes the raw material is treated under medium to high temperature (350–1300 °C) and/or pressure with or without a catalyst. These processes include pyrolysis, gasification, hydrothermal improvement, and combustion (Cherubini et al. 2009; Alvim et al. 2014; Sadhukhan et al. 2014).

Table 1.3 Most common mechanical, biochemical, chemical, and thermochemical processes (Pfaltzgraff and Clark 2014)

Mechanical processes	Biochemical processes	Chemical processes	Thermochemical processes
• Pressing • Milling • Distillation • Extraction • Pelletization	• Anaerobic digestion • Fermentation • Enzymatic conversion	• Hydrolysis • Hydrogenation • Oxidation • Pulping • Transesterification and esterification	• Pyrolysis • Gasification • Steam explosion • Supercritical • Combustion

- *Chemicals*: These processes are used to modify the chemical structure of a substrate. They may need high temperature and pressure. They need to maintain the catalyst temperature and the operating pressure at moderate levels to increase the conversion of reaction and the yield and purity of the desired product. Some examples of these processes are hydrolysis, transesterification, hydrogenation, oxidation, and pulping (Cherubini et al. 2009; Alvim et al. 2014; Sadhukhan et al. 2014).
- *Mechanical/Physical*: These processes are mainly used to carry out size reduction, raw material densification, or separation of components and products, without changing the chemical structure of the biomass components (Cherubini et al. 2009; Alvim et al. 2014; Sadhukhan et al. 2014).

Given the above, it is evident that the concept of biorefinery is very comprehensive and encompasses all aspects of biomass use, whether for the production of biofuels or for the production of other products (Table 1.3).

1.2.3 Biorefinery Platforms

The platforms are the most important features in this classification approach. They are essential intermediate elements between raw materials and final products and can connect different biorefinery concepts with target markets (Jong et al. 2020).

The platform concept is similar to that used in the petrochemical industry, where crude oil is fractionated into a large number of intermediates that are further processed to produce energy and chemicals (Cherubini et al. 2009). The processes are capable of generating products through a building block called platform.

The platforms are generated from the fractionation treatment or preconditioning of the biomass, depending on the nature of the feedstock and type of products to be produced. More than one platform can be present in a biorefinery configuration and the number of platforms is indicative of the complexity of the biorefinery (King et al. 2010; Sadhukhan et al. 2014).

The most important platforms that can be found in energy-powered biorefineries are as follows:

- *Syngas*: The synthesis gas (or syngas) is a gaseous mixture of carbon monoxide (CO), hydrogen (H_2), methane (CH_4), nitrogen (N_2), and carbon dioxide (CO_2), as well as light hydrocarbons such as ethane and propane, and heavier hydrocarbons such as tars (Molino et al. 2016). It is produced from biomass gasification. After cleaning, the synthesis gas can be converted by thermochemical catalysis into alcohols (methanol and ethanol), fuels such as Fischer–Tropsch diesel, and chemicals such as dimethyl ether, isobutene, organic acids, and ammonia, among others (Sadhukhan et al. 2014; Jong et al. 2020).
- *Biogas*: It is produced from the anaerobic digestion of organic materials. This waste is decomposed producing a mixture of gases. Other main products resulting from the decomposition are methane (between 50 and 75% of the total volume) and carbon dioxide (between 25 and 50% of the total volume). At lower concentrations, gases such as hydrogen sulfide, water vapor, hydrogen, and ammonia, among others, are also generated. This biological process is used as a renewable substitute for commercial natural gas and has an estimated conversion efficiency of 70% (King et al. 2010; Sadhukhan et al. 2014).
- *Bio-oil*: The term bio-oil is mainly used to refer to liquid fuels obtained from organic materials (agricultural, forest, and urban waste) through biochemical or thermochemical processes. Bio-oil is a multicomponent mixture of oxygenated hydrocarbons, produced from the fast pyrolysis of biomass (Sadhukhan et al. 2014). According to Demirbas (2009), bio-oils can be separated into heavy and light fractions, which can be upgraded through hydrodeoxygenation to liquid biofuels and chemicals.
- *Sugars C5/C6*: The sugar platform is one of the key platforms and is currently considered, by volume, the largest platform for the production of chemical products from biomass (Jong et al. 2020). Sugar is the basis for a large number of traditional biorefinery processes and consolidated industries. C5 sugars are released from the hydrolysis of hemicellulose. These sugars (e.g., xylose and arabinose) can also be used to produce biofuels and chemicals. C6 sugars (e.g., glucose, fructose, and galactose) are released from the hydrolysis of sucrose, starch, and cellulose. This platform is mainly used for the production of bioethanol and other chemical products with various functionalities, such as furfural, acetic acid, and formic acid, among others (Sadhukhan et al. 2014).
- *Lignin*: Lignin is a very complex natural compound and offers a significant opportunity to improve the operation of a lignocellulosic biorefinery (Jong et al. 2020). It is produced from the fractionation of lignocellulosic biomass. It has a wide range of possibilities for the use and production of different bioproducts, such as fuel for boilers or composite material. According to Aro and Fatehi (2017), it is estimated that more than 95% of the lignin produced annually is used internally in the pulp industries for energy generation. The added value of lignin includes the production of chemicals such as vanillin and phenolic-based aromatic compounds (Cherubini et al. 2009; Sadhukhan et al. 2014).
- *Fats and Oils*: They are found in oilseeds, algae, and animal fat and oil-based residues. They can be converted into fuels such as biodiesel and jet fuel. Due to their chemical functionalities, these can also serve as reagents for the production

of biodegradable lubricants (Sadhukhan et al. 2014). According to Jong et al. (2020), approximately one million tonnes of oils and fats are used annually in Germany for the production of chemicals.

- *Hydrogen*: It can be obtained from the gas shift reaction of water, steam reforming, and fermentation. Hydrogen can be used as a fuel and also as a chemical reagent for the hydrotreatment of oils, hydrogenation of sugars, and in the production of ammonia, for example (Sadhukhan et al. 2014).
- *Organic solutions*: A green biorefinery processes green (wet) biomass such as grass, clover, alfalfa, or immature cereals (Kamm et al. 2006). The first step involves the fractionation of green biomass into a rich nutrient juice called "organic solution" and lignocellulosic filter cake rich into fiber. This organic solution contains compounds such as carbohydrates, proteins, free amino acids, organic acids, minerals, hormones, and enzymes, depending on whether the biomass used as raw material is fresh or silage (Jong et al. 2020).
- *Electricity and heat*: they can be used internally to meet the biorefinery's energy needs or they can be marketed to the power grid (Cherubini et al. 2009; Sadhukhan et al. 2014).

1.2.4 Biorefinery General Products

The products of a biorefinery can be classified into energy products and those used as materials for different industries or human needs. The definition of the set of products will depend on their potential to generate revenue and the potential for avoiding emissions by replacing similar functionalities to fossil-derived products (Cherubini et al. 2009; Sadhukhan et al. 2014). A description of these products is as follows:

- *Biorefinery systems for energy production*: the biomass is mainly used for the production of alternative energy (biofuel, energy, and / or heat). Other products, such as animal feed, are sold or modified to generate bioproducts with greater added value, aiming to improve the economic and ecological performance of the entire biomass supply chain (Cherubini et al. 2009; Sadhukhan et al. 2014).
- *Biorefinery systems focusing on obtaining bioproducts*: generation of bio-based products. The process waste may be subjected to further processing to obtain other products or energy (for internal use or sale). Some examples of these bioproducts are biomaterials, lubricants, food, feed, chemical products, nutraceuticals and food ingredients, pharmaceuticals, fertilizers, biodegradable plastics, surfactants, fibers, adhesives, and enzymes, among others (Cherubini et al. 2009; Sadhukhan et al. 2014).

Energy products such as combined heat and power (CHP) and biofuel are the least valuable. However, due to the large production volume, the revenue generated by this production may be greater than the production of other products. On the other hand, the production of polymers, food, and pharmaceutical products are the ones

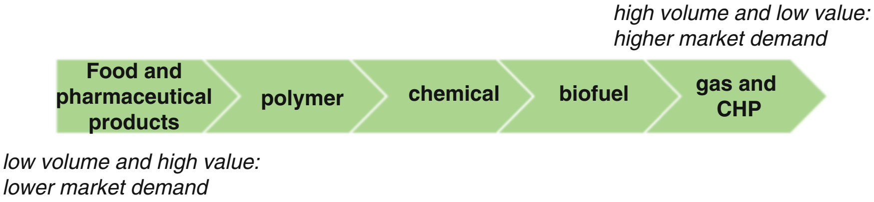

Fig. 1.4 Biorefinery products and their market drivers

with the highest added value. However, with smaller volumes produced, the challenges to find these products in the market are greater. Figure 1.4 shows the market drivers of some products obtained in a biorefinery.

According to Sadhukhan et al. (2014), to add value to each product a biorefinery can combine several technologies using a sequential approach to extract chemicals before it is converted into biomass energy.

1.3 Current Scenario, Challenges, and Future Trends

1.3.1 Challenges and Trends in Biorefining

As is the case for any science and engineering field, the complexity inherent to waste biorefineries' production technologies gives rise to equally complex challenges and business models. Thus, similarly to other fields, it is feasible that more than one solution may be feasible for a given situation. Additionally, these installations do not exist in a vacuum and to attain profitability the installations must adapt quickly to market fluctuations.

In this section, we intend to demonstrate some challenges that are generated when planning, commissioning, and operating biorefineries as a whole, and how waste biorefineries face these. It should be noticed that the situations presented in the following text are not meant to be an exhaustive list, nor the most pressing issue to a particular installation. These are, in the opinion of the authors, the most common issues faced in this industry, both in technical and in financial realms, and possible solutions to these hurdles when available.

1.3.1.1 Plant and Products Sustainability

As previously stated in this chapter, the drive to develop biorefineries stems from the necessity of establishing a circular economy (CE) manufacturing and consumption model as soon as possible to deter further impacts to the environment. Therefore, it is clear that to assure that the intended biorefinery is maintained within a sustainable business model, it is necessary to guarantee that all materials and processes used within the plant are also sustainable.

This may seem trivial at first glance, yet, it becomes increasingly more complex upon closer inspection. One clear issue is the utilization of fossil-based chemicals or those that require considerable energy to be produced, as it is likely that the used energy is also fossil-based. These are important points when designing a plant, and their prominence could potentially put another severe and underestimated issue in the background, the sustainability of the biomass feedstock in itself, and the extent to which it is used.

1.3.1.1.1 Natural Resources Usage

It is important to notice that it has become increasingly common to assume that all biomass, animal or vegetable, are renewable sources. However, this may not be true for all biomasses, particularly those that are grown exclusively to produce goods and/or energy.

This is the main contingency point of a traditional debate when considering biomass-based energy or goods, the commodity–food nexus. This connection between products and food is generated because the same land, or the biomass itself, may be used for food manufacturing or energy-products manufacture. This may generate unhealthy competition for the area between the crops for food crops for commodities.

Experts claim that competition for land can increase food prices and food scarcity, especially in underdeveloped territories. It has been suggested that due to this competition, the price of cereals can grow by 24% in the near future, 27% for other types of crops, and up to 6% for livestock (Ho et al. 2014). Therefore, the usage of land to produce biomass for other uses besides human consumption may be considered ethically dubious, especially in impoverished locations. Additionally, another level of complexity may be added to the nexus, by considering the amount of water used within the biorefinery. As potable water may also be used for direct consumption or to produce food crops.

It should be noted that this debate is not recent, and has permeated many biomass-based projects throughout history, from sugarcane-derived ethanol, biodiesel from palm oil, energy from dedicated forests, and other situations, often out of genuine and valid concerns.

One could consider that using feedstock grown in marginal land or with small land footprints (algae and microalgae) may be a manner of steering away from this difficult dynamic. However, this is true to only a certain extent, as all of these feedstocks and the plant itself will still require water and power during culture and processing.

Therefore, one way to veer away from this issue is to use a feedstock that is not fit for consumption, or will not compete for land with crops for consumption, as is the case with waste or residual biomass biorefineries. These suffer less from this type of issue as the main feedstock will not require significant land, energy, or water to be produced since it is a residue from another process. Additionally, using wastes as feedstock also agrees well with CE efforts.

It is clear that even though biorefining is largely considered to be a very promising tool to accomplish a fully CE, severe sustainability issues may be generated from a sub-par project that does not account for the plant's non-supply chain-related impacts. In order to contemplate this dimension of plant design, it is necessary engagement with local stakeholders and experts from the project inception to its operation. Reducing the gap between the location's resources and needs (D'Odorico et al. 2018) and that all aspects of the project are covered by life cycle analysis (LCAs). Additionally, results from the project, whether promising or underwhelming, should be made available publicly, as this type of data is sparse in literature and is extremely useful to steer subsequent projects and may be used to aid future policy-making (Benites-Lazaro et al. 2020).

1.3.1.1.2 Biomass Utilization

Another important parameter to assure that the processing technology is environmentally sustainable is to assure that the feedstock is being used to its maximum extent possible. This translates into making use of all parts of the feedstock, generating little to no residues downstream of the process, a core necessity when going from a linear economic model, where disposal is seen as a normal occurrence, to a circular economic model (Bose et al. 2020). Additionally, making full use of the biomass decreases the plant's natural resources footprint, as no resources were used to produce wastes.

This is not an easy feat to accomplish, not only for biorefineries but for any production plant or manufacturing facility. However, this situation is aggravated when dealing with lignocellulosic biomass, particularly when considering the usage of the lignin fraction.

As previously stated, lignin is a complex structure, which has been underutilized when compared to the fraction of lignocellulose with high sugar content (cellulose and hemicellulose). Currently, lignin is mostly used for power and heat production through combustion. However, it has the potential to substitute several fossil-based products and, thus, strategies for economically feasible lignin valorization have been studied for several decades (Amore et al. 2016).

Routes for the production of several chemical products have been proposed for lignin, from low-value chemicals, such as different acids and solvents, to fine chemicals, such as toluene, xylene, and vanillin. However, routes for the production of fuels, such as mixed hydrocarbons, alcohols, and jet fuel, or biomaterials, such as carbon fibers and polyurethane, have also been proposed from this molecule (Ponnusamy et al. 2019; Wang et al. 2019).

Therefore, one can notice why the drive for feasible techniques to convert lignin has taken proportions not unlike those generated by a gold rush, as a lignin-based installation can be widely versatile, and thus, resilient. However, to enable the production of these products from lignin a series of hurdles need to be overcome, particularly around the development of less cost-intensive routes for lignin depolymerization, through the use of less expensive catalysts and milder reaction conditions, and more efficient products downstream technologies, particularly for bulk chemicals and emerging fuel applications. Once these techniques are developed, it is important that all these technologies routes must also be scrutinized by LCAs to assure that the sustainability of the plant still holds regardless of the products (Sun et al. 2020).

1.3.1.2 Business Model Sustainability

Assuring that the plant and its products are sustainable is the first step toward a strong project. Nevertheless, after this analysis, other important parameters must be observed. One important parameter is the economical sustainability of the project.

It is increasingly evident that a cascade model, utilizing all the portions and generating a series of products, particularly those of high value and low volume, may be needed to assure stability (Budzianowski 2017). Yet, one must also observe if the generated products will have a market once they are available.

One clear example of this trend is the high interest in producing plastics from biomass within biorefineries. Although commendable, the market is relatively small, especially when compared to the fuel markets (Shen et al. 2010). It is feasible that if a series of new installations are constructed to supply the same market, competition between the companies will lead to instability and closures. This is an important situation to be aware of as a collapse of biorefineries could lead to a reversion to rely on unsustainable feedstocks or production technologies.

Contrarily, markets do not occur naturally; they are generated by manipulation of supply and demand. Markets usually start on small scales, where a company may position itself and tend to a particular necessity of a niche group of clients. If the needs of the clients are fulfilled well, volumes may grow and the market expands (Bauer et al. 2017). Therefore, to cope with narrow market positions, it is also feasible for a biorefinery to be established as a small to medium-sized enterprise initially and supply and grow production as needed in the market. This could potentially be a way to increase sustainability for multiple plants. However, it is clear that in already established markets (such as fuels and chemicals) this is not a feasible solution, and competition with fossil fuels will remain the norm for the foreseeable future until regulations and subsidies are adequate to reduce emissions targets.

1.3.1.3 Current Waste Biorefineries

Despite all these challenges that biorefineries as a whole face, there are still quite a significant number of units operating worldwide. To track these institutions, databases with information over their characteristics have been constructed, such as the repositories generated by the International Energy Agency (*https://www.iea.org/*)

and the Office of Energy Efficiency and Renewable Energy (*https://www.energy.gov/eere/office-energy-efficiency-renewable-energy*). Such tools are of vital importance, as one of the key pathways toward a truly circular economy is by improving data sharing between institutions to diminish chances of failure.

However, as it is the case for any industrial field, information over technologies and financial data is, generally, undisclosed. Nevertheless, the following items demonstrate two study cases of waste biorefineries with demonstration plants in different ends of the size spectrum where waste biorefineries may exist.

1.3.1.3.1 Large-Scale Project: BALI™ Biorefinery Demo, Borregaard AS

Borregaard in Sarpsborg (Norway) is a company with over 40 years of experience in operating biorefineries for the production of a series of biofuels and other products. The company developed the Borregaard Advance Lignin (BALI™) process. This is a novel technology that utilizes a series of proprietary processes to achieve a high degree of separation between lignin and the carbohydrate-rich fraction of the biomass, leading to the production of four major products in the plant: cellulose, ethanol, lignins, and vanillin (Rødsrud et al. 2012).

The production of these products bypasses the issues described in the previous items due to the high degree of separation between the fractions. It reduces costs both for the utilization of the lignin for the production of other chemicals and the cost of carbohydrate's fermentation to biofuels or other biotechnological products. Additionally, the process is also extremely versatile, being capable of processing a series of biomass residues, such as hardwood, softwoods, and bagasse (Costa et al. 2020).

Although Borregaard's main activity is the production of lignin-based chemicals, at its peak production, before a recession in the biofuels market, the company was producing 20 million liters of bioethanol per annum (Fevolden and Klitkou 2017). An environmental assessment of the plant demonstrated that the plant's ethanol, produced through its proprietary process, is on a par with other technologies (Modahl et al. 2015).

This company's history and market placement demonstrate that even though there are severe barriers to the production of bioproducts from wastes, particularly those based on lignin, a market section can be occupied by an environmentally conscious enterprise.

1.3.1.3.2 Small-Scale Project: Biokol, Stockholm Biochar Project

Biokol or the Stockholm's Biochar Project (SBP) is a project based in Sweden's capital city that processes park's green waste (garden waste, tree cuttings, and waste wood, mostly) to produce heat, currently generating enough to 80 apartments per year, and biochar for the local community (Avfall 2017).

Biochar is sustainably produced charcoal with several uses apart from solid fuel, particularly used for soil amendment. It is produced through pyrolysis, which is the thermal degradation of biomass in the absence of oxygen (Lehmann et al. 2011). Additionally, biochar also is very stable, suffering small alterations when added to soil, and thus, it has become an emergent manner of performing carbon storage (Spokas 2014).

The SBP was established in 2013 and the produced biochar is used in trees in the city of Stockholm to substitute peat and increase moisture retention in the soil, increasing the tree's health. This project is now being replicated in several locations internationally (Azzi et al. 2021).

The successful replication of this project is explained by two main reasons. First is the low barrier to implementation, as this is waste biorefinery that is generating both energy and products to its community using, relatively, simple technology. The second and possibly main reason for replicability is the willingness of the participants to share information with other parties. The team responsible for SBP has published both a replication manual (Bloomberg 2018a) and a checklist/frequently asked question guide (Bloomberg 2018b) to facilitate implementation. This is a very important task often overlooked by project managers that greatly reduces barriers to implementation in other locations.

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Chapter 2
Zero-Waste Biorefinery

Benjamas Cheirsilp and Wageeporn Maneechote

Abstract Developing technologies to manage natural resources sustainably is a vital start to ensure food security, supply sufficient quantities of raw materials and renewable energy, reduce environmental footprints, and promote a healthy and viable rural economy. Beyond this, it is also important to avoid unnecessary wastes and to recycle unavoidable wastes in useful and efficient ways. The ideal is to have closed-loop systems of production and byproduct reuse. A biorefinery concept can be applied to natural resources, from which different bioproducts and biofuels are produced, maximizing the value of the intermediates and final products, and consequently decreasing the overall costs. Biotechnological processes are inherently cleaner than petrochemical or thermochemical processes. They are performed in a contained environment and have the potential to produce high yields of specific products with low energy use and minimal waste generation. Biotechnology therefore presents unique opportunities for sustainable biorefinery. This chapter aims to summarize current zero-waste biorefinery, emphasize on biotechnological processes, and address the limitation and problems within this field. The innovative techniques for possible solutions and their integration are discussed.

2.1 Introduction

The key issue in industrial production of food, feed, chemicals, materials, and fuels is the sustainability of supplying the natural resources to meet their increasing demands, protect global climate change, and preserve fossil resources. Driven by these concerns, the circular economy based on "zero waste" concept has promoted systematically designing and managing products and processes to avoid wastes and to recover all components from raw materials and byproducts. The zero-waste scope covers many concepts that have been developed for waste management systems

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which include reduction, reuse, redesign, regeneration, recycle, repair, remanufacture, resell, and redistribute. Therefore, a zero-waste strategy receives growing attention and popularity as best practice (ZWIA 2004). Moreover, the benefits of zero-waste management in the environmental viewpoint are: a reduction of using virgin raw materials, an improved efficiency of using raw materials, a reduction of wastes and a reduced negative effect, and an extension of useful life span of sanitary landfills. A reduction of using virgin raw materials in the process involves more careful estimating, using substitutions for materials and processes, and reducing processes. The proper design of processes, practices, and products to avoid or reduce wastes and pollutants is also included (Yoganandam and Udhayasakthi 2017). Other benefits of zero-waste management are better eco-efficiency of the manufacturing processes due to a lower energy consumption and greenhouse gases (GHGs) emission. This strategy also creates chances to produce bioenergy and bioproducts from the wastes, sale carbon credits, support environmental protection, and avoid using toxic materials for the production (Pietzsch et al. 2017).

A zero-waste biorefinery concept also concerns that all components in raw materials, byproducts, and wastes are either recovered or nurtured through bioprocesses, without damaging the environment. Modern societies have been employing integration of waste management systems with productions of useful products (Zaman and Lehmann 2013; Liyanage et al. 2019). It should be also noted that the concept of zero waste is not only limited to optimum resource recovery and recycle but also elimination of unnecessary waste generation at the beginning of product design. Moreover, the reduce/reuse/recycle/recovery of valuable components has been promoted through the developed technologies. Economic gains can then be achieved via interaction of both consumers and producers, in an effort to accomplish zero-waste society and sustainability (Curran and Williams 2012; Korhonen et al. 2018). The procedures to diminish industrial wastes and wasting energy in the production of goods, as well as the recovery of these wastes were employed largely in order to preserve materials and energy. Reduction of the wastes in relation to the number of products will help produce more products from the same amount of raw materials used and protect environment (Dotsenko et al. 2019). Lately, increased consciousness of the environment, concern over ensuring sustainable development, and awareness of the necessity to establish waste managements have contributed to improving the image of recycling as a significant implementation to gain many profits and also indirectly safeguard the environment (Yoganandam and Udhayasakthi 2017). This chapter firstly introduces a zero-waste biorefinery concept and summarizes current biorefineries. The current and biotechnological approaches for zero-waste biorefinery are discussed. Their limitations and possible solutions are also addressed.

2.2 A Zero-Waste Biorefinery Concept

A biorefinery is the technique that incorporates conversion processes and apparatuses to yield food, feed, chemicals, and fuels from natural resources. The biorefinery concept is similar to petroleum refineries that yield multiple products along with fuels from petroleum. Industrial biorefineries have been recognized as the most powerful means to create a new-curve bio-based industry. By harvesting multiple products, a biorefinery can make use of diversity in material components and their intermediates to maximize the value of natural resources. In addition to zero-waste concept, biorefineries also contribute to developing circular economy as they use green and clean technologies to increase the value of the residuals by converting into high value-added biofuels and bioproducts (Maina et al. 2017). It is among one of the most crucial strategies for the bio-based circular economy that help close the loop of natural resources, i.e. water, minerals, and carbon. New technologies in bioprocessing and biorefinery can help maximize the value of natural resources for the production of products and metabolites with high marketing value (e.g., bioactive compounds, biomaterials, lipids, proteins, and carbohydrates) (Leong et al. 2021).

The valorization of wastes and byproducts for the production of value-added bioproducts such as biofuels, biochemicals, and biopolymers could possibly substitute the use of fossil resources as the raw materials and guarantee an ecologically friendly carbon flow. This approach is considered as a zero-waste biorefinery which would greatly contribute as a clean, green, and economical waste disposing ways. Moreover, the bio-based industries possess environmentally caring properties such as non-toxic, biocompatible, and biodegradable which support an ecologically friendly movement, and hence globally promote a greener environment. Bioprocesses valorizing wastes into value-added biofuels and biomaterials can greatly avoid using fossil resources as feedstocks and this help prevent the natural resources depletion. This strategy does not only preserve the energy environment but also contribute to reducing GHGs emissions from burning fossil resources and mitigation of carbon footprints. Moreover, the involving bioprocesses can be merged with other managing systems such as waste and wastewater treatments. Recently, various wastes have been valorized into pharmaceuticals, chemicals, biofuels (e.g., biogas, bioethanol, biodiesel, and biohydrogen), biopolymers (e.g., polyhydroxybutyrates and polyhydroxyalkanoates), and animal feed which are environmental friendly bioproducts (Zeng et al. 2015; Ferreira et al. 2016; Li et al. 2018; Dahiya et al. 2018; Mishra et al. 2019a, 2019b; Leong et al. 2021). These strategies greatly contribute to the zero-waste biorefinery concept for recovery of all components in natural resources for production of high-value products (Fig. 2.1).

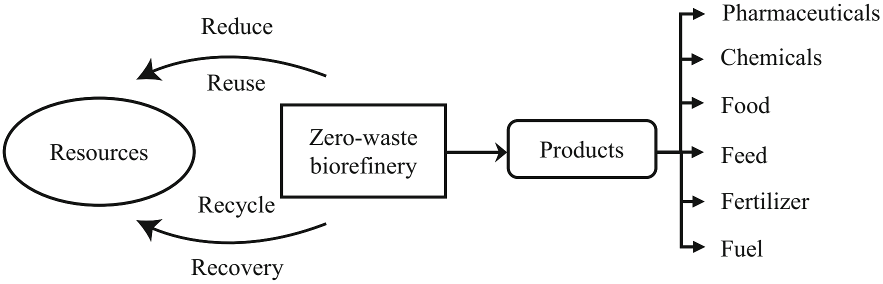

Fig. 2.1 Conceptualizing zero-waste biorefinery for recovery of all components in natural resources for production of high-value products

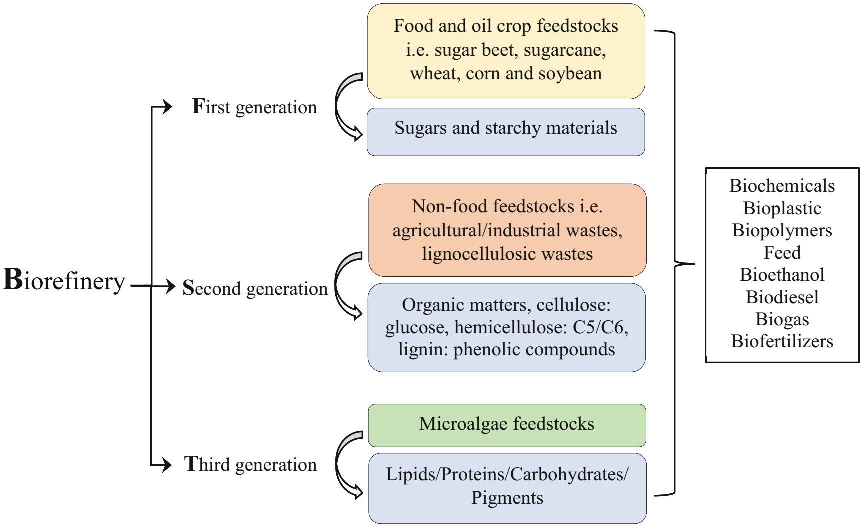

Fig. 2.2 Different feedstocks used in the first-, second-, and third-generation biorefinery for producing biofuels, biochemicals, and feed

2.3 Current Biorefineries

Based on the type of natural resources used, current biorefineries can be categorized into 3 generations which are the first, second, and third generation (Fig. 2.2). For the first-generation biorefinery, the refined materials mainly in sugar and oil forms took from food crops are used. On the other hand, for the second-generation biorefinery, the feedstocks took from non-food sources, mainly lignocellulosic wastes from agricultural and agro-industrial wastes, wood and crop residues, are used. For the third-generation biorefinery, renewable plant and algal resources which are more favorable for sustainable biorefinery process are used (Parada et al. 2017; Gutierrez et al. 2017).

2.3.1 First-Generation Biorefinery

The first-generation biorefinery generally uses the refined feedstocks from food crops such as cassava, wheat, corn, barley, soybean, sugar beet, sugarcane, sweet sorghum, etc. The bioproducts and biofuels from these first-generation feedstocks are the first-generation bioproducts and biofuels such as biochemicals, biopolymers, bioethanol, biodiesel, and biogas. The straight vegetable oils and biomethanol are also included in this category. In the first-generation biorefinery, bioethanol can be produced from refined sugars and starchy materials such as sugar beet, sugarcane, and starch crops (Cherubini 2010; Martin 2010). Subsequently, these feedstocks could be processed using either biological or chemical transformation to other biochemicals such as propionic acid, lactic acid, 1,3-propanediol, polyhydroxyalkanoate/polyhydroxybutyrate, poly-γ-glutamate, biofuels like ethanol and butanol (Yang and Yu 2013). In contrast, wheat, soybean, and corn require additional pretreatment steps (steam pretreatment followed by enzymatic starch hydrolysis using amylase), thereafter biofuels and biochemicals are produced using suitable microorganisms. Several co-products as food additives (high fructose corn syrup, corn steep liquor, oil, and proteins) and animal feed (dry distillers grains and solubles (DDGS), residual cake, and gluten meal) could be also produced (Bothast and Schlicher 2005; Rosentrater 2006). Other bio-based products are also generated in the first-generation biorefinery. These include polymers, paint pigments, paper, cardboard, sorbents, adhesives, detergents, and dyes (Cherubini and Ulgiati 2010).

The advantages of first-generation biorefinery involve high yield and productivity of crops as raw materials, a fully developed cropping pattern, easiness to extract fermentable components, and developed technology for bioconversion of them into biofuels and bioproducts. Production chains for many biofuels have been evaluated by Life Cycle Assessment (LCA) method in order to emphasize their environmental impacts (Gasol et al. 2007; Quintero et al. 2008). Most LCA have shown a net decrease in GHGs emissions and consumption of fossil-based energy when conventional diesel and gasoline are replaced with bioethanol and biodiesel (Kim and Dale 2005). However, the first-generation biofuels are in competition with food and feed industries. Therefore, the use of food crops and agricultural land lead to the ethical consequences: a larger quantity of crops or agricultural land is devoted for biofuel production instead of food production. Therefore, the sustainability of the first-generation biorefinery has been strongly challenged. Their potential obtainability is restricted by soil fertility and yields per agricultural land. In addition, the reduction in GHGs emissions and consumption of fossil-based energy are restricted by the high energy input for crop plantation and subsequent bioconversion to bioproducts and biofuels (Marris 2006; Lange 2007; Mueller et al. 2011).

2.3.2 Second-Generation Biorefinery

Second-generation biorefinery utilizes a variety of non-food crop feedstocks such as lignocellulosic materials/residues from agro-industry, agriculture, forestry, and devoted lignocellulosic crops. According to the literature, the wording of second-generation biorefinery indicates utilization of a wide variety of non-food feedstocks, conversion means (e.g., physicochemical, hydrothermal, enzymatic methods), and value-added intermediates and products. Lignocellulosic biomass/wastes have high potential as renewable energy sources which contribute to mitigation of GHGs and climate change. The use of residues/wastes for the production of high-value bioproducts can avoid environmental pollution and reduce negative effects of their combustion on the field. This strategy also stimulates country economies and supports energy security. However, the cost-effective conversion of lignocellulosic wastes into biofuels and value-added bioproducts is highly challenging due to their very complicate structure and recalcitrance. In the second-generation biorefinery, lignocellulosic wastes are fractionated using a series of bio/chemical processes prior to conversion into fuels and chemicals (Clark and Deswarte 2008; Patel and Shan 2021).

Lignocellulosic wastes can be categorized into forest materials, energy crops, agricultural residues, aquatic plants, and organic solid fraction of municipal wastes (Zabed et al. 2017). Main components of lignocellulosic wastes are cellulose at 35–50%, hemicelluloses at 20–35%, lignin at 5–30%, and other extractive compounds at 1–10% based on dry weight (Menon and Rao 2012; Patel and Shan 2021). Cellulose has a rigid structure containing long chains of glucose molecules (C6 sugar). The difference from starch is the configuration of the bonds across oxygen molecule joining two hexose units. Starch can be easily hydrolyzed by enzymes or acids into glucose monomers, while cellulose is much harder to be hydrolyzed into glucose monomers. Hemicellulose is a relatively amorphous fraction which is easier to be hydrolyzed into a mix of C6 and C5 sugars using chemicals and/or heat than cellulose fraction. Lignin is made of phenolic polymers and is primarily the glue that offers the overall rigid structure for plants and trees. Cellulose and hemicellulose are polysaccharides that can be hydrolyzed to sugar monomers prior to bioconversion into biofuels and bioproducts, while lignin cannot be used biologically converted. But it is useful in other applications such as energy generation and chemical extraction (Schutyser et al. 2018).

Major driving forces for the lignocellulosic biorefinery for production of biofuels and bioproducts include renewable and sustainable domestic supply of energy for the growing economic and less dependence to import energy sources, low carbon footprint, establishing bio-circular-green economy (Valdivia et al. 2017; Oh et al. 2018). Lignocellulosic biorefinery should be developed for supplying multiple feedstocks and producing various bioproducts. In lignocellulose biorefinery, the preparation of feedstocks could be 50% share in production of bioproducts (Junqueira et al. 2016). Process integration, product selection, precise master plan, analysis of cost sensitivity and risk factors, safety, regulation, and reproducible economic modeling are key factors for scaling up biorefinery (Sanford et al. 2016). Integration of lignocellulosic biorefinery is a promising strategy to produce second-generation products at a competitive price. However, there is a pressing need to overcome encounters for the commercialization of this integrated lignocellulosic biorefinery (Patel and Shan 2021). Some bioproducts from second-generation biorefineries can be given as follows:

2.3.2.1 Second-Generation Biofuels

Biofuels are the main part of the biorefinery concept as sustainable, renewable, and alternative fuels (Amoah et al. 2019a, 2019b). Biofuels are mainly derived from wastes and residues that can be categorized as second generation, because its feedstock is not in competition with food and feed. Second-generation biohydrogen is produced using various biological methods and the selection of method has a great influence on the production yields from various feedstocks. Various fermentative microorganisms have been widely used to produce biohydrogen (Kotay and Das 2007). Under anaerobic fermentation, biohydrogen is produced as a byproduct from oxidation reaction of organic substrates through the sequential neutralization of excess electrons by the activity of endogenous hydrogenase. This ordinary phenomenon has been applied for the systematic production of second-generation biohydrogen. The actual yield of second-generation biohydrogen is commonly lower than the theoretical one because a significant amount of substrates are consumed in microorganism growth (Vignais et al. 2001). The production of second-generation biohydrogen by dark fermentation also obtained acetic and butyric acids as the main co-products. Interestingly, these organic acids could be low-cost alternative carbon sources for supporting heterotrophic growth of microalgae (Moon et al. 2013; Ren et al. 2014).

Second-generation biomethane is produced by a set of microbes denoted as methanogens. However, a limited number of the methanogens are known to assimilate organic acids such as acetic acid for biomethane production (Qiao et al. 2014). There are three main types of second-generation feedstocks that have been systematically studied for their prospective conversion to second-generation biomethane. These include municipal wastes, agricultural wastes, and industrial wastes. The second-generation biomethane production greatly depends on the microbial communities and dominant species found in the wastes (Shin et al. 2004). The hydrogenesis process is commonly competing with methanogenesis process as methanogens consume hydrogen for methane production. This has led to the two-step process development for biohydrogen production in the first stage and biomethane production in the second stage (Wu et al. 2015; Xiao et al. 2018). In the first stage, the hydrogenase activity in the acidogens produces organic acids as byproducts and in the second stage these organic acids are then assimilated by the methanogens. Greater yields of biomethane produced in this two-stage process over that in the one-stage process have been reported (Xiao et al. 2018).

Bioethanol is one of the most interesting second-generation biofuels due to its positive impact on the environment (Kar and Deveci 2006; Pickett et al. 2008). Bioethanol can be blended with gasoline to operate a growing number of vehicles (Martin 2010). E10 blend also shows 2% decrease in GHGs emission, 3% decrease in fossil-based energy usage, and also 6–6.6% decrease in petroleum usage (Chen and Fu 2016). The second-generation ethanol gives higher combustion efficiency than that of gasoline due to its high oxygen content (34.7%). Currently, bioethanol is mostly produced from sugar- and starch-containing raw materials. However, various available types of lignocellulosic biomass can serve as feedstocks for bioethanol but they require an efficient pretreatment and acid/enzymatic hydrolysis for production of fermentable sugars to be fermented into bioethanol by the yeasts. As lignocellulosic raw materials are renewable, low cost, and do not compete with food and feed chain, their use for bioethanol production is then promising and also promote the sustainability.

2.3.2.2 Hemicellulose-based Bioproducts

Hemicelluloses are likely to degrade during pretreatment steps such as hydrothermal treatment, steam explosion, acid hydrolysis, and organic solvent treatment. Hence, the fraction of hemicelluloses is seemed to be the most underutilized fraction during the conversion of lignocelluloses to bioproducts. This vulnerable fraction can be value added by pre-extracting it before processing of cellulose fraction (Zhang et al. 2011). Several bioproducts from the hydrolysate of this hemicellulose fraction are as follows:

Lactic acid (LA) is a well-known industrial organic acid that can be used as feedstock for various valuable products, especially cosmetics, chemicals, pharmaceuticals, and biopolymers, namely poly-lactic acid (PLA) (Rahman Mohan 2016). PLA could be a promising candidate to substitute petrochemical-based plastics for fabrication of prosthetic equipment, packaging, and delivery of drug due to its high biodegradability and biocompatibility (Cubas-Cano et al. 2019). LA can be mainly produced through microbial fermentation of both C6 and C5 sugars (Patel et al. 2004) but when sugars from hemicellulose hydrolysate are used the detoxification of potential inhibitors might be needed (Moldes et al. 2006). To valorize hemicellulose hydrolysate for bioproduction of LA, in most cases the heterofermentative lactic acid bacteria are used (Patel and Shan 2021).

Xylitol is another predominant product from hemicellulose fraction. It can be used as a low-calorie sweetener supplemented in chewing gums, toothpastes, and products for diabetics. Because of its low-caloric and potent anti-carcinogenic functions, it is also applied in food industry as sugar substitutes (Irmak et al. 2017). As the biological method is more eco-friendly, sustainable, and requires low energy consumption, the conversion of xylose into xylitol by microbial fermentation is recognized as a promising alternative to the current chemical process at commercial scale. The biological production of xylitol from hemicellulose fraction involved pretreatment step of lignocelluloses by acid/enzymatic hydrolysis, harvesting and detoxification of hemicellulose hydrolysate (xylose), subsequent bioconversion of xylose into xylitol, and downstream process for purification (Mussatto 2012; Cortez et al. 2016).

Xylooligosaccharides (XOS) are composed of xylose-oligomers linked with β-1,4-glycosidic bonds. XOS are recognized as soluble dietary fibers which can enzymatically be produced from hemicellulose fraction, specifically xylan, in crop stalks, straws, and wood. XOS has also been considered as potential prebiotics and other health-care products. Prebiotics are defined as non-digestible fibers that have health benefits to host through selective stimulation of the growth of beneficial bacteria, namely probiotics, in the colon (Gibson and Roberfroid 1995; Carvalho et al. 2013; Faryar et al. 2015). This biological activity of XOS depends on the polymerization degree varying from 2 to 12. XOS with polymerization degree less than 4 can stimulate the growth of probiotics in the human colon like bifidobacteria. In addition, the assimilation of XOS by bifidobacteria also enhances the production of short chain fatty acids which involve in prevention of colon cancer (Carvalho et al. 2013). XOS containing uronic acid as branches has biological properties as anti-allergic agent and antioxidant (Jain et al. 2015).

Polyhydroxyalkanoates (PHA) are biodegradable bio-based polymers that have potential in an integrated biorefinery (Snell and Peoples 2009). PHA can substitute commercial plastics like polypropylene and polyethylene due to their high biocompatibility and biodegradability. However, the industrial PHA production cost is still high due to the high cost of raw materials used for PHA production (Dietrich et al. 2017). The production of PHA from hemicellulose fraction is a potent approach to make second-generation biorefinery more feasible and help contribute to reduction of production cost. PHA are mainly produced by heterotrophic bacteria. One of the commercially available PHA is polyhydroxybutyrate (PHB). PHBs are found as intracellular components of bacteria. Their content may exceed 8% of dry biomass under nutrient-starvation and high ratio of carbon to nitrogen (Troschl et al. 2017). Among photosynthetic microorganisms, several cyanobacteria and microalgae have been found to be able to accumulate PHA under their mixotrophic growth and nutrient-limitation (Samantaray and Mallick 2014).

Furfural is a derivative of pentose sugars from second-generation feedstocks during pretreatment/hydrolysis of hemicellulose fraction (Mathew et al. 2018). Furfural can act as a platform chemical for the production of furfuryl alcohol, levulinic acid, and tetrahydrofuran and can be applied in various industries such as for production of inks, fungicides, nematicides, fertilizers, flavoring compounds, plastics, antacids, and adhesives (Raman and Gnansounou 2015).

2.3.2.3 Lignin-based Bioproducts

Lignin is one of the main compositions in lignocellulosic biomass with considerable amount of 15–25% based on dry weight and is also the second most abundant terrestrial biopolymer. It is a high-volume end product from lignocellulosic-based industry. It can be extracted from wood, dedicated crops, and agricultural wastes by different processes. Lignin is mainly composed of three phenylpropane monomers including coniferyl, p-coumaryl, and sinapyl alcohols. These monomers are cross-linked by different types of stable chemical bonds making them hard to be degraded by microorganisms (Achyuthan et al. 2010; Aadil et al. 2019). The lignin can be valorized to higher-value products such as coatings and binders and also as a functional ingredient (Fache et al. 2016). Lignin fraction is recognized as a low-value byproduct obtained from the production of second-generation ethanol. Therefore, the valorization of lignin should be integrated to pursue sustainable and cost-effective biorefinery (Schutyser et al. 2018). It is a challenge to use lignin for the production of commercially high-value products due to its complex structure. Based on the specific characteristics of lignin, different industrial commodities can be produced. These include aromatics, resins, carbon fibers, fuels, adhesives, and dispersants (Azadi et al. 2013).

2.3.2.4 Lignocellulosic Biomass-based Biochar

Biochar is a black carbon obtained from pyrolysis process of lignocellulosic biomass and can be used for construction materials, soil amendment, catalysts in a fuel cell, and for bioenergy production, and also contribute to CO_2 sequestration (Sharifzadeh et al. 2019; Yang et al. 2019). Current researches revealed that biochar with large pore size and specific surface area could improve its adsorption feature. Modification of substrate-induced uncertainty by biochar has been reported to significantly improve anaerobic digestion and also reduction of GHGs emission (Fagbohungbe et al. 2017; Masebinu et al. 2019).

2.3.2.5 Crude Glycerol-based Products

Crude glycerol is a byproduct generated approximately 10% (w/w) of the biodiesel produced via transesterification reaction. The impurities in crude glycerol depend on the type of catalyst used, oil-alcohol ratio, recovery method, and conversion yield. The amount of crude glycerol generated greatly increased along with the increasing biodiesel production. Therefore, many researchers are attempting to valorize crude glycerol into high-value products. Crude glycerol can also be used as supplement in animal feed (Kerr et al. 2007). It has been used as a promising feedstock for bioproduction of various biofuels and bioproducts like syngas, butanol, citric acid, 1,3-propanediol, docosahexaenoic acid, and polyhydroxyalkanoates (Yang et al. 2012). Other studies also show that glycerol can be used as a carbon source for production of microalgal biomass and lipids (Katiyar et al. 2017). However, these crude glycerol-based products still need further studies to make them economically feasible for incorporation into biorefinery (Mishra et al. 2019a, 2019b).

2.3.3 Third-Generation Biorefinery

Third-generation biorefinery can be called advanced biorefinery because of the feedstocks and techniques used to proceed. The third-generation biorefinery uses specific microorganisms, microbe, and microalgae as its feedstocks (Gonzalez and Kafarov 2011). Microalgae are photosynthetic single cell that can be found in various environments, under a wide range of environmental conditions. They can grow at 20–30 times faster growth rate than food and oil crops and also throughout the year in various climates. Their biomass productivity is then much higher than those of land crops (Chisti 2007). Not only biofuel, microalgae are also known as photosynthetic microorganisms using solar energy for production of other high-value bioproducts (Leu and Boussiba 2014; Venkata Mohan et al. 2015). Microalgae can be cultivated in various cultivation modes, i.e. photoautotrophic, heterotrophic, and mixotrophic systems (Devi et al. 2013; Chandra et al. 2014). Third-generation biofuel production has been established as integration of upstream and downstream processes. However, some major limitations still remain in downstream process such as harvesting and dewatering of microalgal biomass those require intensive energy and cost. Because of relatively low biomass productivity from photoautotrophic cultivation modes, microalgae bioprocesses have been shifted toward heterotrophic and mixotrophic modes and implemented for production of multiple products through biorefinery concept (Rohit and Venkata Mohan 2016; Yen et al. 2013).

Integration of third-generation biorefinery with wastewater treatment would achieve effective utilization of waste stream for production of microalgal biomass which helps reduce overall waste components and support sustainable economics. The residual microalgal biomass after extraction of lipids and pigments that contains high content of starch can be digested anaerobically to produce either biohydrogen or biogas. This biorefinery approach is more economical attractive than extraction of only one single product. The composition of microalgal biomass is also critical for the production of multiple bioproducts such as human food products, cosmetics, pharmaceuticals, nutraceuticals, biofuels, and animal feed. The suitable microalgae species should be selected and their cultivation conditions should be optimized (Brennan and Owende 2010; Fasaei et al. 2018). Recently, microalgal exopolysaccharides (EPSs) have gained considerable attention in the viewpoint of growing demand for the use in a wide range of medical, biotechnological, and industrial applications as potential antibacterial, antioxidant, and emulsifier. In addition, microalgal cell surface-attached EPSs have also attracted attention due to their effects on flocculation property, dewatering of biomass as well as water quality (Xiao and Zheng 2016; Liu et al. 2016). As microalgal EPSs are composed of various monomers such as sugars, proteins, nucleic acids, and lipids, they are also interesting products in the third-generation biorefinery (Xiao and Zheng 2016).

The microalgal biomass after valuable component extraction can be further used in a wide range of bioprocesses such as feedstocks for fermentation and anaerobic digestion to produce biohydrogen and biomethane (Subhash and Venkata Mohan 2014). Thermochemical conversion has been used to convert microalgal biomass into biochar and bio-oil (Agarwal et al. 2015; Sarkar et al. 2015). Microalgal biomass with high content of glucose-based carbohydrates is likely the most promising feedstock for production of third-generation bioethanol. Other high-value co-products would contribute to third-generation biorefinery as well as support the economics of the processes (Venkata Mohan et al. 2015). To preserve other high-value co-products the suitable extraction methods and steps should be carefully selected (Gerardo et al. 2014).

The potential of microalgae in third-generation biorefinery has gained much attention for the production of pharmaceuticals, biofuels, food, and feed (Faried et al. 2017). Recently, oleaginous microalgae have been evaluated as zero-waste biorefinery feedstocks. An efficient zero-waste biorefinery process for oleaginous microalgal biomass was attempted to extract pigments, produce biodiesel and fermentable sugars. This process includes acetone extraction for pigment recovery, subsequent direct transesterification of microalgal lipids into biodiesel, and acid hydrolysis of carbohydrate content in lipid-free residual microalgal biomass residues (LMBRs) to produce fermentable sugars (Mandik et al. 2020). LCA is required to quantify all resources needed for production of microalgal biomass and also downstream process such as biomass harvesting, extraction and purification methods for each component. The GHGs emissions and their impact on environment should be calculated as well. Beyond this, the economic analysis is also a key factor to carry out the third-generation biorefinery. These tools help understand the feasibility of the selected scenarios and provide potential pathways to accomplish the industrialization of third-generation biorefineries (Koyande et al. 2019).

2.4 State of the Art

In a resource biorefinery, fractionation of the resources into their structural components, i.e., cellulose, hemicellulose, lignin, carbohydrate, protein, lipids, and fiber, is very important for their further valorization. The fractionation methods used in the zero-waste biorefinery should be able to separate each component while facilitate their recovery with high yield and minimize subsequent purification. Examples of fractionation methods are hydrothermal, alkali, dilute acid, steam explosion, use of organic solvent and their combinations. In the second-generation biorefinery of biomass feedstock, pre-extraction of hemicelluloses and lignin and subsequent production of high value-added products like ethanol, sugar-based polyesters, biopolymers, and other chemicals have been proposed as a promising approach for zero-waste biorefinery (Lin and Luque 2014).

Pretreatment is a crucial step for breaking down a firmly intertwined matrix of recalcitrant lignocellulosic biomass. Extraction of lignin, partial or total extraction of hemicellulose as well as reducing crystalline fraction of cellulose and polymerization are required to make biomass more suitable for hydrolysis steps to produce sugar monomers and other fermentable compounds. Several combinations of physico-chemical and biological methods have been attempted to improve the digestibility of biomass (Alvarado-Morales et al. 2009). Production of cellulose hydrolyzable fraction is the first criterion for choosing the pretreatment methods in the second-generation biorefinery. Traditional pretreatment and conversion processes use thermal and/or chemical methods that are relatively energy-intensive processes and pollute the environment (Christopher et al. 2014; Baeyens et al. 2015).

Alternative approaches using biotechnology may be able to address these challenges. Biotechnology is the discipline involving biological processes, and this also includes any other methods that use living cells or cell components for bioproduction or to improve agriculture and healthcare, modify and develop products and living cells for specific use. The growth in the economy requires unlimited energy resources, large-scale practices, and inexpensive feedstocks to produce high-value products (Stuart and El-Halwagi 2012). Biotechnology for bioenergy production has been extensively performed in response to the growing demand for biofuel through biomass conversion as renewable energy sources. Therefore, biotechnology process is considered the best option for substituting chemical processes in biorefinery (Haddadi et al. 2018). A techno-economic analysis has also revealed that it was possible to apply biotechnology for brewer’s spent grain biorefinery by co-production of xylitol from xylose, ethanol from cellulose, and polyhydroxybutyrate from organic acids. This strategy would greatly contribute to zero-waste biorefinery and is feasible in the viewpoint of economic and energy consumption (Davila et al. 2016).

Biotechnological approach in second-generation biorefinery has been challenged to convert hemicellulose and cellulose in the biomass feedstock into biofuel and bioproducts. For such second-generation feedstocks directed biorefinery needs an effective pretreatment technique to enhance the enzyme accessibility and degradation. The pretreatment and enzymatic hydrolysis require effective enzyme cocktails to degrade rigid structure of the polysaccharides and saccharify to monosaccharides. The enzymatic hydrolysis is a specific and environmental friendly approach over thermos and chemical hydrolysis. In addition, as enzymatic hydrolysis occurs at a mild temperature, it does not generate sugar derivatives that potentially inhibit the fermentation microbes during bioproduction. Recently, the pretreatment methods have been developed to reduce the enzyme loading for hydrolysis. Ionic liquids are one of candidates that have been used for biomass pretreatment. This method not only reduces the formation of inhibitors but also has high recovery yield and lower energy requirement (Nguyen et al. 2010; Abe et al. 2010). Ionic liquids tend to change the plant cell wall structure, increase accessibility of cellulose, and decrease crystalline structure of cellulose (Putro et al. 2016). However, the efficient enzymatic conversion is still one of the main bottlenecks for second-generation biorefinery. Therefore, new milder pretreatment, new types of enzymes, processing regimes, recovery techniques, and product development have been attempted for effectively utilizing all major components in second-generation feedstocks to create new products (Fache et al. 2016).

After pretreatment, cellulose fraction in both amorphous and crystalline forms and some oligosaccharides are obtained. Multiple enzymes catalyzing hydrolysis reaction of the respective parts of cellulose should be introduced during saccharification step (Amoah et al. 2019a, 2019b). Simultaneous saccharification and fermentation (SSF) is a process in which cellulose is enzymatically hydrolyzed into sugars and then microbial fermentation converts these sugars into bioproducts simultaneously in a single unit process. This process is possible because the enzymatic saccharification happens at a low temperature at which the microbes can grow and produce targeted metabolites. In addition, this process can reduce product inhibition to the enzymes and catabolite repression to the fermentation microbes. SSF can also decrease the overall production time and prevent contamination (Ballesteros et al. 2004).

In addition to biomass biorefinery, biotechnology has been also applied for oil feedstock biorefinery. The refined oils used for biodiesel production are considered as first-generation feedstock. Its cost could be as high as 60–80% of the total cost for biodiesel production. Therefore, this feedstock results in high price of biodiesel and less competitiveness (Parawira 2009). It should be noted that the traditional chemical process for biodiesel production conducted at high temperature and high pressure, is not environmental friendly. On the other hand, enzymatic biodiesel production presents the advantages of lower energy requirement, higher conversion yield of oil feedstocks that contain free fatty acids (FFA) at high level. This method also yields crude glycerol with high purity which is suitable for further use in other bioproducts. The development of enzymes in immobilized forms provides easier product recovery and enzyme reuse which contribute greatly to the reduction of production cost of biodiesel (Adachi et al. 2013; Christopher et al. 2014; Amoah et al. 2019a, 2019b).

An approach for better understanding of the sustainability of zero-waste biorefinery is the integration of interdisciplinary methodologies involving technical, economic, environmental, social, and politics areas. Several assessments like LCA, techno-economic analysis (TEA), and social environmental analysis (S-LCA) have been proposed. TEA is performed to assess the technical feasibility and the economic sustainability as well as identify the bottlenecks of the process. During product and process design, TEA can help improve the processes by giving the best choices and establishing promising goals (Shah et al. 2016). Although the LCA of third-generation biorefinery shows its better eco-friendly feature than the fossil fuels, the system still needs to address the techno-economic challenges for the sustainability (Mishra et al. 2019a, 2019b). LCA and TEA of a successful biorefinery depend on factors like availability and abundance of renewable sources, demand for biofuels and co-products, and zero-waste possibility. Further interdisciplinary collaborations would promote biorefinery sustainability and more complex models with assessments of multiple criteria and spatial referenced tools can help evaluate the sustainability of a zero-waste biorefinery (Lindorfer et al. 2019; Silva et al. 2017).

2.5 Limitations and Prospects of Zero-Waste Biorefinery

For successful zero-waste biorefinery model, the process should produce high-value chemical/material products as much as possible instead of low-value but high-volume products. In addition, the process should also provide biofuels (Cherubini 2010). Another challenge for zero-waste biorefinery is the development for sequential extraction and bioconversion of the components in the biomass, i.e. lignin which has complex structure, low solubility, and low reactivity. These characteristics hinder its use for extraction and production of value-added products (Park et al. 2018). Recently, lignin has been transformed into either fuels or value-added products via chemical/biological methods (Dragone et al. 2020). However, the zero-waste biorefinery still faces some limitations including technical and economical feasibility, environmental footprints, and geographical location (Dutta et al. 2014). Scaling up biorefinery dealing with a large amount of feedstocks is a challenging step that needs efficient manufacturing operations and downstream facilities. On the other hand, the effective management of processes and regulatory concerns will help facilitate process and product innovations in biorefinery (Sanford et al. 2016).

Biorefinery requires process and product innovations to offer great opportunities for all industrial and economic sectors. Moreover, building bioeconomy can also help overcome present limitations and shift to environmentally benign industry (de Jong and Jungmeier 2015). The innovation sectors should precisely consider the integration of understandings and knowledges in the areas of low carbon societies, sustainability, and closed-loop business goals those are driving modern bioeconomy. The zero-waste biorefinery should be highly energy efficient and able to make use of all components following the zero-waste concept and allow all industrial sectors to manufacture environmental friendly and marketable products with minimal carbon and water footprints. In addition, the zero-waste biorefinery should consider possible unintentional competitions of resources and feedstocks, water supply, product quality, land usage, GHGs emission and impact on biodiversity (Zondervan et al. 2011; Van Dael et al. 2014).

2.6 Conclusion

The developing zero-waste biorefinery plays an essential role in stimulating the production of commodity bioproducts with no underutilized components. Different bioproducts and biofuels are produced while the values of all intermediates are maximized and the overall production costs are reduced. The production process should be designed to separate each component with high yield and facilitate their further purification or bioconversion. During the whole production life cycle, energy requirement should be minimized and the use of hazardous chemicals should be avoided. Moreover, overall processes should be environmental friendly with minimal carbon and water footprints. Biotechnological approach presents great opportunities for sustainable zero-waste biorefinery. The limitations and prospects of zero-waste biorefinery have been summarized.

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Chapter 3
Waste Biorefineries Facilities: The Feedstock Choice

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Abstract This chapter provides an overview of waste feedstocks and their potential applications in new biorefineries. The fundamental aspects of the biorefinery are discussed, focusing on thermochemical, chemical, and biochemical processing methods. Recent literature reports are reviewed, which explore the main feedstock wastes used in biorefineries (lignocellulosic biomass, municipal solid waste, food waste, oil-based wastes, and sewage sludge). The chapter also includes characteristics of biorefineries processes, their pros and cons, conversion processes, and applications. Finally, the chapter presents the main conclusion and appropriate recommendations.

3.1 Introduction

In the face of the economic collapse—the largest since the great depression of the 1930s—driven by the coronavirus outbreak, authorities around the world are currently developing recovery programs at a remarkable scale to shape infrastructures and industries for the next few decades. The major goals are to mitigate unemployment and re-stabilize industry and commerce. However, if well designed, parts of these packages are to enhance the sustainability of the energy sector, with a potential goal to develop a cleaner, more secure, resilient, and cost-effective energy system (Markard and Rosenbloom 2020). In this scenario, waste-based biorefineries can play a vital role in the economic recovery of states.

In a world with finite resources, energy recovery from waste or residues is a key to establishing a sustainable economy. Every year, an estimated 9–11 billion tons of waste are produced globally, which is incessantly increasing day by day (Badgujar and Bhanage 2018; Chen et al. 2020). To meet the growing energy demands and the reduced depletion of fossil resources, the waste-to-energy approach holds a significant role in mitigating the challenges facing waste management. Currently, landfill

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to waste disposal remains the most common method of waste management, particularly in developing countries as this method is simple and relatively inexpensive. While this approach is an effective waste management system, if not managed correctly, non-sanitary landfills become a significant source of greenhouse gases emissions, soil and groundwater contamination, unpleasant odors, leachate generation, and disease spreading vectors, flies, and rodents (Kim and Owens 2010; Rehan et al. 2019).

Several definitions of biorefinery have already been reported in the literature (Cherubini 2010; de Jong and Jungmeier 2015; Solarte-Toro et al. 2021). However, they all refer to the processes that convert biomass into a range of marketable bio-based products and bioenergy (IEA 2008). The feedstock is an integral part of the biorefinery system, and its choice is critical in the definition of techno-economic viability, availability, and sustainability metrics.

Residues from lignocellulosic biomass, organic residues (mainly municipal solid waste and food waste (FW)), oil-based wastes, and sewage sludge are among a few potential feedstocks for waste biorefineries. These types of biorefinery can be employed to produce biofuels, bioenergy, platform chemicals, biofertilizers, soil conditioners, and bioplastics (de Jong et al. 2012; Venkata Mohan et al. 2016). However, the choice depends on the target products, feedstock availability, and facility structure. In this sense, this chapter aims to discuss the main waste feedstocks used in biorefineries, their pros and cons, recent literature reports, and their applications.

3.2 Waste Biorefineries

Understanding the available feedstocks, their compositions, and the target products is crucial to facilitate efficient waste valorization and choose the ideal bioconversion process. Depending on their source, the wastes can present many valuable compounds, which include carboxylic and other acids, carbohydrates, proteins, nitrogen, phosphorus, and metals. When combined with the biorefining process, they can be transformed into high-valuable products such as food additives, chemicals, biodegradable polymers, and bulk products, such as materials and energy. Numerous sources of waste are explored in the biorefinery concept. In this chapter, we focus on the major sources of waste, which are (i) lignocellulosic biomass, (ii) municipal solid waste, (iii) FW, (iv) oil-based wastes, and (v) sewage sludge (Fig. 3.1).

The conversion processes of wastes are grouped into three major categories: (i) thermochemical pathway, where high temperature is applied to feedstock using chemicals as a solvent, such as liquefaction, pyrolysis, and gasification; (ii) transesterification process based on chemical conversion, in which the wastes are treated with chemicals; and (iii) biochemical process, where the waste feedstock is converted into value-added products through enzymes or microorganisms, as in anaerobic digestion and fermentation. Figure 3.2. summarizes these pathways. To

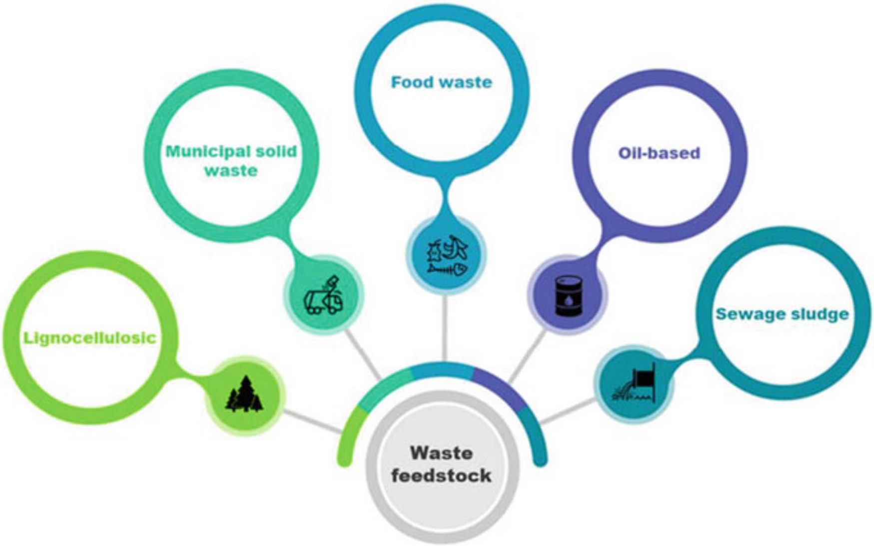

Fig. 3.1 Major waste feedstocks for biorefineries facilities

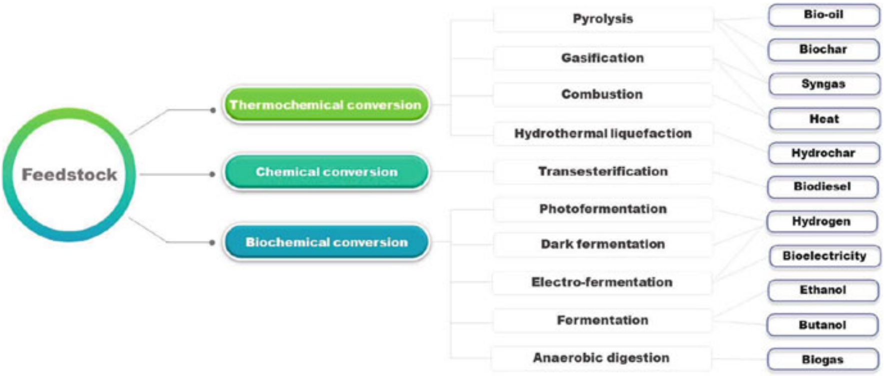

Fig. 3.2 Main waste valorization pathways for energy purposes

improve the biorefinery efficiency, a combination of two or more conversion routes is employed in process integration (Tsegaye et al. 2021).

Thermochemical conversion is considered the most versatile technology applicable to many waste feedstocks. This technology uses severe treatment under high temperatures and in some cases high pressure to generate energy and high-value products (Labaki and Jeguirim 2017). Operating conditions and the end products are the differences between the variants of this category.

Combustion is carried out under severe oxidative conditions and high temperatures (800–1000 °C), to generate heat (Materazzi and Foscolo 2019). As alternatives to combustion, gasification and pyrolysis are the refined thermochemical methods aimed to generate solid, liquid, or gaseous biofuels. Characteristically, for pyrolysis temperatures between 300 and 800 °C are employed and are divided in slow, intermediate, and fast processes, based on their different temperatures, residence times, and heating rates (Santos et al. 2020). Regardless of the type of pyrolysis, the same energy products are generated (bio-oil, biochar, and syngas). For gasification, O_2, CO_2, steam, or supercritical water treatments are applied on the waste feedstock at high temperatures from 800 to 1000 °C. From this reaction, syngas and heat are generated (Lee et al. 2020). Thermochemical liquefaction requires a moderate temperature (250–400 °C) and high pressure to obtain biocrude oil, biochar, and gases, in which the volume of liquid oil generated is higher than that of biochar and gaseous products (Maroneze et al. 2019).

The chemical wastes conversion is the transesterification of catalyzed process, where fats and oils are converted to fatty acid methyl ester, known as biodiesel and glycerol, using catalysts to increase the rate of chemical reactions. This reaction has been widely used to produce biodiesel from waste cooking oil and waste animal fats (WAFs). In the transesterification process, alcohols like methanol and ethanol are used for chemical reactions owing to their low cost and high availability. The transesterification can be performed with many catalysts including alkalis, acids, and enzymes (Tan et al. 2019; Karpagam et al. 2021).

Bioconversion is the conversion of plant or animal waste into value-added products or usable products through the process of waste transformation, using biological agents such as whole cells or purified enzymes. The bio-based production is environmentally sustainable, clean, and eco-friendly as they are bio-processed at room temperatures (or close), using atmospheric pressure and free of harsh chemical catalyzers (Mu et al. 2010). Moreover, bio-based production generates minimal by-products and demands low energy (Bilal et al. 2021). Nevertheless, a prior thermochemical or chemical treatment of feedstocks is vital for efficient bioprocessing (Behera et al. 2014; Kiran et al. 2017). Biochemical transformation of biomass can be achieved through three pathways: anaerobic digestion, fermentation, and enzymatic catalysis. The combination of these processes or only one process can generate a broad range of products such as biofuels, biogases, bioplastics, oligo- and monosaccharides, bioactive molecules, and lignin derivatives (Cho et al. 2020).

Anaerobic digestion is a waste-to-energy technology commonly used at different scales globally to produce energy and fertilizers. It occurs naturally at temperatures between 35 °C (mesophilic) and 55 °C (thermophilic) when high amounts of wet organic matter accumulate in the absence of oxygen (Meegoda et al. 2018). In this bioprocess, anaerobic microorganisms convert different feedstocks, mainly food wastes and animal manure, into biogases comprising 60–70% methane, 30–40% CO_2, and a solid nutrient-rich residue useful for crops applications (Xu et al. 2018).

Fermentation is the most versatile method for bioconversion processes owing to a broad range of available carbon sources, microorganisms, and products. Thus, fermentation is defined as the metabolic process that produces chemical changes, through a sequence of enzymatic actions that microorganisms perform, to generate energy through the oxidation of organic compounds (substrates) and the reduction of an endogenous electron acceptor. Fermentation in the field of biochemistry is an anaerobic process for energy production. However, in its broad definition, it refers to any process where the action of microorganisms brings the desired change in the substrates (Godbey 2014). The products, efficiency, and yield of fermentation depend on the substrate, the catalyst (as isolated enzymes or whole cells), and the process conditions (Tomasik and Horton 2012). Therefore, fermentation is grouped into different subcategories in biorefineries application.

Dark fermentation is a process developed for biohydrogen production performed in the dark under anaerobic conditions using pure cultures or mixtures of microorganisms since it is related to the acidogenic stage of the anaerobic digestion process (Antonopoulou et al. 2011). Photo-fermentation is a process of converting organic compounds such as volatile fatty acids (VFA) into H_2 and CO_2 through the action of photosynthetic microorganisms to produce chemical energy from sunlight to power metabolic enzymatic reactions (Sağır and Hallenbeck 2019). Nevertheless, two-stage processes using sequential dark and photo-fermentation have been used to increase overall biohydrogen yield since this parameter is higher in photo-fermentation systems (Chen et al. 2008). Dark fermentation has lower production costs than photosynthetic methods as it is characterized by ambient temperatures and pressures. Moreover, it uses less expensive photo-bioreactors, such as organic wastes from agroindustry or sewage as substrate (Antonopoulou et al. 2011).

The most applicable bioconversion process in the biorefinery context is the fermentation of carbohydrates, mainly monosaccharides, and products transformation (e.g., organic acids and alcohols) to synthesize organic metabolites of commercial interest. The products spectrum from this type of fermentation is biofuels, organic acids, polysaccharides, amino acids, vitamins, antibiotics, solvents, and proteins (Anderson 2009). In search of bioprocesses with high yields and productivities, the performance of biological catalysts, i.e., microorganisms or enzymes, has been enhanced by genetic and protein engineering, genomic mining, and adaptive laboratory evolution (Utrilla et al. 2012).

3.3 Waste Feedstocks

From a biorefinery perspective, feedstock is any raw material that can be converted into value-added products. Feedstocks are grouped into three main categories: the first generation that uses edible crops; the second generation that uses non-edible crops, agro-industrial residues, and other wastes (e.g., municipal and food), and third generation that are microalgae-based processes (Moncada et al. 2014). First-generation biorefineries are considered sustainable and economically feasible platforms in the USA and Brazil where bioethanol is produced from corn and sugarcane. Nevertheless, some ethical issues still exist regarding the use of edible crops for synthesizing non-edible products (Albonetti et al. 2019. The second- and third-generation biorefineries are also sustainable and economically feasible platforms that avoid the ethical concerns mentioned above (Badgujar and Bhanage 2018).

However, probably the most studied is the concept of second-generation biorefinery, in which the processes generate waste feedstock (Albonetti et al. 2019; De Bhowmick et al. 2018). This waste feedstock includes agro-industrial (lignocellulosic) residues, municipal solid wastes, food wastes, waste cooking oil, and animal fats.

3.3.1 Agro-industrial Waste

With the rapid population growth, the agribusiness industry has experienced accelerated development, recording revenue of 75 billion dollars in 2017. However, this development has turned agro-industrial wastes into an important environmental problem, since more than five million metric tons are produced yearly (Ravindran et al. 2018; Mehmood et al. 2021). Residues from agroindustry and timber are attractive biorefinery platforms because the content of starch, xylan, glucan, and lignin contains useful compounds for bio- and chemical conversions. Lignocellulose comprises approximately half of the plant's biomass, and it is the most important renewable resource (Sánchez 2009). Lignocellulose has three main components: cellulose (35–50%), hemicellulose (20–35%), and lignin (15–25%), and it is a rigid structure organized as an intricate complex of polymers linked by covalent and non-covalent bonds (Fig. 3.3) (Vargas-Tah et al. 2015; Kohli et al. 2019). Other minor components of lignocellulose include vitamins, organic acids, volatile

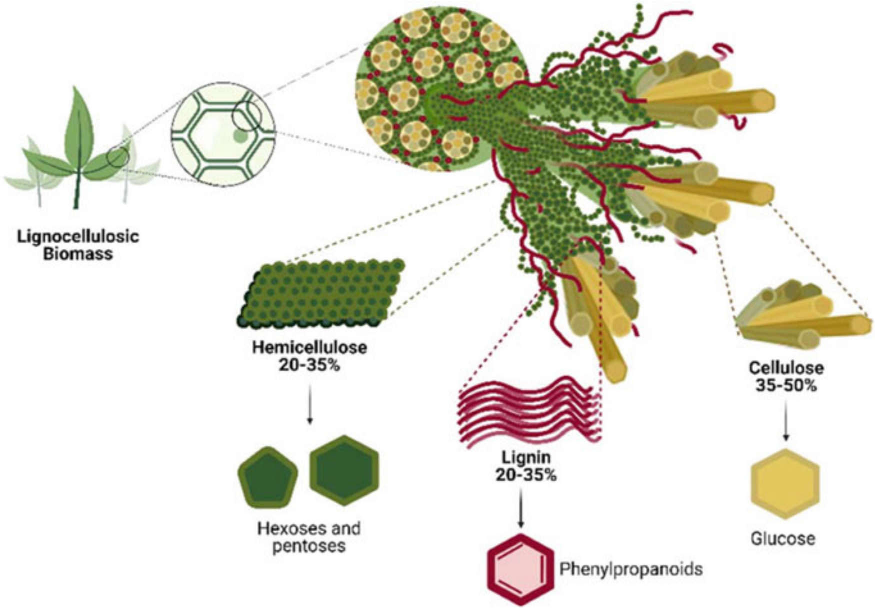

Fig. 3.3 Structure of lignocellulose

compounds, fats, proteins, and inorganic compounds (mainly minerals) (Kumar and Sharma 2017).

Cellulose is a crystalline structure of glucose homopolysaccharides, linked and stabilized by β(1–4) glycosidic and hydrogen bonds, respectively (Kannam et al. 2017). Hemicellulose is a branched acetylated heteropolymer composed of xylose, glucose, and arabinose. Stabilized by hydrogen bonds, hemicellulose contains lower amounts of galactose, mannose, and cellobiose, in a less organized structure than cellulose (Kumar et al. 2019). Finally, lignin is an amorphous aromatic polymer synthesized from monolignols such as guaiacyl, *p*-hydroxyphenyl, syringyl, *p*-coumaryl, sinapyl, and coniferyl alcohols (Uzuner et al. 2018). Lignin is found on the exterior of the lignocellulose macro fibrils, covalently attached to hemicellulose, and acted as a crosslinker for cellulose and hemicellulose. Moreover, lignin facilitates rigidity to the cell wall and protects the cellulose structure (Kumar et al. 2019). Physicochemical and thermochemical treatments are often used to hydrolyze the structure due to the recalcitrance of lignocellulose and mechanical support. Physicochemical and thermochemical treatments also help to obtain hemicellulosic monosaccharides, organic acids mainly acetate, volatile compounds such as furans, phenolic lignin derivatives, amorphous cellulose, and low amounts of glucose monosaccharides (Kumar et al. 2009). Since glucose is the preferred substrate for bioconversion processes, additional steps are required to break the amorphous cellulose into free glucose molecules. Therefore, enzymatic saccharification is often used for this purpose (Guo et al. 2018). A wide spectrum of agro-industrial residues can be used as feedstocks in biorefineries. These include bagasses, straws, corn stover and cobs, seeds, coffee pulp and grounds, grasses, and nuts shells. Timber wastes are another important source of lignocellulosic feedstocks that generate a significant amount of residues such as branches, chunks, and sawdust from the cutting process of soft and hardwoods.

Sugarcane bagasse (SCB) is one of the most available wastes, being Brazil, India, and China the top producers of SCB in the world. Since 270 tons of this residue can produce 1000 tons of processed sugarcane, then approximately 600,000 million tons of SCB are generated yearly (Loh et al. 2013; Martinez-Hernandez et al. 2018). The average compositions of SCB are 40–45% cellulose, 30–35% hemicellulose, 20–30% lignin, and up to 2% ashes (Parameswaran 2009; Cardona et al. 2010; Alokika et al. 2021). The SCB is more advantageous for bioconversion processes owing to its low ash content and the higher yield of 80 t/ha per year, compared to 11–17% ashes and 1–20 t/ha per year of other wastes such as straws, grasses, and woods (Pandey et al. 2000). SCB offers benefits to logistic management as it has already been collected in the sugar mill and bioethanol factories, thereby reducing processing costs. Bioprocess techniques to convert SCB into value-added products are divided into a) liquid fermentation, where the whole or hydrolyzed bagasse is utilized, and b) solid-state fermentation, where the SCB is applied as the carbon source or as inert support (Pandey et al. 2000). Although SCB has mainly been used for bioenergy and biofuels production, its versatility in cultivating microorganisms enhances the development of the synthesis of alcohols, composites, polymers, fibers, proteins, etc. Table 3.1 summarizes some processes from SCB to the synthesis products.

Table 3.1 Production of value-added compounds from different lignocellulosic sources

Agro-industrial waste	Conversion process	Product	Yield/Titer	Region	Reference
Sugarcane bagasse	TCH/ES/fermentation	Fuel ethanol	78%	Asia	Yu et al. (2018)
Sugarcane bagasse	TCH/ES/fermentation	Fuel ethanol	77%	South America	Wanderley et al. (2013)
Sugarcane bagasse	TCH/ES/fermentation	Fuel ethanol	92%	South America	de Araujo Guilherme et al. (2019)
Sugarcane bagasse	TCH/fermentation	D-lactate	~100%	North America	Utrilla et al. (2016)
Sugarcane bagasse	TCH/ES/fermentation	2,3-butanediol	70%	Asia	Zhao et al. (2011)
Corn stover	TCH/ES/fermentation	Fuel Ethanol	76%	North America	Vargas-Tah et al. (2015)
Corn stover	TCH/ES/fermentation	Fuel Ethanol	74%	Europe	Öhgren et al. (2006)
Corn stover	TCH/fermentation	Carboxylic acids	55%	North America	Thanakoses et al. (2003)
Rice straw	TH/ES/fermentation	Ethanol	81%	Asia	Wi et al. (2013)
Rice straw	TCH/fermentation	Butanol	13.5 g/L	Asia	Ranjan et al. (2013)
Oat straw	TCH/fermentation	Biohydrogen	2.9 mol H_2/mol_{hexose}	North America	Arriaga et al. (2011)
Wheat straw	TCH/ES/fermentation	Fuel ethanol	47%	North America	Saha et al. (2005)
Wheat straw	Chemo-mechanical	Nanocomposites	–	North America	Alemdar and Sain (2008)
Wheat straw	TCH/fermentation	Xylitol	59%	South America	Canilha et al. (2008)
Barley straw	TCH/fermentation	Acetone, butanol, ethanol mixture	27 g/L	North America	Qureshi et al. (2010)
Barley straw	TCH/ES/fermentation	Fuel Ethanol	70%	Europe	Paschos et al. (2020)
Sorghum straw	Pulping/bleaching/acetylation	Cellulose acetate	–	South America	Andrade Alves et al. (2019)
Corn cobs	TCH/ES/fermentation	Ethanol	78%	North America	Pedraza et al. (2016)
Avocado seed	TCH/fermentation	D-lactate	94%	North America	Sierra-Ibarra et al. (2021)
Softwood	Co-pyrolysis with zeolite	Aromatic hydrocarbons	86%	North America	Qian et al. (2021)

(continued)

Table 3.1 (continued)

Agro-industrial waste	Conversion process	Product	Yield/Titer	Region	Reference
Aspen	TCH/fermentation	Fuel ethanol	94%	North America	Lawford and Rousseau (1991)
Oak	TCH/fermentation	Fuel ethanol	72%	Asia	Nigam (2001)
Eucalyptus	Aqueous two-phase extraction	Antioxidant phenolics	1.89 mg/100 $\mathrm{mg_{wood}}$	Europe	Xavier et al. (2017)
Eucalyptus	TCH/fermentation	Xylitol	26%	South America	Villarreal et al. (2006)
Eucalyptus kraft pulp	ES	Caffeic acid	233 mg/L	Asia	Kawaguchi et al. (2017)
Cedar	Alkaline copper oxide–peroxide reaction	Vanillin	8.5%	Asia	Qu et al. (2017)
Pine	Oxidation	Vanillin	6.8%	Europe	Mathias and Rodrigues (1995)

TCH thermochemical hydrolysis, *TH* thermal hydrolysis, *ES* enzymatic saccharification

Straw crops include corn, rice, barley, oat, sorghum, wheat, and other grains. However, the straw wastes consist of the remaining dry stalk of the cereal plants after the extraction and removal of grains (Santulli 2017). Straw wastes are abundant since they constitute approximately half of the total biomass of the harvested grains. For example, 1661 million tons, 975 million tons, and 529 million tons of corns stover/cobs, rice straw, and wheat straw, respectively, are annually produced worldwide (Smil 1999; Agwa et al. 2020; Tan et al. 2021). The lignocellulosic content of straw biomass is divided into 32–47% cellulose, 19–27% hemicellulose, 5–24% lignin, and 13–20% ashes (Zaky et al. 2008; Palvasha et al. 2021). The relatively high amount of ashes may be a major drawback for some biotechnological transformations as it decreases the efficiency of thermochemical pretreatment and enzymatic saccharification (Huang et al. 2017). However, the integration of pre-washing steps has improved the global processing efficiency (Singhal et al. 2021). Other processes where straw wastes are widely used to avoid the effect of high ash content include power generation, biogases production, composites, and usage as supporting or filtering materials (Table 3.1).

Forestry wastes are widely used in biorefineries across the North Hemisphere since they are one of the most available agricultural wastes in this region (Galbe and Zacchi 2002). Several studies have recently reported their use around the world. Widespread in most regions are wastes from woods such as oak, aspen, eucalyptus, poplar, teak, pine, cypress, spruce, and cedar, commonly used to produce different value-added products (Table 3.1). Another important fraction of woods is bark, commonly used as solid fuel but with interesting and recently reported content of bioactive and antioxidant components (Vangeel et al. 2021). Wood from timber can be divided in two main groups: hardwoods and softwoods. Hardwoods are produced by angiosperm trees, comprising of complex structures and vessels (Wilson and White 1986). Hardwoods are used for a large range of applications that include furniture making, musical instruments, boat building, fine constructions, barrels, and manufacture of charcoal (Merkle and Nairn 2005). Softwoods are woods from gymnosperm trees commonly used in the construction industry and paper pulp (Khana and Ahring 2019). The chemical composition of soft and hardwoods depends on the species, age, and growing conditions. However, the respective average composition of softwoods and hardwoods is 43–45% and 40–55% cellulose, 20–23% and 13–40% hemicellulose, and 28% and 18–25% lignin (Galbe and Zacchi 2002; Dziekońska-Kubczak et al. 2018). Despite the high polysaccharides content that makes timber wastes attractive for fermentation, the high content of lignin-derived phenolic compounds is the main constraint for the biotransformation of these materials as they are toxic for various microorganisms and inhibit saccharification enzymes (Clark and Mackie 1984; Martinez et al. 2000; Palmqvist and Hahn-Hägerdal 2000; Kumar et al. 2012). However, this constraint can be turned into benefits to produce other high-value aromatic chemicals such as lignosulphonates, vanillin, and antioxidants (Table 3.1).

3.3.2 Municipal Solid Waste

The escalating population growth has increased the consumption of energy and goods, generating more than two billion tons of municipal solid wastes globally, being India, the USA, and China the major producers (Waste Atlas 2018). Unfortunately, 33% of these residues collection or recycling are not effectively managed (Nanda and Berruti 2021). Municipal solid wastes (MSW) comprise residues from households, offices, educational institutions, and commercial enterprises, and they vary according to the region and income (Funk et al. 2013). However, a general classification organizes them into recyclables, compostable organic matter, toxic substances, and solid wastes (Millati et al. 2019). The MSW treatment includes landfilling, composting, waste-to-energy conversion, recycling, and incineration (Rao et al. 2017). Of these management strategies, only the transformation of MSW into energy is applied to the biorefinery context. The energy is produced from biohydrogen or methane through the organic fraction of MSW, composed predominantly of food wastes, minor quantities of office paper, yard wastes, and corrugated newspapers (Ghosh et al. 2020). The high variability of organic MSW and the reluctance of people to separate their wastes are the major challenges facing biogas production (Appels et al. 2011). A more detailed review of value-added products synthesis from food wastes is presented below.

3.3.3 Food Waste

The Food and Agriculture Organization of the United Nations (FAO) defined food waste (FW) as food and inedible parts removed from the human food supply chain in the following sectors: food products manufacturing, food/grocery retail, food service, and households (FAO 2011). The organization estimated that one-third (approximately1300 million tons) of food produced for human consumption is lost or wasted every year, generally dumped or incinerated with municipal solid waste (Xu et al. 2018). These wastes are characterized by high moisture content that generates dioxins from incineration, whereas dumping in open areas is associated with huge social, environmental, and economic problems.

The FW composition presents a high energetic value, consisting mainly of 30–60% carbohydrates, 5–20% proteins, 10–40% lipids (w/w), and traces of inorganic compounds (Kwan et al. 2016; Dhiman and Mukherjee 2021). However, the composition varies by source. For example, animal-based wastes are rich in lipids and proteins, whereas plant-based wastes are full of starch and carbohydrates (Ravindran and Jaiswal 2016). The characteristics associated with their homogeneity make these residues excellent candidates in waste biorefinery as they can be converted into a spectrum of biofuels, bio-commodity chemicals, and bio-based materials (Battista et al. 2020; Tsegaye et al. 2021). Table 3.2. presents the process and waste origin of some of these products.

The food manufacturing industries, commercial and households kitchens, and agricultural waste are the major sources of FW. Among the food processing industries, those with the greatest impact are the fruits processing industry as well as vegetables, cereals, meat, dairy, poultry and eggs, seafood, and aquatic products industries. However, approximately 85% of overall FW originate from plant-based products, and only 15% are from animal products chains (Li and Yang 2016).

Plant-based wastes from the food industry are particularly interesting for the renewable energy sector, as it is mainly of a lignocellulosic nature, with high cellulose and lignin content (Ravindran and Jaiswal 2016). These wastes include fruit and vegetable residues (peelings, stems, seeds, shells, and pulp), cereal residues (mainly paddy, wheat, and corn), starch, and sugar. Since this waste is easily obtained with high yield, the production of ethanol through fermentation with *Saccharomyces cerevisiae* is the most common approach for FW valorization. However, many bioproducts can be recovered through different approaches, such as biohydrogen from dark fermentation (Yun et al. 2018), bioplastics and enzymes from fermentation (Tsang et al. 2019), biogas from anaerobic digestion (Xu et al. 2018), and high-value products (e.g., carotenoids, phenolic compounds, nanoparticles, and pectin) from different extraction methods (Ravindran and Jaiswal 2016). As these wastes are mostly made up of complex carbohydrates, a biological hydrolysis processing method is always required. The processing is achieved using acids or alkali. However, substances released may inhibit biological conversion. Thus, enzymatic hydrolysis is the preferred method. In addition to the biological

Table 3.2 Bioproducts from food waste using different conversion methods

Food waste	Process type	Product	Production/ Yield	Reference
Tomato residue	Pyrolysis	Insecticidal bio-oil	37.8%	Cáceres et al. (2015)
Mango seed	Pyrolysis	Bio-oil	28–38%	Lazzari et al. (2016)
Carrot discard juices	Fermentation	Bioethanol	11.98 g/L	Clementz et al. (2019)
Vegetable wastes	Fermentation	Bioethanol	251.85 mg/g	Chatterjee and Mohan (2021)
Kitchen waste	Immobilized lactate oxidase/Fermentation	Bioethanol	30 g/L	Ma et al. (2014)
Beer fermentation waste	Fermentation	Bioethanol	102.5 g/L	Khattak et al. (2013)
Bakery/mixed waste	Fermentation	Lactic acid	230–270 mg/g	Kwan et al. (2016)
Shrimp waste	Solvent extraction	Astaxanthin	0.284 mg/g	Dave et al. (2020)
Dairy wastewater	Microalgae culture	Single-cell oil	0.8 g/L	Ummalyma and Sukumaran (2014)
Bakery hydrolyzed waste	Microalgae culture	C-Phycocyanin	22 mg/g	Sloth et al. (2017)
Catshark viscera	Fermentation	Hyaluronic acid	2.26 g/L	Vázquez et al. (2015)
Shrimp waste	Alkali-acid treatment	Chitin, chitosan	510; 410 mg/g	Khanafari et al. (2008)
Fish skin	Solvent extraction	Acid soluble collagen	25–45%	Bhuimbar et al. (2019)
Shrimp waste	Solvent extraction	Astaxanthin	0.0406 mg/g	Sachindra et al. (2007)
Fish waste	Pyrolysis	Bio-oil	57.1%	Fadhil et al. (2017)

conversions, FW hydrolysates are also an option for growing medium for microalgae, useful in producing a wide range of bioproducts (Kiran et al. 2017).

Animal-based food wastes are from meat, poultry, seafood, and dairy industries. The meat processing industry mainly generates wastes such as horns, hooves, bones, contents of the gastrointestinal tract, hair, and deboning waste (Jayathilakan et al. 2012). In addition, slaughterhouse wastewater contains a high organic load and polluting potential, as it is made up of protein, animal fat, blood, and detergent residues (Maroneze et al. 2014). The seafood industry generates an important source of relevant biomaterials in their wastes, which generally includes viscera, shrimp shells, crab shells, skins, prawn waste, and fish scales (Sharma et al. 2020). Dairy residues consist of complex organic milk constituents, such as fat, casein, lactose, inorganic salts, detergent, and sanitizer residues (Dongre et al. 2020). Residues from the vegetal origin and those of animal origin also present a vast exploitation potential. Any of these sources can be converted into heat, power, or bio-fertilizer through anaerobic digestion. Lactic acid fermentation is used to process meat and poultry waste that produces lactic acid and lactic acid bacteria, which has been applied as probiotic supplements (Ashayerizadeh et al. 2017). Dairy and slaughterhouse wastewater are excellent culture media for microalgae-based processes owing to their high nutritional composition and the absence of inhibitor compounds (Maroneze et al. 2014; Queiroz et al. 2018). The seafood waste is an excellent source of different products and molecules through chemical and biological processing of protein, enzymes, glycosaminoglycans, chitin, astaxanthin, hyaluronic acid, and marine peptones (Vázquez et al. 2013; Sharma et al. 2020).

Besides the potentialities, the lack of techno-economic evaluation of FW data in biorefineries is a challenge. Moreover, the inconsistency in the composition and structural complexity of these feedstocks also make it difficult to use them. Several variables, including the location where the FW was produced, time of picking, and diversified food habits of different cultures, are some of the major factors that significantly affect the composition of the waste (Karmee 2016). Although FW is a zero-value resource, the costs related to collection and transport are a bottleneck that must be considered (Dhiman and Mukherjee 2021).

3.3.4 Oil-Based Wastes

Oil-based waste biorefineries are one of the main refineries, with some liquid fuels such as biodiesel and bio-jet fuel being the main energy added value products (Becerra-Ruiz et al. 2019). Currently, biodiesel production is carried out using feedstocks such as edible vegetable oils (edible feedstocks), non-edible vegetable oils, single-cell oils (microbial lipids), waste cooking oils (WCOs), and waste animal fats (WAFs) from non-edible feedstocks (Adewale et al. 2015). Unlike edible vegetable oils, from which approximately 95% of this biofuel is obtained, WCOs and WAFs contribute to 10% and 6% of biodiesel production, respectively (Mathew et al. 2021). However, the processing of edible and non-edible vegetable oils is restricted in some countries as some of them are considered food products intended for human consumption and for the limited availability of arable land (Pinzi et al. 2014). As the processing of WCOs and WAFs has become relevant for the biofuels production and the pollutants expelled into the environment mitigation, economic and environmental strategies are required to address the problems associated with global renewable energies (Chen et al. 2021).

The sources of WCOs are from fried foods prepared in the food segment (restaurants, households, hotels, etc.), where edible oils (e.g., soybean, canola, corn, olive, and others) and some animal fats (mainly leaf lard) are used for deep immersion cooking (Chen et al. 2021; Singh et al. 2021). As many countries do not have suitable policies for disposing of oily liquid waste, cooking waste oils produced can massively contribute to the pollution of water resources (Gui et al. 2008; Moecke et al. 2016; Singh et al. 2021). WCOs obtained directly from cooking edible food and oil are classified as yellow grease and characterized by a free fatty acid (FFA) content of 8–15% (w/w). However, the WCOs obtained from grease traps processed in sewage facilities to separate grease and oil from wastewater are classified as brown grease and have an FFA content greater than 15% (Adewale et al. 2015; Pinzi et al. 2014; Talebian-Kiakalaieh et al. 2013). In 2019–2020, approximate consumption of edible oils reached 191.71 million tons, in which WCOs production was estimated to reach 57.51 million tons (~30% yield) (Jiang and Zhang 2016; Singh et al. 2021). In green fuel production, waste cooking oils are a possible substitute to other feedstocks owing to their low manufacturing cost compared to conventional edible vegetable oils (2.5–3.5 times lower) (Nanda et al. 2019; Rezania et al. 2019). Different methods are used to produce biodiesel from residual cooking oil, which includes base or acid transesterification (homogeneous, heterogeneous, and enzymatic catalysis), dilution or blending, micro-emulsification, thermal cracking, or pyrolysis, among others. However, due to the high free fatty acids (FFAs) and water content, this waste cannot be used directly, a pretreatment process should be performed, which consequently affects the overall processing costs (Rezania et al. 2019; Singh et al. 2021; Yusuf et al. 2011).

WAFs are obtained as end products from tanneries, slaughterhouses, and meat processing units, serving as a potential cheap feedstock for biodiesel production. In industrial biodiesel production, the most used WAFs are tallow (veal and beef), lard, chicken fat, and fish oil (Adewale et al. 2015; Pinzi et al. 2014; Sander et al. 2018). Animal fats comprise chemical structures similar to vegetable oils, but with a different distribution of fatty acids and an FFAs content ranging from 10 to 25%. This has been one of the main limitations of biofuel production (0.5% w/w FFAs admitted content), and it is an essential parameter in the viability of the biodiesel production process (Alajmi et al. 2018; Bianchi et al. 2010; Veljković et al. 2021). Another technical drawback of using WFAs as feedstock is the high cloud point that limits its use in areas where temperatures do not fall below 4 °C (Bagheri 2017). Despite the above limitations, WAFs have low unsaturated fatty acids, offering several advantages, such as high calorific value, high cetane number, and high oxidation stability (Adewale et al. 2015). In addition, biodiesel production using WAFs as feedstock is the most economical option (USD 0.4–0.5/L) compared to the traditional vegetable oil transesterification (USD 0.6–0.8/L) (Demirbas 2009).

3.3.5 Sewage Sludge

Sewage sludge is an inevitable by-product of the wastewater treatment released from various sources such as houses, industries, medical facilities, street runoff, and businesses (Harrison et al. 2006). Along with the growing world population, industry, and agriculture, the quantity of sewage sludge increases yearly and presents a major ongoing disposal challenge for water management authorities globally. Lack

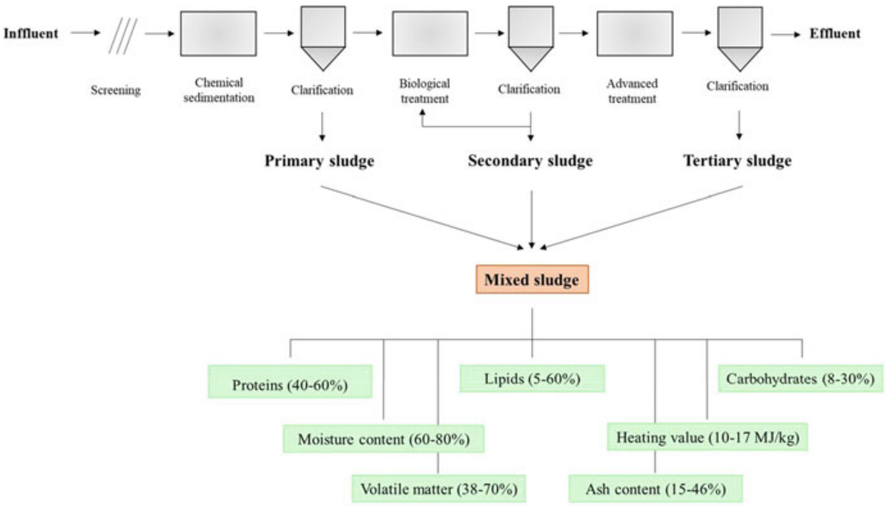

Fig. 3.4 Schematic of the wastewater treatment process and typical composition of sewage sludge (on dry basis). References: Thipkhunthod et al. (2006); Banerjee et al. (2020); Naqvi et al. (2021)

of waste generating data, treatment policies, and use policies of this waste further aggravates its sustainable management. According to Gao et al. (2020), the global sewage sludge production rate was recorded as 45 dry MT per year in 2017.

Sewage sludge contains many harmful elements, such as heavy metals, non-biodegradable organic compounds, pathogens, and dioxins (Zhang et al. 2020). They may also contain chromium, lead, copper, nickel, and other metals of approximate concentrations of between 0.1% w/w and 0.3% w/w (Agrafioti et al. 2013). Inadequate disposal facilities of these wastes cause serious environmental problems and, consequently, affect human health. The treatment and management of sewage sludge comprise approximately 50% of the wastewater treatment cost and 40% of greenhouse gas emissions (Banerjee et al. 2020). Nevertheless, sewage sludge is biomass rich in organic carbon, nitrogen, phosphorus, and inorganic compounds such as silicates and aluminates, in addition to having a high calorific value and a good volatile content. Thus, a promising and alternative way to manage sewage sludge is to use the waste as feedstock using a biorefinery approach (Villalobos-Delgado et al. 2021).

The origin of the wastewater defines the characteristics of the final sewage sludge. Furthermore, the processing stage in which the sludge was removed (primary, secondary, and tertiary) also influences its composition. Figure 3.4 presents a schematic basic wastewater treatment process with a typical composition of produced mixed sewage sludge.

In primary treatment, suspended solids and scum are removed in sedimentation tanks. After this process, the primary sludge will consist of debris, bulk material, and sand. The secondary treatment aims to reduce the biodegradable material, carried out through a biological process, such as activated sludge, moving bed biofilm reactor, sequencing batch reactor, upflow anaerobic sludge blanket, and stabilization ponds. The solid residue originated from this step is mainly composed of extracellular polymers, organic pollutants, heavy metals, nutrients, and microbial assemblages (Banerjee et al. 2020). The tertiary treatment or advanced stage is applied when high-quality waste is required, involving the chemical removal of dissolved nutrients, mainly nitrogen and phosphorus. The sludge collected in this step presents a high concentration of nutrients like NO_3, PO_4, and SO_4, in addition to heavy metals in many cases (Demirbas et al. 2017). Finally, the mixed sewage sludge consists of a mixture of organic, inorganic materials, and moisture (Naqvi et al. 2021).

Due to its composition, the main disposal routes for this waste include land applications such as fertilizer. However, direct use in agriculture is controversial due to the presence of heavy metals, pathogens, and micropollutants, which can aggregate the food chain (Herzel et al. 2016). Fortunately, different conversion methods have been proposed to convert sewage sludge into energy and chemicals, which include thermochemical and biochemical processes or a combination of the two platforms. According to Werle and Dudziak (2019) and Naqvi et al. (2021), the thermochemical conversion of sewage sludge (incineration, gasification, and pyrolysis) appears to be the most promising alternative for its management and energy production in the future. This is due to the significant volume (up to 90%) reduction, mass (up to 70%) reduction, and the sterility of the final by-product (Ducoli et al. 2021).

Sewage sludge incineration is the most practiced thermal technology with the ability to recover energy and residual ash. The ash is rich in CaO_2, SiO_2, Fe_2O_3, and Al_2O_3 and can be disposed into landfills or can be used as a raw material substitute in cement industries (Ducoli et al. 2021). Moreover, the recovered heat can be used for drying raw sewage sludge in other biorefining processing. However, it is a source of harmful emissions of toxic compounds, in addition to being a costly alternative (Banerjee et al. 2020).

The gasification process is an alternative to using sewage sludge as a raw material for biorefineries. As this is a reducing process, it eliminates the problem of emitting gaseous contaminants to the atmosphere, unlike incineration. The main products from gasification are synthesis gas, a hydrocarbon-rich combustible gas suitable for burning and generating energy. Another by-product is the biochar, a carbon-rich solid material, that can be used for catalyst, adsorbent, or nutrients recovery. However, due to the excessive moisture and ash content of sewage sludge, the quality of gasification products is low. Thus, gas cleaning and high energy consumption are the main bottlenecks to overcome. A viable option is to combine energy production with phosphorus recovery (Werle and Dudziak 2019).

Pyrolysis of the sewage sludge produces liquid bio-oil, combustible gases, fixed carbon, ash, and water vapor. Pyrolysis is considered a favorable sludge management option, since it converts this feedstock into liquid bio-oil, combustible gases, and biochar, with low emission of pollutants, in addition to demanding cheaper equipment (Gao et al. 2020; Vali et al. 2021). The bio-oil produced in a yield is in the range of 51–80 wt%, comprising of a complex mixture of water, organic compounds, and other components that can be used as biofuel and chemicals, including fertilizers, resins, and light aromatics (Djandja et al. 2020). This solid product (yield between 35 and 80 wt%) has a high potential to be applied as an adsorbent of pollutants such as H_2S or NOx in gaseous streams or as a reducer in metallurgical processes or as a fuel to maintain the process (Fonts et al. 2012).

In summary, despite having high moisture, ash, and heavy metal content, sewage sludge is a promising feedstock for energy and chemical recovery, especially if we consider that the feedstock becomes a zero-waste material. However, it requires preliminary dewatering to decrease the liquidity of the feedstock to up to ~20% and increase its organic matter concentration, which significantly increases the costs of these processes. Even so, Shahbeig and Nosrati (2020) showed that sewage sludge was economically feasible to produce bioenergy from municipal sewage sludge pyrolysis. However, the lack of technical-economic information in the literature is another challenge related to sewage sludge biorefining.

3.4 Concluding Remarks

It was clearly demonstrated that there are a wide range of waste feedstocks that offer exploration potential to produce a large spectrum of by-products, especially bioenergy. This is a very interesting outlook for biorefineries, given that a portfolio of products amplifies economic viability and confers adaptability to a process. However, there are several key points of technical and economic difficulty that must be addressed and dealt with in order to consolidate such bioprocesses.

The high cost, necessity of pretreatment in most cases, and current low oil prices limit the industrial application of wastes as a biorefinery feedstock. Nevertheless, it is crucial to consider that these processes not only increase additional value to the waste but also solve environmental problems. Thus, to make the valorization of these resources commercially viable, it is important to conduct additional R & D in this domain, in addition to support from government agencies, through investments, subsidies, tax credit, etc.

This chapter demonstrated that each residue has its benefits, limitations, specificities, and possibilities. Thus, choosing the appropriate feedstock is challenging as it depends on demand, availability of resources, and geographic position, among others. Thus, for the viable development of a waste-based process, we recommend conducting a careful analysis based on the information presented and the processing requirements.

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Chapter 4
Emerging Pretreatment Technologies Applied to Waste Biorefinery

Bahiru Tsegaye, Swarna Jaiswal, and Amit K. Jaiswal

Abstract The increasing amount of waste generation along with population growth poses a great challenge and risk for the environment. In many countries, wastes are disposed of in landfill mode and/or incinerated, which contributes to additional air pollution and other environmental problems. Therefore, eco-friendly, cost-effective, and green technologies are required to dispose of and utilize the bulk waste generated every year. This helps toward the achievements of the zero-waste goal or circular economy goal set by some regional powers like the European Union. Many scholars attempted toward this goal by converting waste into energy and other value-added products. This chapter aims to present the current state of the art of waste-based biorefinery and to present the potential and prospects of waste biorefinery. These emerging processes are important alternatives for converting waste into fuels, chemicals, and other bio-based materials.

4.1 Introduction

According to United Nations (UN) projection, the world population is expected to reach 9.4 billion by 2050 of which 70% of them are living in cities (United Nations 2014). The continued concentration of population in urban areas is posing huge challenges for providing food and energy as well as managing the bulk waste generated annually (Lehmann 2011; Satchatippavarn et al. 2015). Today the global energy system is dominated by fossil fuel which roughly accounts for 85% of energy

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consumption in 2020. However, the need to address the adverse environmental consequences and sustainability issues is driving many countries and regional powers to shift into the circular economy. According to European Commission (EC), the circular economy is targeted in maintaining the values of products, materials, and resources into the product cycle by minimizing waste generation (Spatial, Foresight; SWECO; ÖIR; t33; Nordregio; Berman, 2017). In the circular economy, zero-waste generation, reusing, and recycling as well as ensuring the sustainability of supply are the core concepts. In this context, waste conversion to energy by applying the concept of the biorefinery is a crucial tool to achieve the target of renewable energy goal as well as decarbonization of the energy system.

Waste generation is directly linked to population growth and the level of economic growth. Food waste (FW), agricultural waste (AW), industrial waste (IW), and municipal waste (MW) are among the most common type of wastes generated every day. According to Food and Agricultural Organization report, 14% of food produced was lost in the postharvest stage alone and 1/3 of total food production was wasted annually (Food and Agricultural Organization (FAO), 2019). The monetary value of food waste was estimated to be United States Dollar ($) 936 billion annually without accounting for the environmental and societal cost (FAO 2014). In EU alone, the monetary value of FOOD WASTE is estimated at Euro (€) 146 billion based on 173 Kilogram (kg) per capital loss (Åsa et al. 2016; Tonini et al. 2018). The generation of bulk quantities of waste is a major concern and proper utilization will reduce the environmental pressure as well as advances in economic developments (Dahiya et al. 2018). Recycling of municipal waste alone has been estimated to generate $410 billion; however, only one-fourth of the waste is recovered and recycled (Guerrero et al. 2013; Zakir Hossain et al. 2014). Therefore, applying the concept of biorefinery for the proper valorization of the bulk waste into biofuels and other high-value chemicals will contribute to the advancement of the circular economy. However, the diverse type and composition of the waste hinder the effectiveness and efficiency of conversions of waste to energy and other platform chemicals.

Various pretreatment and processing methods are used for waste biomass conversion to value-added chemicals and bio-based materials. Among them are thermochemical conversion, biological conversion (Tsegaye et al. 2018a, b, 2019a), alkali pretreatment (Tsegaye et al. 2019b, c), acid pretreatments (Solarte-Toro et al. 2019), microwave pretreatment (Binod et al. 2012; Tsegaye et al. 2019d), hydrothermal liquefaction (Cantero-Tubilla et al. 2018; Dimitriadis and Bezergianni 2017), ultrasound pretreatments (Hassan et al. 2018), organosolv pretreatments (Tsegaye et al. 2020a, 2020b; Zhao et al. 2009), and combination of the pretreatments (Dimitriadis and Bezergianni 2017; Tsegaye et al. 2019d, 2020a, b) are among the pretreatment methods developed for biomass conversion to advanced fuels. Generally, all the approaches are currently lacking breakthroughs in goals to achieve for cost-effective, eco-friendly, and commercial-scale production due to their limited products produced. Therefore, the integrated biorefinery approach is the best alternative to achieve the sustainable development goal.

The generation of energy and other high-value chemicals by applying the concept of biorefinery on waste materials is a decisive approach to solve the issues of sustainability and climate change (Dahiya et al. 2018). Integrations and cascading are at the core of the circular economy. Various types of waste origins can be used as a substrate through the integration of processes and products in the biorefinery systems to produce advanced biofuels and other bio-based chemicals and materials. Many scholars have been applied biorefinery on food waste (Battista et al. 2020; Patel et al. 2019), spent coffee grounds (Zabaniotou and Kamaterou 2019), organic waste (Moretto et al. 2020), integration of anaerobic waste and microalgae (Chen et al. 2018) to produce biofuels and other high-value chemicals and materials. The application of the biorefinery approach is limited to food waste and sewage sludge (SS) for the production of biofuels, biogas, and compost excluding other platform chemicals and bio-based materials (Nghiem et al. 2017). The potential of production of hydrogen, methane, ethanol, volatile fatty acids, biopolymer, bioplastic, polyhydroxyalkanoate, and other specialty chemicals is not well-reviewed. This chapter presents the current state of the art applied to waste biorefineries for the production of advanced biofuels, chemicals, and other bio-based materials.

4.2 Waste Generations and Waste Biorefineries

Waste is described as unwanted and useless materials arising from human and animal activities. Waste can be classified based on material nature such as glass, plastic, metal, paper, and organic waste. According to the World Bank report of 2019, 2.01 billion tons of waste was generated from cities across the world in 2016 (Kaza et al. 2018). The world average waste generation is 0.74 kg/person/day while it ranges from 0.11 to 4.54 kg/person/day (Kaza et al. 2018). The high-income countries that account for 16% of the world population generate 34% (683 million tons) of the world's total waste generation. The percentage of waste generated by region is given in Table 4.1.

East Asia and the Pacific region lead in the total amount of waste generation by region that accounts for 23% of the global waste generated. The detailed total

Table 4.1 The shares of waste generated by regions throughout the globe annually

Serial number	Region	Percentage of waste generated (%)
1	Middle East and North Africa	6
2	Sub Saharan Africa	9
3	Latin America and the Caribbean	11
4	North America	14
5	South Asia	17
6	Europe and Central Asia	20
7	East Asia and Pacific	23

Source: Kaza Silpa et al. (2018)

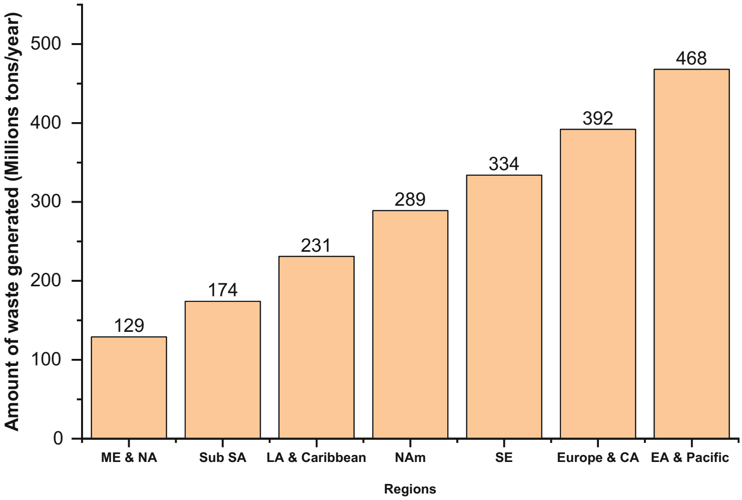

Fig. 4.1 The total amount of waste generated by region (millions of tons/year)

Table 4.2 The current and future scenario of waste generation rate per capita by region

		The regional average waste generation rate (Kg/capital/day)		
Serial number	Region	2016	2030 (projected)	2050 (projected)
1	Middle East and North Africa	0.81	0.90	1.06
2	Sub Saharan Africa	0.46	0.50	0.63
3	Latin America and the Caribbean	0.99	1.11	1.30
4	North America	2.21	2.37	2.50
5	South Asia	0.52	0.62	0.79
6	Europe and Central Asia	1.18	1.30	1.45
7	East Asia and Pacific	0.56	0.68	0.81

Source: Kaza et al. (2018)

amount of waste generated by region is shown in Fig. 4.1. The amount of waste generated is predicted to increase with the increasing world population. It was anticipated that 3.40 billion tons of waste will be generated by 2050. The low-income countries are expected to generate more than three times the current waste generation rate (Kaza et al. 2018). The current and future scenario of the average regional waste generation rate per capita by region is shown in Table 4.2.

The waste generation rate is positively correlated with the level of economy and quality of life. As the level of economy and quality of life increases, the amount of waste generated per person increases and vice versa. Cities and more tourist destination countries are also uniquely experiencing higher waste generation rates than the regional average. The current and anticipated waste generation by region is shown in Fig. 4.2 (Kaza et al. 2018). Therefore, a strong focus should have to be taken on how to properly utilize the enormous amount of waste generated.

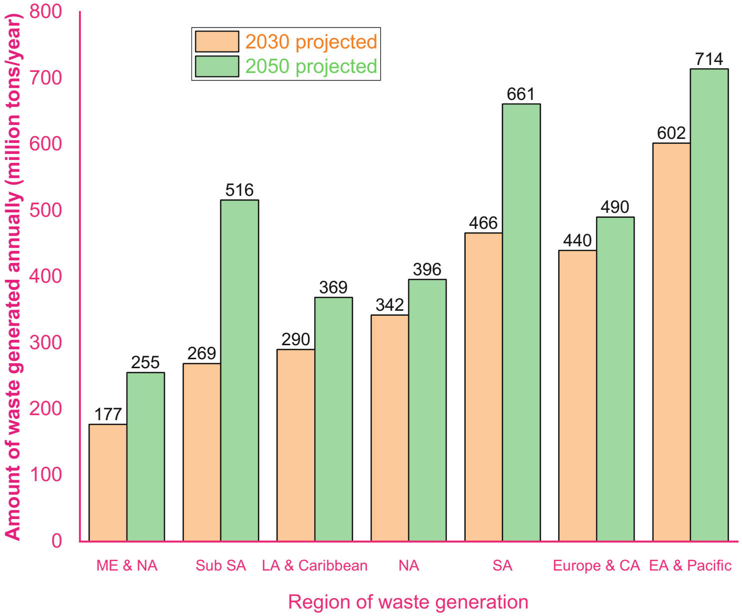

Fig. 4.2 Anticipated waste generation by region

The demands for energy, food, and material are significantly increasing with the growing world population that directly contributes to the enormous amount of waste generations (Venkata Mohan et al. 2016). The increasing amount of waste generation across cities in the world posed a serious concern of waste management and related environmental impacts. Traditionally, waste has been controlled in varieties of ways in the world from well-designed sanitary landfills to open-air dumping and burning (Kaza et al. 2018). However, the increasing amount of waste generation along with increasing populations make it difficult to follow the traditional ways of waste management. Therefore, shifting from the linear path of raw material utilization to a circular path (closing up the loop) may solve the global concern of waste management and climate issues.

Energy recovery from waste biomass ensures sustainable consumption and production which is in the framework of the circular economy that solves the issue of climate change and waste management. The application of the biorefinery approach fosters and realizes the "closing the loop" strategy for economic and environmental benefit (Maina et al. 2017). Waste biorefineries are established on three main processes:

1. The thermochemical processes include gasification, liquefaction, pyrolysis (fast, slow, and flash pyrolysis), torrefaction, carbonization, and incineration (combustion).
2. The physicochemical process includes the use of chemicals such as transesterifications.

3. Biochemical processes include the use of biological agents to convert biomass into bio-products, biofuels, and biomaterials. It includes fermentation, microbial and enzymatic hydrolysis, biodelignifications, anaerobic digestion.

Each biorefinery process can produce a product based on the type and content of the biomass or feedstock (Venkata Mohan et al. 2016). Therefore, an integrated approach of the biorefinery concept must be employed to convert the bulk waste into chemicals, biofuels, biomaterials, and other bio-based products.

4.3 Biorefinery System Classifications

Generally, four main features are considered to classify biorefinery systems. These features are:

1. *Platforms*: this type of classification depends on the types of intermediates produced starting from the raw material processing to the final product production. The most common intermediates are biogas from anaerobic digestion, pyrolysis oil from pyrolysis, syngas from gasification, hydrogen from steam reforming, water-gas shift fermentation, and water electrolysis, lignin from lignocellulosic biomass, carbon 5 and 6 sugar from hydrolysis of starch, cellulose, and hemicellulose.
2. *Products*: this type of classification depends on the types of final products produced. It is further divided into two subgroups: energy-driven biorefinery system (where the products are power, biofuels, and heat) and material-driven biorefinery system where the products are mainly bio-based materials.
3. *Feedstock*: the classification is based on the type of feedstock used in the biorefinery system; based on this classification system, the biorefinery system can be classified as dedicated energy crops feedstock (which includes cereals, marine biomass, and grasses) and residues which includes agricultural residues, organic residues, and lignocellulosic residues.
4. *Processes*: this classification depends on the pathway followed to produce the final product; according to this classification, the biorefinery system can further be categorized into four categories:

    A. The physical/mechanical process includes separation, pressing, distillation, milling, grinding, etc.
    B. The biochemical process; this pathway includes the application of enzymes or microorganisms for transforming the biomass.
    C. The chemical process includes pulping, hydrolysis, hydrogenation, oxidation, transesterification, and.
    D. The thermochemical process includes the application of high temperature and pressure with or without using a catalyst. This process includes pyrolysis (slow, fast, and flash), gasification, and liquefaction (hydrothermal liquefaction, plasma liquefaction, and solvent liquefaction).

4.4 Pretreatment Technologies Applied for Waste Biomass

The pretreatment step is the most vital step for depolymerization of waste biomass into their respective components to produce lower molecular weight chemicals and advanced fuels. Many common pretreatment methods such as alkali pretreatment, acid pretreatment, ammonia fiber expansion (AFEX), thermochemical pretreatment, liquid hot water (LHW), biological pretreatments, ultrasonic pretreatment, plasma-enabled liquefaction, ionic liquid pretreatment, etc., have been developed for conversion of lignocellulose biomass into biofuels and other value-added chemicals (Chen et al. 2018; Ong and Wu 2020; Siqueira et al. 2020; Sirohi et al. 2020; Tsegaye et al. 2020a; Zhu et al. 2020). Most of the methods are under laboratory or pilot scale and breakthroughs are required for successful commercialization. All the pretreatment approaches have their advantage and side effect. The comparative advantage and disadvantages of the common pretreatment methods are given in Table 4.3. Therefore, an integrated approach to processing and production must be followed to overcome the existing problems.

4.5 Emerging/Advanced Pretreatment Technologies Applied to Waste Biorefinery

The biomass pretreatment step has been known as the heart of the depolymerization process and a technological bottleneck for the commercialization of lignocellulose biomass and/or waste-based products. To overcome these challenges, a biorefinery concept was introduced for efficient utilization and conversion of waste to advanced fuels, chemicals, and bio-based materials. The biorefinery concept is the integration of biomass conversion processes for the production of multiple products to overcome the cost and technological barriers. According to International Energy Agency (IEA) biorefinery is defined as “the sustainable processing of biomass into a spectrum of marketable products and energy” (IEA bioenergy task 42). The application of the concept is showing promising results and has great potential to efficiently convert the bulk waste generated every year. Therefore, the adoption of the concept will solve the issues associated with bulk waste generation and related environmental and health issues.

Hydrothermal liquefaction, plasma liquefaction, pyrolysis, gasification, applications of green/organic solvents, microwave heating for waste biorefinery, ionic liquids, ultrasound pretreatments, electron beam, gamma-ray, deep-eutectic solvents are among the emerging biorefinery processes used to produce bio-crude (bio-oil). However, the bio-crude needs to be refined and/or co-refined with petroleum to produce fuel and other chemicals (Djandja et al. 2020; Saber et al. 2016).

Table 4.3 Comparison of common pretreatment methods

Pretreatment Method	Effects	Advantage	Disadvantage	References
Mechanical milling	Reduce the particle size and crystallinity of lignocellulosic materials	Control of final particle size, make handling of material easy	High energy consumption	Maurya et al. (2015)
Acid	Hemicellulose and lignin fractionation	Enzymatic hydrolysis is sometimes not required as the acid itself may hydrolyze the biomass to yield fermentable sugars	High cost of the reactors, chemicals are corrosive and toxic, and formation of inhibitory by-products	Jönsson and Martín (2016)
Alkaline	Lignin and hemicelluloses removal	This leads to less sugar degradation than acid pretreatment	Generation of inhibitors	Zhang et al. (2016)
Organic solvent	Lignin removal and hemicellulose fractionation	Produce low residual lignin substrates that reduce unwanted adsorption of enzymes and allow their recycling and reuse	High capital investment, handling of harsh organic solvents, formation of inhibitors	Nitsos and Rova (2017)
Oxidation	Removal of lignin and hemicelluloses	Lower production of by-products	Cellulose is partly degraded, high cost	By Anuj Chandel et al. (2013)
Ionic liquid	Cellulose crystallinity reduction and partial hemicellulose and lignin removal	Low vapor pressure designer solvent, working under mild reaction conditions	Costly, the complexity of synthesis and purification, toxicity, poor biodegradability, and inhibitory effects on enzyme activity	Yoo et al. (2017)
Liquid hot water	Removal of soluble lignin and hemicellulose	The residual lignin put a negative effect on the subsequent enzymatic hydrolysis	High water consumption and energy input	Zhuang et al. (2016)
Ammonia fiber expansion	Lignin removal	High efficiency and selectivity for reaction with lignin	It is much less effective for softwood, cost of ammonia, and its environmental concerns	Bajpai (2016)

Source: Hassan et al. (2018)

4.5.1 Hydrothermal Liquefaction

Hydrothermal liquefaction is a type of thermochemical conversion through which lignocellulose biomasses are exposed to hot pressurized water for some time to solubilize the biomass completely. It is classified into three major categories:

1. Hydrothermal carbonization (below 247 °C) is used to produce hydrochar.
2. Hydrothermal liquefaction (between 247 °C to 374 °C) is used to produce bio-crude.
3. Hydrothermal gasification (above 374 °C) is used to produce synthetic fuel.

High carbon efficiencies are achieved during hydrothermal gasification due to the lower carbon content of the water phase (Nallasivam et al. 2020). Upgrading or modifying the bio-crude is required for using it in the fuel market (Djandja et al. 2020; Saber et al. 2016). Moreover, treating the aqueous by-product is also vital for sustainable production. High bio-crude yield (50%–60%) was observed in continuous flow reactor systems of algae liquefaction (Elliott et al. 2015). However, the processing and operating conditions are highly specific to the feedstock type and contents used. Therefore, developing processing and operating conditions for each biomass type and conducting techno-economic analysis are crucial for successful commercialization.

4.5.2 Plasma Liquefaction

Plasma is the fourth state of matter. Plasma-enabled liquefaction is an eye-catching and promising technology for lignocellulose biomass conversion (Levchenko et al. 2018; Liu et al. 2017; Mei et al. 2019). The process generates many high energy and excited electrons at ambient conditions initiating the biomass to dissolve at a much faster rate due to the formation and reaction of highly reactive species in the biomass. The process is easily switched off and started instantaneously, which has a positive advantage for commercial-scale production. Several studies have been studied for the conversion of corn cob, rice straw, and sawdust (Liu et al. 2020; Mei et al. 2020), wood (Sun et al. 2020), corn cob (Mei et al. 2020), algae (Tan et al. 2015). However, all the studies are not focused on exploring the effects of feedstock contents, type, and concentration of catalyst, and post bio-crude refining (upgrading of bio-crude). Therefore, a biorefinery approach should have to be targeted to enhance the yield and quality of bio-crude, optimize process parameters, study the effects of each parameter on the quality and yield of bio-crude, upgrade the bio-crude to transportation fuels and feasibility study analysis should have to be done.

4.5.3 Pyrolysis

Pyrolysis is one of the most promising thermochemical processes that are performed under elevated temperatures in the absence of oxygen. The pyrolysis process leads to changes in the physical state of the organic matter as well as the chemical composition. Multiple reactions (aromatization, dehydration, charring, depolymerization, decarboxylations, and isomerization) are taking place in parallel and/or in series during the pyrolysis process (Collard and Blin 2014). The process produces three kinds of the product (liquid, char, and gases) depending on the reaction condition. The char (biochar) is the solid phase product of pyrolysis and it contains aromatic compounds. The liquid phase is commonly cold bio-oil or bio-crude and it contains phenols, hydrocarbon chains (both aliphatic and aromatic), hydroxy acetyl aldehyde, water, levoglucosan, and aldehydes. The gaseous phase contains diverse ranges of gases such as syngas (hydrogen and carbon monoxide), carbon dioxide, methane, and short hydrocarbon chain gases. The reaction and process condition of the pyrolysis as well as the type of biomass used determines the percentage and compositions of the products (Hu and Gholizadeh 2019). Pyrolysis is categorized into slow, fast, and flash pyrolysis depending on the reaction temperature and residence time.

Slow Pyrolysis is accompanied at low temperature (300–700 °C), lower heating rate (0.1–2 °C/sec), and longer residence time (30–60 min). The typical product during slow pyrolysis consists of 35% wt of gas & biochar and 35% of bio-crude. Moreover, the average elemental composition of the typical slow pyrolysis product consists of 53–96% carbon, biochar yields of 30–90%, and higher heating values (HHVs) of 20–36 MJ/kg depending on the biomass content and type (Ahmad et al. 2014; Demirbas 2004). Slow pyrolysis is favored for the production of higher biochar yield. Therefore, applying slow pyrolysis on waste biomass enhances the production of biochar.

Fast Pyrolysis is accompanied by a higher heating rate (10–200 °C) and a short residence time (0.5–10 s) intended to produce bio-crude (bio-oil) and biogas. It produces bio-oil yields between 50% and 70 wt %, 12%–15% biochar, and 13%–25% gases (Demirbaş and Arin 2002; Kan et al. 2016). The bio-crude is further improved/refined to produce liquid fuels and other chemicals. Generally, fast or flash pyrolysis is preferred for a high yield of bio-oil production. The core principle for the fast pyrolysis is a very high heating rate usually between 10^3 °C and 10^5 °C at moderate heating temperature between 450 °C and 650 °C, very short vapor residence time, <2 s, the particle size of <2 mm and more importantly suppressing the formation of secondary gases by rapidly quenching the pyrolysis gases (Balat et al. 2009; Bridgwater 2012; Kan et al. 2016). To enhance the yield of bio-crude, the biochar produced should have to be removed very rapidly (Isahak et al. 2012).

Flash Pyrolysis is operated between 400 °C and 1000 °C accompanied by a fast heating rate (10^3–10^4 °C) and a very short residence time (0.1 s–0.5 s). The main product of flash pyrolysis is a higher yield of bio-oil, 75%–80% (Amutio et al. 2012; Demirbaş and Arin 2002; Jahirul et al. 2012) and 12%–13% biochar (Balat et al. 2009; Jahirul et al. 2012; Kan et al. 2016). The basic requirements for flash pyrolysis

Table 4.4 Types of pyrolysis process based on temperature range and heating rate

Type of pyrolysis	Reaction time (s)	Temp. range (°C)	Heating rate (°C/s)
Slow pyrolysis	30–60 min	300–700	0.1–2
Fast pyrolysis	0.5–10	650–950	10–200
Flash pyrolysis	0.1–0.5	400–1000	1000–10,000

are higher heating temperature between 800 °C and 1000 °C and particle size of <0.2 mm (Balat et al. 2009; Jahirul et al. 2012; Kan et al. 2016). Generally, the choice of the process depends upon the desired final products. The pyrolysis classifications based upon operating temperature and heating rate are given in Table 4.4.

4.5.4 Gasification

Gasification is a process by which biomass, organic waste, or fossil-based raw materials are converted to fuel gases (syngas) by applying a controlled amount of oxygen and/or steam at elevated temperature, >700 °C. A typical gasification process for a biorefinery plant comprises five main sub-classifications:

1. **Biomass preparation stage**; the biomass feedstock undergoes drying, heat treatment, and grinding to make it ready for gasifier.
2. **Gasification unit stage**; the biomass is partially oxidized and transformed to gases (CO, CO_2, CH_4, H_2O, H_2, H_2S, HCN, tars) at atmospheric or pressurized conditions under a temperature of 1300 °C.
3. **Air separation unit stage**; in this stage, N_2 rich and O_2 rich streams are separated under cryogenic conditions and raw syngas is produced.
4. **Cleaning and conditioning stage**; in this stage removal of impurities such as H_2O, CO_2, H_2S, HCN takes place. The cleaning and conditioning treatments depend on the intended purpose of the syngas (CO and H_2).
5. **The exploitation of syngas for the desired final product**; in this stage, the refined syngas is used to produce biofuels, biochemicals, heat, or power.

Slezak et al. (2019) studied syngas production from spent mushroom gasification using steam between 800 °C and 900 °C. They achieved a higher yield of H_2 at 800 °C (42.9 mol H_2/kg) by utilizing 50 vol% of steam concentration. Ninõ-Villalobos et al. (2020) studied the simulated biorefinery approach for hydrogen and biodiesel production from a mixture of Palm and Jatropha biomass. They suggest that the combination of the mixtures of the biomass reduces the environmental impact as well as improved the production of biodiesel and hydrogen. The use of catalysts in the gasification process improves the yield of the product either by reacting with the biomass or by cracking with newly formed tar in a secondary reactor (Grams and Ruppert 2017). 92.3% conversion rate of tar was reported by using Ni-Fe catalyst during rice husk gasification at optimized reaction conditions

(Shen et al. 2015). Significant improvement of hydrogen yield was obtained from bagasse gasification by applying Ni-Fe/y-Al_2O_3 (Jafarian et al. 2017). Generally, the use of catalysts significantly improved the yield of the desired product during the waste gasification process.

4.5.5 Microwave Irradiation

Microwave is a non-conventional energy source and is electromagnetic radiation with wavelengths between 1 mm and 1 m and frequencies between 300 MHz and 300 GHz. Ionic conduction and dipole rotation are the two main working principles of microwaves interactions with reacting media (Constant et al. 1996; Kostas et al. 2017; Tsubaki et al. 2018; Whittaker and Mingos 1994). The relative advantage of microwave irradiation (the very fast and efficient and controlled heating as well as the very short reaction time, uniform heating, and heat generations throughout the material) attracts waste biorefinery application. Microwave is applied in biorefinery in two ways: i) pretreatments assisted by solvents at mild temperature (<200 °C) and ii) microwave-assisted pyrolysis held at a higher temperature, above 400 °C (Dhar and Vinu 2017; Hassan et al. 2018; Tsegaye et al. 2019e; Xu 2015).

The application of microwave in waste biorefinery is highly dependent on the dielectric properties of the biomass (ability to store and convert electromagnetic energy) as well as the size and shape of the biomass (Hassan et al. 2018; Tsegaye et al. 2019d; Waheed et al. 2017). Enhancement of reducing sugar yield (74.15% cellulose yield) was reported by microwave-assisted alkali pretreatment of wheat straw (Tsegaye et al. 2019d). Dhar and Vinu (2017) applied microwave heating on lignin to produce phenolic compounds using dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) solvent at 100 °C and achieved a maximum yield of 20%. Sun et al. (2019) observed that increasing the applied microwave power increased lignin depolymerization in ILs. Kostas et al. (2020) evaluated the production of biochar and bio-oil from microwave pyrolysis of olive pomace. They achieved 71.9% bio-oil production which consists of mainly acetic acid and good quality biochar at optimal conditions (200 W microwave power, energy input of 3.6 KJ/g, and reaction time of 3 min). Higher hydrolysate content (46%) from harmful algal blooms using microwave-assisted hydrolysis was achieved by microwave irradiation (Kumar et al. 2020) whereas high-quality cellulose and pectin were extracted from waste mango peel using microwave hydrothermal treatment (Kumar et al. 2020). The application of microwave heating in waste biorefinery is rapidly increasing to produce platform chemicals and bio-based materials from waste biomass. Many researchers are focused on fruit peel waste and very little work has been done on other waste residues. Therefore, if it is extended to other waste biomass such as food waste, agricultural residues, etc., it has a great potential to significantly contribute toward the achievements of zero-waste goal.

4.5.6 Ionic Liquids (ILs)

Ionic liquids are normally salt in a liquid state with melting points lower than 100 °C. Ionic liquids are considered as catalysts, solvents, or reagents, or combinations of them in many chemical processes. Ionic liquids are categorized into task-specific ionic liquids (Kumar et al. 2020), room temperature ionic liquids (Hallett and Welton 2011; Lei et al. 2014), supported ionic liquid membranes (Wickramanayake et al. 2014), and polyionic liquids (Qian et al. 2017; Rojas et al. 2014). Paul Walden was the first scholar to report the ionic liquid, ethyl ammonium nitrate in 1914 (Walden 1914). Almost after a century, it become a major research area, and the potential of ionic liquids is unveiled for biorefinery.

Borges et al. (2020) studied the catalytic effect of chromium (III) chloride hexahydrate on cupuacu peel, rice husk, and pequi peel for the production of furfural derivative compounds (furfural and hydroxymethylfurfural) by applying 1-butyl-3-methylimidazolium chloride as ionic liquids. They achieved 42.89% furfural, 14.28% glucose, 3.81% xylose, 1.92% hydroxymethylfurfural, and 0.93% arabinose by applying biorefinery concept. Up to a 6.7-fold increase in cellulose hydrolysis was reported from eucalyptus by recycling of the ionic liquids 1-butyl-3-methylimidazolium acetate (b). Meanwhile, Li et al. (2016) achieved 90.53% glucose production using the same ionic liquid after applying NaOH to separate lignin (Li et al. 2016). NaOH pretreatment of sunflower stalk combined with 1-butyl-3-methylimidazolium chloride contributed to the increment of reducing sugar to 69.14% (Nargotra et al. 2018) while corn stalk pretreatment with N-methylpyrrolidinium-2-chloride resulted in 85.94% lignin recovery and 91.81% reducing sugar yield (Ma et al. 2016). Chloride and acetate-based ionic liquids are more favorable for lignin extraction from *Eucalyptus* and *Pinus radiata*. The application of ionic liquids in waste biorefineries is attracting much interest for producing platform chemicals. Therefore, proper choice of the ionic liquid based on the type of feedstock is critical for obtaining optimal and efficient products.

4.5.7 Deep-Eutectic Solvents (DESs)

Deep-eutectic solvents are solvents that are made by mixing two or three cheap and nontoxic compounds that can make a eutectic mixture (having a lower melting point than the individual components). They are commonly considered as new generations of solvents that can overcome the problems observed in ionic liquids, high cost, high toxicity, a complex synthesis that require purification, and non-biodegradability (Abbott et al. 2004, 2006). Hydrogen bond donor and acceptor are the two main principles used in developing eutectic solvents. Even if the application of deep-eutectic solvent was known before Abbott et al. (2003) was the first scholar who introduced the concept of deep-eutectic solvent to describe the formation of low melting point liquid, 12 °C while mixing choline chloride and urea. Considering the range of components capable of forming eutectic solvents, there are vast possibilities of developing new and green solvents.

The integrated approach of rice straw pretreatment, solvent recovery, and reuse by employing natural deep-eutectic solvents (mixture of choline chloride, lactic acid, and water) for ethanol production has been evaluated (Kumar et al. 2018). They achieved 129 L ethanol/ton of rice straw (79.9%, theoretical conversion efficiency) with three times solvent reusability and 86%–90% lignin recovery. Andlar et al. (2021) used choline chloride-based natural deep-eutectic solvent for orange peel waste valorization to extract compounds such as polyphenol, protein, and D-limonene. They developed DES of choline chloride-ethylene-glycerol and obtained 86.8% polyphenol recovery. Ramesh et al. (2020) evaluated *Bambusa bambos* delignification using DESs, choline chloride-urea, and choline chloride-oxalic acid treatments for 4 h at 120 °C. They obtained higher delignification, 25% while applying the deep-eutectic solvent, choline chloride-oxalic acid. Fractionation of empty fruit bunch by choline chloride-lactic acid mixture resulted in 88% lignin removal (Tan et al. 2018) while 69% lignin removal was achieved by cholinium-argininate mixture from grass (An et al. 2015). Choline chloride-based deep-eutectic solvents are commonly used for biomass fractionation. The application of DESs in the integrated biorefinery approach is gaining momentum and the probability of developing a novel and green solvent is very high. Therefore, deep investigations on the solvent might solve the current bottleneck of biorefinery.

4.5.8 Ultrasound

Ultrasounds are sonic waves with a frequency ranges between 20 KHz and 10 MHz. Frequency ranges from 1 MHz to 10 MHz are generally used for medical and diagnostic applications while 20 KHz to 1 MHz of frequencies are used as power ultrasound, chemical processing. Ultrasound technology can be applied for extraction, crystallization, homogenization, filtration, and emulsification (Chemat et al. 2011). Due to the efficient extraction potential of the ultrasound process, food wastes are increasingly utilized for extraction of bioactive and other components by integrating the biorefinery approach. Pingret et al. (2012) evaluated polyphenol extraction from apple pomace waste using ultrasound-assisted extraction. They achieved 30% higher polyphenol content on the lab scale and 15% higher on the pilot scale than the conventional extraction process at optimized conditions (temperature 40 °C, ultrasound intensity 0.794 W/cm, solid to solvent ratio, 150 mg/mL). Moreover, they observed that there was no polyphenol degradation in the extract. Araujo et al. (2013) reported an increase in efficiency of extraction of lipid by sonication of microalgae. Recently, ultrasound assisted by alkali/acid/salt is gaining momentum for lignocellulose biomass treatments. Xu et al. (2017a, b) observed hydrolysis yield of 81% for corn cob, 66% for corn stover, and 57% for sorghum stalk after ultrasound-assisted dilute aqueous ammonia pretreatments. 98% cellulose recovery and lignin removal of 46% were observed after ultrasound-assisted potassium permanganate pretreatment of spent coffee waste (Ravindran et al. 2017). The low energy requirement and the green nature of ultrasound process boost the extraction of valuable components from waste biomasses especially, from food wastes. Therefore, integration of ultrasound process in biorefinery process significantly increases and diversifies products from food wastes and achieves the circular economy goal.

4.5.9 Gamma Radiation

Gamma radiation or gamma-ray is a form of electromagnetic radiation emerging from atomic nuclei of radioactive decay. The energy range of gamma rays from radioactive decay is from a few kiloelectronvolts (KeV) to approximately 8 megaelectronvolts (~8 MeV). Various sources other than radioactive decay such as Cygnus X-3 microquasar release very-high-energy gamma rays (100–1000 teraelectronvolt, TeV). The application of gamma rays in biorefinery is increasingly used for pretreatment to enhance hydrolysis. Wu et al. (2020) studied reduction in milling efficiency and increase in hydrolysis rate of agricultural residues after applying gamma radiation. They observed milling energy reduction of 64.4% in rice straw, 66.62% in corn stalk, and 71.68% in rapeseed straw by applying 600 KiloGray (kGy) of irradiation. Meanwhile, 4.78 times higher hydrolysis efficiency in rice straw, 3.82 times in corn stalk, and 4.35 times in rapeseed straw were observed. Xiang et al. (2016) studied pretreatment of hybrid popular sawdust by irradiation of Cobalt-60 gamma-ray. They observed the increment of reducing sugar yield to 519 mg/g after applying 300 kGy radiation. The integration of gamma-ray with other pretreatment processes is increasingly used in the biorefinery process and gives promising results. Yin and Wang (2015) reported higher biohydrogen production after the dissolution of waste-activated sludge by the combined effect of gamma-ray and alkali treatment at 20 kGy. The potential of gamma radiation for waste biorefinery has been demonstrated by many scholars. Therefore, integration of the technology into the waste biorefinery may advance the goal of the circular economy.

4.5.10 Electron Beam Radiation

Electron beam irradiation is a process that involves the use of high-energy electrons for treatment. Free radicals are generated when energy is transferred from the electron accelerator to the atoms of biomass molecules and contributes to cell wall disruption (Grabowski 2015). Recently the combined solvent pretreatment and electron beam irradiation are gaining interest due to the high efficiency of biomass disruption. Yang et al. (2015) reported 87.97% glucose conversion and 96.8% ethanol yield after the combined aqueous ammonia pretreatment and electron beam irradiation (500 kGy) of Korean *Miscanthus sinensis*. Leskinen et al. (2017)

reported the combination of consecutive pretreatment of Birchwood and Pinewood by electron beam and steam explosion for enhancement of scarification process. Karthika et al. (2013) observed 40% increases in theoretical glucose yield after synergetic mild acid (H_2SO_4) and mild alkali (NaOH) with electron beam processing of hybrid Napier grass exposed to 150 KGy. The soaking of the samples in mild acid or mild alkali facilitates the depolymerization of cellulose during electron beam irradiation. The advantage of lower solvent requirement, higher efficiency, cleanness, and cost-effectiveness of electron beam irradiation is crucial to design and integrate waste biorefinery.

4.6 Conclusion

The application of emerging technologies in waste biorefineries is attractive and has vast potential for the realization of the circular economy. The utilization of waste for energy, chemicals, and other bio-based materials productions is significantly contributing to sustainable development and is promising for the future security of energy and chemicals. Therefore, the emerging pretreatment technologies may be well integrated into waste biorefinery for the designing of green, efficient, cost-effective, eco-friendly, and sustainable production of biofuels, platform chemicals, and bio-based materials. However, further research studies and investigations are required to break through the bottleneck of waste biorefinery commercialization.

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Chapter 5
Waste Biomaterials Innovation Markets

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Abstract Bio-based materials for chemicals and energy markets remain as a reference of global sustainable resources. The Energy-Food-Feed-Chemical-Materials concerns are directly linked with the sustainability matter: given the huge global amount of waste, it has a strong innovation-driven character. The plethora of raw materials can spur research combining industrial biorefineries processes with innovations, creating new innovative sustainability-based markets. We explore the bioeconomic relations between Research and Development (R & D) efforts in technologies for biorefineries and the emergence of "waste" materials markets. The methodology—based on the identification of technological trajectories from patent citation networks—allows the comprehension on how distinct generations of technologies are combined to improve waste processes and the generation of value chains and potential markets. Results show the most relevant industrial areas explored by firms and the emergence of a huge, although technologically immature, pattern of investments. This bio-based industry is very promising: one of its main features is the possibility to combine new inventions with traditional ones, demanding R & D efforts, as well as a variety of policy and regulatory framework provisions. Our conclusions may support R & D policies and entrepreneurial investments, by the identification of emerging areas and allocation of knowledge resources for industrial sustainable development.

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5.1 Introduction

Sustainability is a new civilization milestone, an urgent collective transition goal, once there is the climate change context to deal with. There is much uncertainty regarding the measures to be taken to ensure, simultaneously, a new pattern of economic growth and markets development while maintaining a sustainable global human society (Dal Poz et al. 2021).

The governance of natural common-pool resources—the *Commons* (Ostrom 1990)—is the central point of the sustainability challenge. For this change, technological, organizational, social, financial, and human behavior innovations are needed.

Bioeconomy is an under-construction paradigm for that sustainability transition, offering renewable resources for bioproducts development and production; it demands, at the moment, and will still demand for a long time, R & D efforts and the structuring of new markets.

Human economic activity is a large waste generator—huge quantities of materials that are not used, as agricultural waste, or those that are barely used, as food packing. The global waste management market and the waste management concerns worldwide. Companies and even countries must adapt themselves to the rapid technological changes faced in knowledge economy. This adaptation process requires the ability to anticipate competitive scenarios before they happen, and the capacity to combine internal and external knowledge sources for innovation opportunities.

In this context, this chapter maps the global production of technical solutions for the use of waste as a source of energy and materials.

The bioeconomy applications for waste products can be considered an under-construction paradigm for the sustainability transition. Hence, this is a preliminary study to characterize this emerging paradigm. We adopt two approaches to achieve this goal: the first is a review of the previous literature about bioeconomy, waste-to-energy technologies, and biorefineries; in the second approach, we use a patent citation network to map and identify the main technological trajectories, as a foresight procedure for waste innovation emerging patterns.

Patent network methodologies are important methodological tools that are being used to analyze technological frontiers, emerging areas, and the future paths of industrial knowledge. The uniqueness present in this approach is in the ideas of complexity that involve the development of knowledge and the diffusion of innovations. In particular, they are new approaches that explain the process of knowledge in the context of technological changes, which lead to the process of economic development. With this, recent studies on the role of knowledge in contemporary capitalism have advanced significantly and focus on issues such as technological change, interaction, innovation networks (Cowan 2005; Krafft et al. 2011; Bueno et al. 2018), and methodologies for the treatment of diffusion of innovations (Morone and Taylor 2010; De Nooy et al. 2018).

This chapter aims to understand and relate technological global generation of bioeconomic innovations aiming at the use of these materials for energy and chemical purposes. The use of these materials is inserted in the field of innovation in bio-based materials and bioenergy, a challenging issue in scientific, technological, and economic order. The role of renewable sources—if on screen—and biodegradable raw materials brings a new dynamic to the activities of knowledge generation and R & D, involving a change in the technological route of traditional fossil materials for the biological basis. One of the fundamental characteristics of this model is a quantitative reduction in the use of productive raw materials, and the qualitative change in raw materials, which requires not only to produce new technical solutions, but to understand the insertion of new products and industrial processes in an economic context. Biorefineries platforms are the ultimate facilities for this: the industrial plants that integrate the processes and equipment to convert biomass for the purpose of fuel, energy, and chemical production.

The bioenergetics of renewable sources and biomaterials-based industry meet a new productive model, based on four assumptions: (1) energy can be restored over time; (2) raw materials are clean and renewable; (3) their sources are resulting from production processes or from human activities; and (4) produce quantities much smaller greenhouse gases compound generators, when compared with traditional sources (Demirbas 2001, 2007, 2009; Demirbas and Demirbas 2007)—its production is the only Carbon capturing system, from photosynthesis. Biomaterials can be used both for chemicals substitution and energy production; the use of waste as feedstock relates to the debate on bioenergy and the expansion of biofuels in many countries (Lal 2007), as well as for renewable resources for the actual petrochemical sources of rawmaterials. But the cost of waste treatment is considered, now, extremely high, reducing the competitiveness of those alternatives. Environmental concerns—including reducing emissions of green house gas—and food security are relevant issues that determine the debate on economics of biofuels and biomaterials.

The drivers for waste materials markets are (a) the favorable initiatives concerning clean energy and biomaterials use, (b) the increasing rationale against gas emissions, and *c)* the rising of (new and old) energy and materials demands.

According to the NASDAQ forecasting, this market expected revenues may shift from USD 20.9 billion (2015) to USD 44 billion[1]/USD 33.46 billion (2023).[2] So, both developed and developing countries have been investing significantly in the development of technologies needed to make the production process more energy efficient in environmental and economic terms. This is the so-called “biorefineries model,” an industrial plant that integrates the processes and equipment to convert biomass with the purpose of fuel, energy and chemical production.

Due to this “new” market challenges, they should be evaluated: *a)* in the context of the potential displacement effects and other markets, such as the electricity of multiple traditional sources and from the potential of the co-generation through

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[1] According https://www.statista.com/statistics/480452/market-value-of-waste-to-energy-globally-projection/

[2] According https://globenewswire.com/Index, according to the report by Global Market Insights, Inc.

biomass and *b)* the allocation of resources for R & D and the adoption of new technological trajectories (Gan and Smith 2006). In sum, there are economic and environmental motivations towards the use of waste materials as feedstocks. Hence, to fully seize these opportunities, reinforce technological assessment capabilities and formulate better policies, it is necessary to understand the technological frontier and the new trends toward the conversion of residuals to chemical products and energy sources.

In this context, this chapter is organized as follows:

The *State of Art,* composed by:

- Section 5.2.1, discussing a bioeconomy scenario context analysis, focusing on bioeconomy markets emergence aspects, and
- Section 5.2.2, presenting a waste bio-based innovation markets emergence demonstration study, based on technological foresight techniques through Patent Citation Network (PCN) (Hall et al. 2001) analysis; this methodology is applied for several fronts of technological trajectories on *waste*, exploring the global efforts in some emerging industrial R & D areas.

As *Conclusions*, the *waste* reduction technological efforts and the potential markets emergence are presented; mapping these scenarios seems essential as a first step—in the field of bioeconomy, such as decision support on the fronts of waste use R & D, regarding industrial sustainable-raising policies and enterprises initiatives.

5.2 State of Art

5.2.1 Bioeconomy-Based Markets

Waste biomaterials markets are inserted in the bioeconomy area, as an applicable issue of the climate change challenge. This set of concerns is part of the ongoing *adaptative economy*, in which renewable and re-usable material and energy practices are essential to the planet's future. Waste materials have been seen, in this context, as economic assets, and not as something to be eliminated, meaning heavy costs.

According to Ratner et al. (2012), *biomaterial science* addresses the design, fabrication, testing, application, and performance as well as nontechnical considerations integral to the translation of synthetic and natural raw material. It is a *convergence paradigm* that pushes multidisciplinary science and market efforts, since it depends on the integration of innovation policies, research and development in areas such as molecular biology, chemical engineering, process, and production engineering, among others.

Understanding the dynamics of markets based on new materials complement this multidisciplinarity. In this context, analyzes in innovation economics, which rehearse biomaterials markets through *new* and *old* dynamics competition, can collaborate to those new materials scale and long-term use.

This section seeks to characterize how the debate around climate change and bioeconomy—and its bioproducts and biorefineries platforms—are interlinked. In addition, it aims to provide subsidies for the Chapter's main goal, which is to discuss the emergence of innovative markets from waste biomaterials.

Bioeconomy is the production system based on biological resources and their conversion into food, feed, bioenergy, and bio-based materials. It composes an innovative market—in the sense that it is a biologically-based knowledge "sector."[3]

The climate change issue is the prime mover through this economic approach emergence, which is supposed to drive a sharp promotion of sustainability transitions within a new economic and societal dynamics.

The is a new development context in which a collective logic of exploration and use of natural resources of common property arise, the so-called *Commons*. It brings us back to the "Tragedy of *Commons*" (Hardin 1968) issue versus the current efforts—as this chapter does—through the bioeconomy emergence perspective—to deny that such a natural resources exhaustion is in fact destiny. On the contrary, following the logic of the analysis efforts about the possibility of implementing systems for "Governing the *Commons*" (Ostrom 1990)—orchestrating the use and exploitation of common-pool natural properties and resources, this chapter collaborates with the ongoing rationale about the entangled challenge to think about a sustainable future. Bioeconomy is concerned as a very promising way for this.

The problem of the disorderly and unlimited use of resources shared by various economic agents, which can range from pastures to consumer markets, was resumed in an emblematic way from the discussion proposed by Garret Hardin (1968); this author argues that no agent will exhaust resources only before an authority (public or private) that appropriates the good and impose rules of use. This authority would also be fundamental to the "free-rider" problem, exposed by Mancur Olson (1965), when addressing the problems collective action, where some agents take advantages of others and only reap the rewards, discouraging other to cooperate (Olson 1965). What Ostrom (1990) will assert in the face of these assumptions is that, if we consider that authority is never omniscient, it is unable to exercise this control. So that a collective monitoring within rules and governance system that respects certain conditions (the collective concerned rules) would be more efficient in the control and would provide a more lasting learning for new sustainable contexts. Bio-based markets or the bioeconomy can be inserted in this context, demanding a big set of new organizational forms of production, market dynamics and agent's agreements, rules and behaviors implementations.

That is why bioeconomy is an innovative market.

There are a multitude of shared resources, related to the matrix of subtractability of use versus the difficulty of excluding potential beneficiaries (Ostrom 1990). At the intersection between high levels of these two factors, the common-pool resources are

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[3] Biotechnology and its market's applications, as the so-called *bioeconomy*—are not exactly economic "sectors" but sets of knowledge-based research and development efforts that can alter mature markets or create new ones.

positioned. This approach follows exactly the chapter's main heuristic: the transition for sustainability is an evolutionary, interactive, and interactive process to be permanently performed by a huge diversity of actors, at many layers of policy demands and actions levels, involving a sort of geographical spheres and levels of integration.

And bioeconomy plays a fundamental role in this transition once its main character is to be based on renewable resources. This happens in terms of raw material resources as well as in terms of an ecological economics approach—once the resilient character of the systems.

That said, the governance of shared resources would be focused on the collective regulation of two basic aspects of resources: the difficulty of "exclusion" of beneficiaries and the "subtractability" of resources. The "exclusion" deals with the limitations to use, especially in the selection and who and how many will have access to the resource, regulating the offer; the "subtraction" refers to the flow, of how Much the use of a unit decreases the quantity available for new uses.

Bioeconomic approaches, in this context, represent a shift in that unlimited use of commons' *rationale*: it represents the conservative, resilient and progressive views of economic management of natural *Commons*. It is not only because it is based on biomaterial resources, but on an evolutionary ecosystemic adaptative system since both the raw material can be reused and the productive system—as natural ones—has recovery capacity.

It is plainly an *institutional change* demand, assuming institutions as a broad set of human behaviors, culture, and modes of common-pool natural or technological resources use.

That is why a precise and parsimonious definition of *bioeconomy* is a challenge. The term relates to economic activities of diverse character, nature, analytical and practical dimensions. Different sets of actions for the exploitation of biological resources in bioeconomy—and their consequent innovative market organization demand planning and implementing new products and processes innovations, new sets of economic organization, as regulatory, financial, and labor aspects and forms of competition, among others.

More specifically, in relation to the nexus between the bioeconomy and the phenomenon of climate change, the transition to bio-based approach is a complex system. It involves a lot of new contexts social, political, and market measures, efforts and measures. Performing permanent and strong actions and at sustainable policy analysis, policy decision-making, and policy frameworks proposals cross the bioeconomy challenge, as well as conceptual use and adaptation of all the elements and relationships that interact in the production, diffusion and use of new useful knowledge for bioeconomy future.

The Paris Agreement (according to IPCC 2013) sealed the global commitment to reduce the emissions of greenhouse gases to mitigate climate change and thus limit the increase in earth's temperature to just 1.5 ° C above pre-industrial levels (IPCC 2013; WMO 2019).

A new geopolitical interaction arises from the climate change control challenge: bio-resources are even more seen as sustainable alternatives, and the field of bioproducts is no longer of interest only to leading countries, involving other countries that dominate different links in the production chain of enabling technologies to products that replace those already produced in a conventional way (drop in) and those radically new (drop out) (Bozell and Petersen 2010; Ferrari et al. 2021). As previously pointed, institutional changes, involving regulation changes, incentives policies, etc., for the reduction of greenhouse gases will shape the productive configurations associated with the bioeconomic segment.

Given this evolution of the knowledge and technology frontier (involved in bioeconomy *exploration* efforts) and the *exploitation* of the new technology uses demanded by the bioeconomy shift. This is what Winskel et al. (2014) call *layers that define learning pathways.*

Therefore, it is necessary to think about the bioeconomy in its various positive externalities, focusing on the real reasons for its development and aspects related to the transition to sustainable economic systems.

The global interests for the pursuit of the bioeconomy reveal its multifaceted character as an emerging sector of the economy (McCormick and Kautto 2013; Souza et al. 2017). The movements associated with the interaction between bioeconomy, climate change and biorefineries date back to the 1990s, when the general framework of this analysis involved purely environmental and economic dimensions. However, there were progressive changes around the future of generations and social inequality issues. At that time, the European Comission launched its *White Book* (CE 1994), "Growth, competitiveness, employment: challenges and paths to enter de twenty-first century." It is a book focused on economic development and the competitiveness of economies in the long term, but many views on the role of bioeconomy (despite the term *bioeconomy* was not directly used) in the transition to sustainability are already appearing: "We are experiencing a new industrial revolution, responsible for a very rapid change in techniques, Jobs and skills" and "Europe's competitiveness would come from the need for knowledge-based investment and the role of biotechnology in economic growth" (CE 1994, p. 10).

The formalization of this model took place in 2012, with the launch of the document "Innovating for Sustainable Growth: A Bioeconomy for Europe" (European Comission 2012). It is also worth mentioning the formation of the Knowledge-Based-Bio-Economy (KBBE) initiative, from two conferences held in 2005 and 2007, which effectively contributed to conceptualize the bases of bioeconomy (McCormick and Kautto 2013).

In other words, the presuppositions for the global change of a bio-based economy were placed, and the development of the bioeconomy, started to be part of the strategic management of many countries' agenda.

During discussions around the new European Climate Law, for example, the European Commission elected the bioeconomy as a strategic element to achieve the ambitious goal of making Europe the world's first climate-neutral continent by 2050 (European Commission 2019); this plan includes credit and funding programs for bioenergy and other bio-based sustainable technological solutions as the Horizon Europe (Ronzon and M'Barek 2018). The European model for bioeconomy—

through the *European Green Deal* has, as the main goal, to zero greenhouse gas emissions by 2050 (European Commission 2019; El-Chichakli et al. 2016).

The bioeconomy stood out with multiple sources for the production of new sustainable-driven products (Cherubini 2010; Bozell and Petersen 2010); it is formed by a broad set of *enabling technologies*, like gene editing or recombinant RNA-derived techniques, based on a huge variety of bio-raw materials (a big sort of different biochemically biomasses), the potential to develop bio-based platforms for multiple products—as alcohol-chemical trajectories from biomass, to capture and adapt sectorial distinct industrial nature processes. The knowledge complementarity represents a total greater than the sum of the unique capabilities involved in these development and production processes: distinct technologies can draw multiple technological regimes, as waste-to-chemicals or waste-to-plastics trajectories.

Emerging industrial economies, like China, Brazil, and South Africa, see biotechnology as a nascent field of innovation in which these economies can compete. The Brazilian bioeconomic model prioritizes the rational exploitation of local biodiversity through the development of new sources of renewable energy—till the Oil and Gas sector 1970s crisis, when Brazilian Bioethanol Program has been implemented—and offers environmental services and eco-efficient products.

For many other developing countries, the main concern is inclusive rural development and equitable sharing of natural resources (El-Chichakli et al. 2016); for many biodiverse countries, of course, the biodiversity exploration—in the form of resilient agricultural and livestock production, natural resources preservation and bio-based new markets represents a unique challenge. This challenge is not only derived from research and development and market diffusion demands, but, also, it depends on new institutional arrangements, as intellectual property rights sharing, that puts together international enterprises markets agents and indigenous people from rainforests, for instance. The demands for analysis of the differential scientific and value trading capabilities between these actors are clear, and there is an ontological and epistemological gap between the practices of exploration and use of biological resources through entrepreneurship, and the distribution of benefits between these actors involved in this institutional network (Dal Poz and Bueno 2017).

Given this set of aspects involved in the dissemination of the bioeconomy and considering the Sustainable Development Goals (United Nations 2000) five principles, detailed below, were proposed with the aim of coordinating and harmonizing, among different countries, the process of transition to bio-based industries[4] (El-Chichakli et al. 2016).

(a) Knowledge development and transmission across boundaries, concerning the scientific gap capabilities between high-income countries and others; the high

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[4] This paper was published in Nature (2016), after the publication of 40 countries leaders report about bioeconomy development strategies, in 2014; in this year bioeconomy had a US$ 2 tri (El-Chichakli et al. 2016) global performance.

know how found in some biodiverse and middle-income countries is another aspect to put into account.

(b) Creation and management of global networks can perform a central role in defining common protocols—managing information—that pave the way for the bioeconomic industry.
(c) International coordination to overcome the problem of conflicting national priorities—from policy devices as carbon footprint pricing and credit markets—and the so-called *green deals* about fossil fuel's role for countries' development.
(d) Education for sustainability transition, including natural assets preservation and adaptative economics (Dal Poz et al. 2021), and Research and Development efforts, in an international collaboration at innovative projects and goals.

All these factors make bioeconomy an under-construction paradigm for the sustainability transition and address the requests for the bioeconomic market's dynamics deeper understanding efforts.

The sustainable future design, where bioeconomy, through biotechnology and bio-based raw materials plays a central role, is being operated by a variety of efforts to change market modes and rules by which productive and commercialization flows use common-pool natural resources (Dal Poz et al. 2021). At the level of countries' political and social actions or from international initiatives, a common definition is needed to implement and manage the bioeconomy emergence, through instruments of economic, environmental, and social policy. This means to have strong and permanent governance efforts around innovation funding, firm's competition positive environments, funding systems flows, regulatory adaptations for new technologies diffusion, among others. And, by addiction, to see this process as an evolutionary, interactive and interactive process to be permanently performed by a huge diversity of actors, at many layers of policy demands and actions levels, involving a sort of geographical spheres and levels of integration.

The search for new economies, given the demands for transition for sustainability, presumes and addresses efforts that should result in new paradigms, such as the bioeconomy. In turn, the transition to the bioeconomy—as a bio-based economy (McCormick and Kautto 2013)—involves a deep transformation of industry structure and sectors of many product chains, as this is an area still under development. In this sense, Energy-Food-Feed-Chemical-Materials issues have a strong bioeconomy innovation-driven character since raw materials of biological origin are the only renewable ones.

But the emergence of bioeconomic markets is not given through technological innovation, but it depends also on the integration of social, organizational, and institutional innovation (Geels and Schot 2008; Kemp et al. 1998). These processes are supposed to be structured as learning and adaptative based processes, demanding iterative and interactive permanent behaviors as networking, learning-by-doing, and learning-by-interacting cooperative and interorganizational processes (Cohen and Levinthal 1990; Sabel 1993), presenting strong absorptive capacity to understand

and perform new sustainable demands (Mowery and Rosenberg 1989; Arora and Gambardella 1990, 1994).

The technological trajectory of waste-to-plastics, for instance, based on bio-renewable materials, as biomass, can illustrate this market emergence plethora of demands: science development, followed by research and development processes must be followed by new firms' network formation, knowledge sharing[5] and joint work to achieve new market environments, based on regulatory of funding offers. The technological appropriation firm's individual success is a posterior phase, in which other market forces will be put into account—what means there should be a differential *absorptive capacity* to take the new technology as a competitive asset.

This example shows why closed definitions and concepts concerning bioeconomy term can be drawn from three visions:

(a) From biotechnology set of potential technical solutions, emphasizing research and its applications.
(b) From bioecology, focusing on systemic sustainable processes that optimize the nexus between resources such as water, energy, and food production, on the governance of sustainable practices and approaches to natural resources in common use and ownership and on the promotion of biodiversity, and.
(c) From biological resources, that highlights processing as well as establishing value chains for a variety of biorefinery products.

Once more, bioeconomy reveals itself as multifaceted and multidisciplinary area (Bugge et al. 2016; Bonomi et al. 2016), involving and demanding a big set of knowledge areas integration.

In short, the bioeconomy is more than single products development platforms, but integrated systems of technological platforms (Mohan et al. 2016), in which the anthropogenic waste generation can generate new markets. Basic building blocks for materials, general goods, chemicals, and energy are derived from renewable biological resources and from the full use of the industrial plant for the development of a wide variety of products. So, biomass-based biofuels platforms that replace oil-based fuels—the bioenergy industrial plant—also produce other bioproducts, as bioplastics (Bozell and Petersen 2010; Lynd et al. 2011), for instance.

It is necessary to point out that the emergence of new markets or the evolution between "old"and "new" ones is not a linear process and involves analysis about industrial dynamics and technological change. As a technological new regime, we could point to the genetic modified organism's innovation diffusion over the last 40 years. This means to understand not only research and development efforts, but the evolutionary modeling of the links between the microeconomics of innovation, the patterns of industrial change and some observable invariances in industrial structures (Marsili 2001). The innovation diffusion of new technologies leans on

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[5] Sometimes the scientific challenge and the knowledge application efforts are so high that some market rivals—as big plastic raw material suppliers—collaborate at the first Research & Development phases of the new technologies' achievements.

factors as the co-existence of firms (which are the developers or owners of new or mature technologies). They are subjected to pressures derived from demands for learning (Dosi et al. 1995)—which allows, or not, the introduction and diffusion of new technologies in real production processes. The survival of these firms in competitive selection environments depends on numerous other typical factors of market competition. They can be illustrated by cluster formation, change capability of regulatory regimes and, ultimately, manage to change the structure of markets. The weight of the generation of new businesses with high economic complementarity is not negligible.

That is why the oil and gas technological regime—and its lock-in effects—despite its non-sustainable pattern of development, is still the dominant market. Renewable fuel sources, as bioenergy, must overcome the entry barriers outlined in the previous paragraph; this is valid for all the bioeconomy technologies.

From a positive perspective, the bioeconomy has been able to transform many economic sectors, managing to establish new successful technological trajectories. In particular, the economy of rural areas. The main argument (and evidence) is that the wide range of goods and services have been continuously emerging from plant, animal, and forest material to most of production, processing and transport of bioeconomy. This is a significant variable, especially for developing countries, which have a large part of their economies based on agricultural and cattle-raising production.[6]

Unlike other industries, like petrochemicals, bioeconomy is decentralized: there is a wide variety of raw materials, like those for bioenergy—from corn or sugar cane plantations to different sources of waste, like sugar cane bagasse. From these waste materials, another variety of Energy-Food-Feed-Chemical-Materials can be produced, the main theme of this book.

The economy has clearly leaned to renewable raw materials; in the case of energy and chemicals sources, or because, in fact, non-renewable sources have a lower horizon of offering, or, indeed, because the global economy needs more and more energy and materials. This new look at the use of waste to generate new varieties of energy and chemicals has been promoting efforts to find technological routes for the bioconversion under changing trajectories of R & D based on fossil materials for bio-based chemical raw materials (Kamm et al. 2008).

In this context, this chapter describes the innovative market scenarios that are emerging due to new technological solutions able to integrate multiple value chains: Energy-Food-Feed-Chemical-Materials.

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[6] This is the Brazilian case, where agricultural productivity gains have been based on Science and Technology efforts from the last 40 years.

5.2.2 Waste Bio-based Innovation Markets

This section presents the conceptual assumptions (Sect. 5.2.2.1) and methodological procedures (Sect. 5.2.2.2) that can support the bioeconomy markets analysis, as a background ensemble for the waste industrial foresight study, in Sect. 5.2.2.3.

5.2.2.1 Conceptual Assumptions to Draw a Waste Bioeconomy

Methodologies that seek to measure the technological progress are quantitative assessment and analysis tools for the inter-comparisons of activities that generate knowledge and its appropriation, as innovations. They are models of information analysis that specify how the content and the lexical representations of documents are intrinsically related (Croft 2000). The examination of patents and their thematic content is an essential procedure for the analysis of various aspects of technological change (Griliches et al. 1986). It can be used to study long periods of investment in R & D activities, the level of the firm, and its patent profile, yielding a view about the "technological space" of a company or groups of them.

According to Zitt and Bassecoulard (2006), the design of technological fields is essential for studies of decision support, for the evaluation of positions of industrial development of institutions or countries, to understand the dynamics of Science, Technology & Innovation, and the strategic position of certain actors. Geisler (2000), for the evaluation of science and technology, points that there is only one viable method: the measurement of indicators. The verifiable data measurement is represented by lexicographical content indicators such as the incidence of Chapters in each period of time, publication of specific areas, authorship and collaboration, incidences of citation and relationship between cited and audiences, such as, for example, the characteristics that are observed in patents to evaluate the production of technological innovation.

The methodological assumptions are that Patent Citation Indicators (number of citations[7] received by a patent, from others, resulting in Patent Citations Networks—I-PCN) because patent citations allow one to study spillovers, and to create indicators of the "importance" of individual patents, thus introducing a way of capturing the enormous heterogeneity in the "value" of patents. This is considered as a robust approach for analyzing the patenting strategies of firms, an economic indicator that is able to vouch for the patent efforts as economic agents trajectories persecuted to reach some innovation goal; this approach demonstrates an industry evolution (Verspagen 2007).

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[7] Hall et al. (2005) point that this is not a final indicator for S & T & I economic analysis. Other approaches to understand the "citation dynamics" related to economic value of Technologies could be applied; due to this Chapter's profile, only the "indegree" indicator of forward citations received by a patent—is explored, which gives us a preliminary scenario for economic valuation of the waste technologies efforts performed by firms.

Complementary, PCN indicators provide a proxy of a given patent of the network (inasmuch the *graph theory*, according to Barabási and Albert 1999) to lead new technological developments. Patent sequencies that perform a *main path*[8] from a PCN have been considered as proxies of technological trajectories performed by economic agents in R & D efforts; the network can be seen as the *ex post* projection of those efforts (Mina et al. 2007; Verspagen 2007; Fontana et al. 2009; Martinelli and Nomaler 2014). This approach is a proxy of economic interests in technologies and that allows analyzing, from a technological point of view, areas and subarea of efforts in R & D and its investments.

This chapter assumes that PCN approach enables a broad understanding of: (i) economic agents' efforts at tangible, intangible, and complementary assets through innovation; (ii) industry inward competition concerning rivalry and cooperation relationships among firms and (iii) the knowledge variety that a stated sector needs to reach a new pattern of innovation (Saviotti 2009). So, PCNs provide an overview not only about waste R & D efforts, but it permits to select the most enabling technological trajectories, or, at least, the emergence of some technologies, which is a *proxy* of the bioeconomic ensemble of the "waste industry" global efforts.

5.2.2.2 Methodological Procedures

In order to explore the economic significance of PCN structures, we use two complementary procedures:

(a) The Thomson Innovation Platform, to identify the more active patenting market players in this technological area, focusing on the International Patent Classification Indicators (IPC). IPC scenarios, combined with the mapping of the most active patent holders, give us a broad market effort proxy in the technological area.
(b) The Search Path Link Count (SPLC) indicator introduced by Hummon and Doreian (1989) in their networks' main path analysis. According to Martinelli and Nomaler (2014), these indicators "evaluate the connectivity of a citation by measuring how many downstream and upstream patents are connected throughout such citation."

With this, it was possible to verify which forms to reduce waste are receiving more attention in terms of the production of knowledge potentially applicable to the technological development based on "waste" materials and consequently may mean technological trends.

The search system and data aggregation were performed by the following tools:

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[8] The *main path* of a network of patent citations is a given path in which the connectivity index of the archs reaches its maximum value (Hummon and Doreian 1989).

(a) The central search query for patents was composed by the word "waste" (at patent's abstract descriptor) and the word "energy"[9] (at patent's abstract descriptor)[10]; the period of patents was 1976 to 2018 (from the US Patent and Trade Office, USPTO).

(b) The information technology tools used to obtain data for this chapter, and to get a broad technological scenario, the same search query has been submitted to:

- We use the Thomson Innovation Platform to build a lexicographical map of patent documents. Thomson's algorithms extract sentences and expressions from these documents and categorizes them into topographic clusters on the basis of the similarity of the text. This procedure looks for industrial technological areas—using the IPC approach—concerning the term "waste" and the main market technological diffusion map, through enterprises activities.
- The Vantage Point Platform, to reach the identification of trajectories—by Depth Procedure (Batagelj et al. 2014), and SPLC criteria (Verspagen 2007), once the last one is a proxy of patent's effectivity to generate new knowledge flows, contributing to a technological development path.

5.2.2.3 Waste Technological and Market Foresight Study

The International Patent Classification (IPC) approach ensembles the following clusters of waste technological classes, as Fig. 5.1 presents.

The Class C07C relates to the core business of real industrial sales of organic materials into energy sources. The Class C10 and its subdivision C10G are closely linked to industrial processes that have as raw material the "waste," as well as the C10J. The Class C10L refers to semi-finished products—post-first phase of degradation of raw material. In this set, the Class C12P is the one that most closely approximates the generation of innovations, because it combines the processes of fermentation or enzymes that perform with the synthesis of compounds or compositions, *i.e.,* technologies are able to process the raw material that went through pre-treatment and transform it in biofuels.

The patenting activities—beginning in 1982, become relevant in 2003, and it has a clear maximum point between 2011 and 2017.

From this point, we will explore the map from an enterprise perspective, selecting the most relevant patents—concerning this chapter's methodology, the PCN approach—and, then, in terms of market technological diffusion (Table 5.1).

A giant Patent Citation Network component—shaped by 2204 patents—has emerged from the queries—as central nodes—and 8645 linking lines—has been formed.

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[9] This lexical composition (waste+energy) has proved to be able to capture the biorefineries-based patents, once waste can be used as chemical raw material or for energy production.

[10] ABST/waste AND ABST/energy—1841 patents at USPTO.

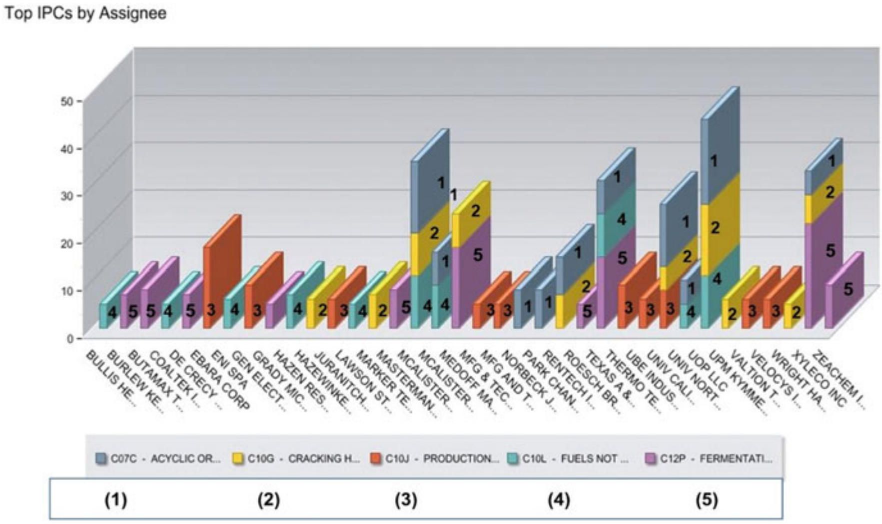

Fig. 5.1 Technological Areas in "Waste" Patents. Legend: Green (1)—C10 L** (fuels, not otherwise provided for; natural gas; synthetic natural gas); Yellow (2)—C10G* (cracking methods of hydrocarbon oils); Red (3)—C10J (production of gases containing carbon monoxide and hydrogen); Blue (4)—C07C (organic chemistry, acyclic or carbocyclic compounds); Purple (5) C12P (fermentation or enzyme). Source: Authors, through Thomson Innovation. Database: from USPTO patents, 1976–2017.

Table 5.1 Technological areas of the patent lexicographical scenario and leading companies

Technological Area	Leading Companies in terms of number of patents
A—cellulosic + lignocellulosic + corn + pulp + sugars + enzymes + fermentation	Xyleco Inc. (USA)
B—fermentation + microorganisms + ethanol	Butamax Advanced Biofuels LLC—joint venture British Petroleum and Du Pont.
C—enzyme+encoding-cell + culture + microorganism + culture	Sapphire Energy Inc. and The Scripps Research Institute (USA)
D—solar + electrical + carbon dioxide	McAlister Technologies LLC (USA)
E—fuel cell + electricity + cathodes	EBARA Co. (Japan) and McAlister Technologies LLC (USA)
F—carbon-dioxide-dissolving	McAlister Technologies LLC (USA)
G—burner-gasifier-gasification	Rem Engineering INC.
H—carbon + monoxide + methane + gasification	University of California
I—cellulosic + pulp + paper	Reclaim Resources Limited
J—gasification + gasifying + wall	Biothane Corporation (USA) and Valtion Teknillinen Tutkimuskeskus (VTT, Finland)

Source: Authors, through Thomson Innovation

Table 5.2 Main density indicators

Density1 [loops allowed] = 0.00172294
Density2 [no loops allowed] = 0.00172370
Average Degree = 7.71875000

Table 5.3 SPLC Sources Ranking

Sources/Startpoints	SPLC	Rank_SPLC
4,338,199	0,196	1
3,961,913	0,103	2
4,301,750	0,022	3
3,973,043	0,019	4
4,334,997	0,018	5
4,205,613	0,013	6
4,291,636	0,010	7
4,311,593	0,010	8

Table 5.2 shows an abstract of the main density indicators; it is important to point out that 0,17 of the potential links (full ranked) have been completed.

This original network has been filtered, using a sub-network extraction tool. A huge, dense and acyclic PCN, even after this procedure, has emerged. We identify several triads as well as some network paths made up of three or more highly cited patents.

This specific network pattern have been detected, which means there is still a deeper investigation about potential clusters of integrated technologies involved in technological packages that could be the final technical solutions for the several technological demands on *waste* The SPLC procedure has been calculated, to generate a *partition.* The paths over 1% were than considered as a valid sample for new partitions. At least 13 layers of this new core network presents sub-trajectories.

For this chapter, the main technological trajectory (or trajectories), the filter procedures—performed by network's partitions application, reveal at least 3 critical paths, in which with, at least 6 *depths,* concerning these indicators is first search algorithm used to detect and represent the mainstream of an interconnected set of nodes in a network.

Four aggregation procedures have been applied, to establish the technological trajectories:

Step 1: SPLC calculation to sources identification:

The 2204's patents PCN presents 67 nodes sources, or startpoints. SPLC for each startpoint has been calculated (SPLC Table 5.3).

Step 2: Technological Trajectories Identification, through startpoints:

The SPLC procedure has been calculated, to generate a partition. The paths over 1% were then considered as a valid sample for new partitions. Among the 67 startpoints, 8 central nodes have been identified (up to 1%), revealing the most important technological paths.

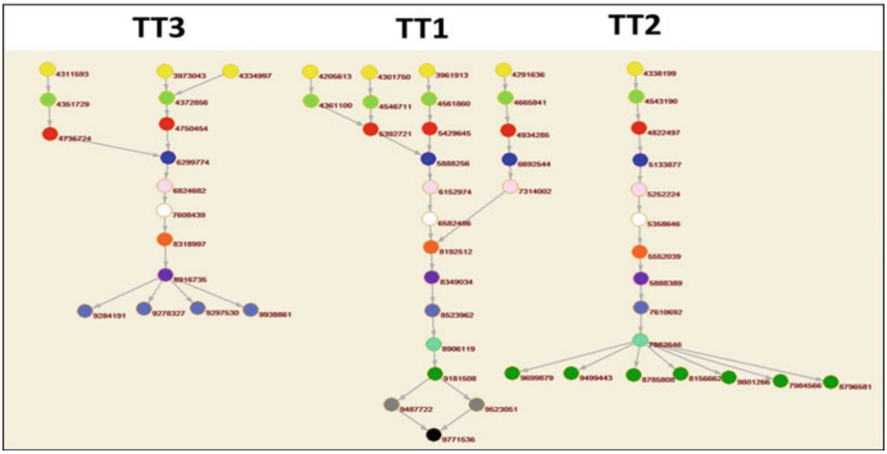

Fig. 5.2 Three Main Technological Trajectories (TTs) on “Waste”—main patents identified by Patent Number (USPTO)

Step 3—Technological Trajectories (TTs).

Hummon and Dereian (1989) algorithm was assumed for each startpoint, according to Verspagen (2007).

Step 4—Technological Trajectories Organization, through depth partition.

Depth partitions were used to organize the sources once: *i)* sources registrate depths and *ii)* for intermediary further nodes, the *depth* reveals the maximum geodesic distance of each node, in relation to a source.

The methodological procedures described above made it possible to design a 57 patents sub-network, with 3 trajectories (Fig. 5.2):

(a) Sources n° 2 (Pat. 396,191), n° 3 (Pat. 4,301,750), n°6 (PAt. 4,205,613) and n° 7 (4291636) have converged to the same path, or trajectory (TT1).
(b) Sources n° 4 (Pat. 3,973,043), n° 5 (Pat. 4,334,997), n°8 (PAt. 4,311,593) and n° 7 (4291636) have converged to the same path or trajectory (TT3).

From these results, the next procedure is to analyze the contents of each drawing patents of the waste technological trajectories—TT1, TT2 and TT3.

5.2.2.4 TT1: “Waste” Pyrolysis and Combustion

USPTO Patent 3,961,913 (1976) is the founder of TT1—*pyrolysis*, *combustion and oxidation* trajectory through liquid carbonaceous fuel methods for treating the organic fraction of solid waste material at an elevated temperature. Acid treatment is very frequently used in these technologies, especially in the trajectory first steps. This condition remains from the yellow branch of the TT1 trajectory, followed similarly by the second branch (in red). The next branches (pink, pale pink and orange) reveal a variant of the same trajectory, with densification of waste materials as a technique for packages of pyrolysis industrial technologies; the last technologies are concerned with the same industrial processes, demonstrating some sophistication of the pyrolysis process. These are incineration processes that produce bio-oil, combustible gas, and char.

The main assignees of this trajectory, the majority are companies of the USA, and all existing companies are:

- Accordant Energy, LLC (Rutland, VT)
- Pirelli Ambient S.p.A. (Milan, IT)
- Union Carbide Corporation (New York, NY)
- Combustion Equipment Associates, Inc. (New York, NY)
- Pan American Resources, Inc. (San Diego, CA)
- Outokumpu Oy (Helsinki, FI)
- Ecosystems Projects, LLC (Albany, NY)
- Re Community Energy, LLC (Rutland, VT)
- MPH Energy LLC (Rutland, VT)

5.2.2.5 TT2: "Waste" Plasma-Based Technologies

This is a remarkably interesting trajectory, once it began in the 1982 year, with oxidizing methods, and evolves for waste materials treatment; many patents from 2014 offer a very sophisticated cluster of long-action technologies, concerning waste treatment. At first, this trajectory is related to treatment of water, wastewater, sewage and sludge focusing greengas emissions reduction and solid waste transformation. From the beginning (1982) through 2011, it is related to systems and methods for conversion of high moisture waste materials to dry or low moisture products for recycle or reuse; in this middle trajectory area, technologies are at the nexus between treatment of water and energy production (using heat or not) by some integrated industrial processes of material separation, biomass drying, chemical or biological purification; some industrial products are energy, "green pellets" and fertilizers. Toxic waste treatment is a particularly important industrial work front, at this level.

From 2011, the ultimate carbon capture technologies—related with plasma methods for carbon capture as a solid material reveals a clear inflexion at the trajectory. Higher valued products make up the shelf of more recent technologies, composed of activated carbon composites. It is, obviously, a differential branch of TT2: carbon dioxide capture is linked with electric markets, and it is a mitigation process for global warming. It is also a new energy carrier resource based on Hydrogen Enriched Natural Gas (HENG). Thus, by converting from one energy carrier to another, you have effectively slowed down and stored power that would have been curtailed to stabilize the electrical grid. So, it is upstream carbon capture while delivering a zero-emission energy carrier downstream to end users such as refineries, power plants, H2 fuel stations and residential consumers of gas.

This ensamble permits to mix, to match or to configure that spark plug operated on wind/solar charged batteries of a whirlpool formed with a turbocharger turbine volute attached to a polyethylene (PE) tank using a stadium light parabolic reflector. Biorefineries—from the new chemical compounds' perspective—are linked to this trajectory, at this point.

It is a radical innovation trajectory, once a wind or battery-powered plasma spark plug natural gas cracker for converting electricity and natural gas to hydrogen while capturing solid carbon.

It could be related to a machine intentionally designed to perform a simple task in an indirect and overcomplicated fashion (that Rube Goldberg Machine).

The main assignees of this trajectory, not all existing companies or institutions, are:

- Modar, Inc. (Natick, MA) (it is not an active enterprise).
- Modell Development Corporation (Framingham, MA) (it is not an active enterprise).
- EarthRenew, Inc. (Half Moon Bay, CA)—(acquired by Valencia Ventures Inc. in 2017).
- Foret Plasma Labs, LLC (The Woodlands, TX).

5.2.2.6 TT3: Waste for Renewable Fuels, Wastewater and Biomass Treatment Through Biological Processes

This trajectory is performed almost by 100% of biological treatment of water, waste and sewage, characterized by microorganisms use. It is based on enzymes, microbiology (principally anaerobic digestion processes), and biocatalysis. That is why it is also composed of some filtering and microorganisms selection industrial processes.

The principal products are related with *biorefineries, once the platforms are typically those from the* renewable energy from biomass and carbon byproducts; it includes syngas—that may be converted to alcohol which may be stored, sold, used, or fed directly to a reactor for production of biodiesel. Methane, as well as other energy-valued gases, as biogas are some of the profiled materials from this trajectory.

Fertilizers are another branch of those bioproducts trajectory, in which the waste material is used, concerning the reuse of agricultural industrial processes byproduct as molasses, typical of sugar cane ethanol industries.

Biomass waste use, while sequestering carbon, is an important character of this trajectory. It involves carbon fiber or graphene materials products, a revolutionary new material.

The main assignees of this trajectory, not all existing companies or institutions, are:

- ExxonMobil Upstream Research Company (Spring, TX);
- McAlister Technologies, LLC (Phoenix, AZ).

5.3 Conclusions

This investigation has generated qualified technological scenarios for the industrial bioeconomy sector, concerning the “waste” innovation efforts.

By combining the IPC analysis with the Hummon and Doreian (1989) method for selecting patents in citation networks, we were able to reconstruct the three main technological trajectories for biorefineries while ensuring minimal interference by the researcher. From these trajectories, it is possible to bridge current streams of innovation on the “waste” frontier.

The “Pyrolysis/Combustion” technologies (TT1) has followed a long-established trajectory within a mature industry. However, these products are not related to very well-established markets, and the existing fossil oil and gas markets are highly competitive and offer very thin margins for the emerging pyrolysis industry. Further investigation, concerning these aspects, is obviously needed. The key advantage of the pyrolysis platform is that bio-oil and biochar are intrinsically greenhouse gas-neutral energy products, and any bio-oil cogenerated with biochar that is used as a soil amendment is a greenhouse-gas-negative energy product. The market advantages are that pyrolyzers can be scaled from small to large, pursuing economies of scale. This condition is associated to the management of production and processing of large volumes of biomass, at a large, centralized facility or network of facilities and mills, reducing other production costs in the production chains—as biomass transportation, storage and handling costs that accrue from processing biomass through a distributed network of small facilities located close to the biomass source.

TT2, the “Plasma Technologies” presents the most interesting knowledge and industry technological spill over evolution. First, because it is related to a broader cluster of markets, as energy from electricity or fuels; it enables, too, a greater market penetration since these secondary energy carriers are compatible with gas turbines and gas engines, characterized by a high electrical efficiency. Second, because the cost savings associated with landfill avoidance and the added value of the potentially marketable products are the main economical advantages of plasma gasification. And third, there are advantages from an environmental point of view, once plasma systems have the potential to offer a viable alternative to landfilling and conventional incineration, with lower air pollution and virtually no residual waste streams requiring final disposal.

These three competitive advantages are linked with an important innovation diffusion dimension, the complementary assets needed to go to market, which are still present at current markets, and can be managed in favor of the plasma company. So, this trajectory is composed of the most market-driven solutions.

TT3, the “Renewables Through Biological Processes” Trajectory encompasses some mature and available technical solutions. It has the broader spectrum of raw material use and prime products interrelationships, once it can transform waste into syngas, biodiesel, methane and graphenes. This characteristic may be an extremely competitive one, despite the still demanding frontier given by the biological-based processes, which are more science-based. The potential for further biogas or methane production is remarkably high, once these industrial plants have two sources of raw materials: municipal and agricultural waste. And, of course, it has the same TT2 characteristic, because it is related to a broader cluster of markets, as energy from electricity or fuels, too.

In sum, the PCN approach was successful in identifying a set of complementary technologies that can provide new technical opportunities/solutions for waste biorefineries. These findings tend to reinforce some propositions present in Cherubin (2010). The author stated that biorefinery platforms encompass a broad set of bio-raw materials (including, generically, "waste") that can be converted to bio-based products and energy through jointly applied enabling technologies.

Our results concerning the three technological trajectories may help to point out the main waste-to-energy and waste-to-chemical conversion technologies that should be prioritized by private R & D efforts and by industrial policies focusing on bioeconomy applications. This should be further investigated through the relevant market evolution of the companies revealed in the technological trajectories.

The second investigation procedure was able to demonstrate other facts about the waste biorefinery technologies pathways. The investigation revealed, through IPC analysis, a broader and emerging group of technological areas that have been applied for new challenge: the waste markets. This is a new R & D ensamble, performed by a new knowledge variety: from 2003, there was a clear emergence of the organic chemistry and biological techniques, as well as new methods of biological molecules cracking and modification, using microrganisms enzymatic industrial processes. Waste-to-energy production seems to be the main goal of those processes, followed by a second one: biorefineries branch of chemical products, a bioeconomic waste-derivated compounds industry.

Further investigation must put efforts into the understanding of the motives for this shift, represented by the knowledge spillovers into a bioeconomy approach. Of course, the first interpretation is that environmental and climate changes pressures on industry performance. Moreover, there are methodological limitations to be considered in our approach. We use a general patent search query, i.e., the words "waste" and "energy." For this reason, we encourage other researchers to use this study to find more specific search filters (e.g., "Waste Pyrolysis," "Plasma") that may help to paint a more accurate picture of the main biorefineries technologies. Despite these limitations, our results indicate that industry evolution is taking the newest path, the bio-based one, at TT3, from biological processes; this seems to be an overly complex technological emerging area, and further investigations will be needed, to search and understand its industrial and innovation future potential.

In this context, it is possible to remark that the Waste Energy-Food-Feed-Chemical-Materials technological trajectories are embedded in future markets.

Managing innovative waste materials markets is to take into account the complex system of factors that must be considered in innovation diffusion as an uncertain and highly risky set of phenomena. The uncertainty around the conditions that could transform new technologies into mature markets can be qualified from three dimensions.

The first one is a micro-institutional approach, in which the firms' activities are placed at service of the innovative transition, that is, the efforts, at the level of introducing new industrial routines involved in the implementation of new businesses and production systems. Innovation diffusion models—that can illustrate those efforts, involve five factors at the firm's level[11]:

(a) Strategy—to enter new markets, to overcome competitors, to surpass market entry barriers; this means to mobilize new funding and investment procedures and new sorts of transaction costs to manage.
(b) Organization—to change old intra-mural routines of production or implement new routines and managing processes around the new technological trajectory production systems.
(c) Process—to implement new production processes and all the business adaptions they demand, as supply chain organization, regulatory adaptations, etc.
(d) Learning—to create new cycles of cognitive rules (according to the new market's demands) among the firm's actors and stakeholders; this implies managing learning-by-doing, learning-by-adapting, and learning-by-interacting in new internal routines, with the consequent learning costs.
(e) Networking—once innovative markets entry behaviors demand new marketplaces dynamics of relationships: to search, select and internalize complementary skills, to access new sources of knowledge, to establish new kinds of contracts, managing new patterns of property rights safeguarding, to cite just a few of the steps needed to set a new standard of market's interactions behaviors that draw a new networking configuration. It is important to point that the level of networking demanding behaviors, in themselves, is greater than in the cases of industrial activities with mature technological trajectories.

For each new potential emerging business of the trajectories, a complex set of innovation management demands will emerge. These emerging technological solutions in the fields of waste management and waste to energy (e.g. electricity plants from waste, electricity cogeneration from sugarcane bagasse, biogas, etc.) are affecting several sectors, some with positive, others with negative effects on competitiveness. Efforts to protect intellectual property rights must be high, but there is also the derivative effect of *ownership of the new*, the so-called "temporary monopoly of the new," that can break down some entry barriers or generate new markets. Other kinds of efforts, as the new industrial production processes planning, validation and implementation, are costly, but they mean, for the firm, the epistemic construction of new governance capabilities, which represents, once again, intangible assets of great competitive value.

In the same way, learning costs can reveal themselves as new knowledge-based assets of start-ups companies or old companies' spin-offs enterprises: innovation-driven costs and efforts can result in the leverage of the company's value, in terms of the addition of new valuation criteria for intangible assets.

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[11] Quoting Tidd and Bessant 2009.

The second dimension—at the meso-level of the firm—is contiguous to the networking factor: it is related to the "fences" that separate the firm unit of analysis from the market. It is related to a long-term firm's performance planning and operating fiscal and tax issues, raising funds behaviors and experimentations, taking advantage of economic incentives, and acting as a central actor in the changes of new regulatory standards demands by the diffusion of new productive and commercial forms and behaviors. Illustrations can be found, again, in waste-to-energy agricultural emerging sectors: if, at the micro-level, the innovation diffusion is focused on firm's routines, at the meso-level, network behaviors are not simply useful for innovation catch up, but as a search and selection learning space in which enterprises can apply experimentation cycles about the real effectiveness of their current supply chain network, identifying potential network adverse ou positive effects. Complementary, a new network of stakeholders or shareholders can emerge from this kind of effort, generating a new network whose rationality is positive for the adoption of new technologies and the emergence of new markets. Competitors may not have experienced the learning cycles necessary to outlive these scenarios, which means an additional advantage for the innovative firm. That is why investments in innovation management—despite the risks—can make the company more competitive.

These innovative efforts can change market conditions dramatically. This happens due to the adaptive pressure of innovation on incumbent firms.[12] New markets emergence starts in this meso-level layer: sustainable industrial processes have received from countries' governments and from international institutions oriented for the sustainable transition, attention in terms of public policies innovation-driven funding resources. Financial innovation is an interesting example of this spin off effect of innovative systematic behaviors, at the meso-level: the payment for ecosystemic services funding, and Carbon capture markets tools are good examples.

The broader and third dimension, at the macro-level, refers to the long-term effects of those set of innovation management systematic collective efforts: the sustainable transition goals.

Waste to energy-food-feed-chemical materials industry, conformed especially by the bioeconomy, demonstrates a high potential for the sustainable transition, once it represents the full renewable adaptative long-term cycles of natural resources uses and exploration.

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[12] This change can or not happen, but applying these efforts increases the chance of change.

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Chapter 6
Step Forward on Waste Biorefineries: Technology Bottlenecks and Perspective on Commercialization

Rafaela Basso Sartori, Rosangela Rodrigues Dias, Leila Queiroz Zepka, and Eduardo Jacob-Lopes

Abstract Biorefinery is a concept analogous to the current refineries of fuels and petroleum derivatives. For this promising technology to become doable, it must be considered the use of abundant biological raw materials, such as residual biomass. However, based on the current maturity of waste biorefineries, unfortunately, they are not competitive on a large scale. In this sense, it is important to identify the technological bottlenecks so that they become sustainable and can produce products with market potential. Noteworthy, given the global ecological awakening, the waste biorefinery as a technology capable of mitigating or even eliminating the environmental impacts of a determined product has reached a featured position. Thus, this chapter bedding an overview of biorefineries, the main technological bottlenecks found for their establishment, as well as an understanding of the state of the art and the possibilities of achieving the technical and economic viability of waste biorefineries.

6.1 Introduction

Due to the rapid growth of the world population and the global increase in energy demand, new and fully sustainable energy sources are sorely needed (Fozer et al. 2017). According to estimates by the International Energy Agency, the demands for fossil fuels, trade flows, and greenhouse gas (GHG) emissions will not be sustainable until 2030. In order to consolidate the principle of climate justice and deepen the discussion on the best ways to orchestrate the transition to carbon neutrality, government policies have been adopted in recent years to drive global innovation in clean energy products with the purpose of making them widely accessible (IEA 2016; Mathieu 2016).

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Biomass produced from residual sources is considered the principal future alternative raw material to replace fossil, suppling a various of materials and energy products. In line with the vision of the bioeconomy, waste biorefineries are the ones with the greatest potential for added value to production chains today (Meyer 2017). A waste biorefinery is a facility analogous to an oil refinery and represents a genuine waste management approach. This is because it allows the utilization of waste resources to produce a variety of valuable chemicals and energy and this mitigates the utilization of natural resources (Carneiro et al. 2017). However, for the implementation of a successful waste biorefinery, it is necessary to consider environmentally and economically sustainable processing units and supply chains (IEA 2019).

Despite the obvious advantages associated with waste biorefineries, the most effective operating conditions of the cultivation systems and the commercialization of the resulting co-products, aimed at competing with resilient petroleum refineries, have not yet been established (Deprá et al. 2018). There has been a lot of discussion about high energy requirements, high water consumption, complicated pre-treatment, and insufficient market value when compared to fossil fuels (Fozer et al. 2017). Therefore, the proper selection of a better operating system and the development of these facilities on a large scale remain a major challenge for current research.

In this sense, this book chapter aims to discuss the technological bottlenecks in the establishment and commercialization perspectives of waste biorefineries. Initially, it presents the main assessments of biorefineries in general and provides a more detailed view of microalgae biorefineries. Finally, it highlights its bottlenecks and explores some of the emerging and developing technologies that are being applied to overcome current technical and economic barriers, as well as the process integration supported by the bioeconomy and life cycle assessment (LCA).

6.2 Biorefinery Assessment

Waste biorefineries have global interest, as they are part of the expanding bioeconomies. They are capable of increasing the added value involving biomasses of different raw materials, improving the perspectives related to environmental, social, and economic factors. Thus, waste biorefineries are defined as “the sustainable processing of biomass in a spectrum of bio-based products (food, feed, chemicals, materials) and sources of bioenergy (biofuels, energy and/or heat),” being a concept described by the International Energy Agency in the Bioenergy Task 42 (IEA) program (Aristizábal-Marulanda and Cardona Alzate 2019).

In the 1980s, Marchessault et al. (1988) started publications on the subject. Today, there are already several reviews addressing biomass conversions, refining them into various forms of bioenergy and other high-value products, also assessing the economic and environmental impacts generated by raw materials from different sources (Caldeira-Pires et al. 2013).

As of 2015, the search for the exploration of emerging technological efficiency began, where the focus is on the maximum use of biomass and, consequently, the reduction of the emission of greenhouse gases and other pollutants, obtaining products that are potential substitutes for those traditionally produced by conventional sources (Jungmeier et al. 2015). Therefore, through these researches, it seeks to mitigate them in a promising way, in order to contribute to the high demand for energy (fuels, energy, and heat), food, feed ingredients, medicines, chemicals, and other materials. However, there is an impasse in the commercialization of these biorefineries, largely due to the lack of adequate comparison involving different technologies and raw materials (Liu et al. 2021a).

6.3 Waste Biorefinery Feedstocks

Bioprocessing of waste in the production of value-added bioproducts and metabolites is not just about energy and environmental safety issues, but also about better waste stream management (as it focuses on recycling and reusing these wastes) (Leong et al. 2021). Therefore, it is an ecologically and economically viable platform, as the raw material for production is sustainable and of low cost, which in this case can be the link between environmental protection, the economy, and the circular economy promoted by government policies (European Commission 2015; Venkata Mohan et al. 2016).

The chemical composition of various types of biomass makes them suitable for different conversion systems. All types of waste can be used as a raw material to produce a considerable amount of high-value products through a variety of bioprocesses (Karunanithi et al. 2016). Figure 6.1 illustrates the main raw materials used in waste biorefineries. Among them, those considered in the literature for waste biorefineries are industrial waste, crops and agricultural waste, municipal waste, aquatic organisms, wood waste, herbs, and fertilizers.

6.3.1 Agricultural Wastes

The generation of organic waste from agriculture is currently highlighted due to the urgent need to discover new research and development solutions, as it represents a gigantic source of waste generation allocated to the environment. Among the main responsible crops, most of these residues refer to the production of rice, soybeans, wheat, cotton, and corn, or it refers to any other type of lignocellulosic residue produced by the agro-food industries in their daily operations, such as leaves, roots, stems, bark, bagasse, and seeds (Nizami et al. 2017). Animal waste (e.g., slaughterhouse waste and manure) also represents another significant source of pollution in this class, particularly due to greenhouse gas emissions (contributing about 20% of

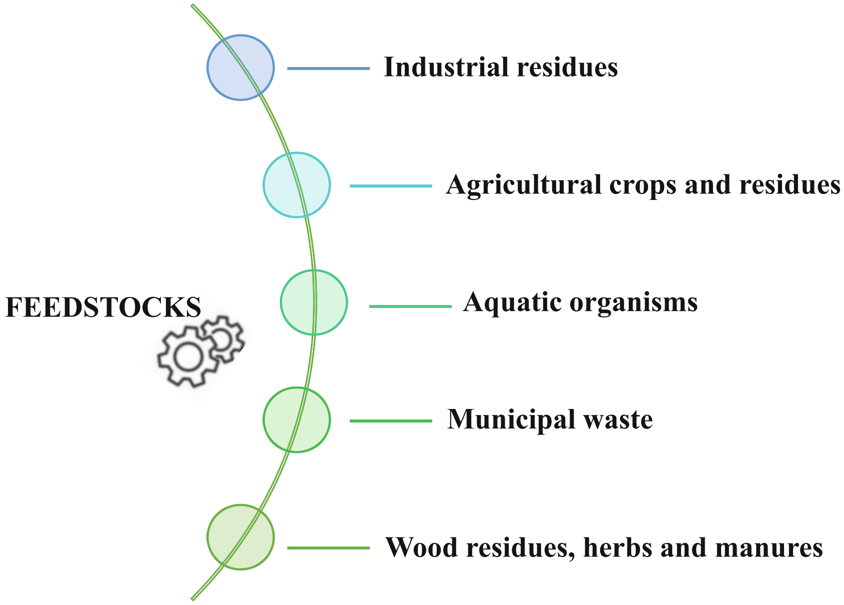


Fig. 6.1 Different sources of raw materials. Modified from Liu et al. (2021a, b)

total methane emissions in the world) and contamination, as it is often dumped directly for estuaries and rivers without any pre-treatment (Sorathiya et al. 2014).

Although these residues represent a major source of pollution (most often produced by manure, agricultural and silage residues, wood chips, oil processing, veterinary drugs, pesticides, and fertilizers) they provide a widely available, renewable, and practically biomass free for use in biorefineries (Sharma et al. 2019). Globally, 140 billion tons of biomass from the agricultural sector are generated each year. This volume of biomass can be transformed into large amounts of energy and raw material, which is equivalent to approximately 50 billion tons of oil and which can substantially move fossil fuels and reduce greenhouse gas emissions. Furthermore, as raw material, agricultural residues have potential attractiveness for conversion into various fuels and value-added products, such as bioethanol, activated carbon, biochar, organic fertilizer, natural fiber compounds, and nanocomposites (Forster-Carneiro et al. 2013; Liu et al. 2021b).

6.3.2 Wood Residues, Herbs, and Manures

In particular, the composition of plant-based agricultural residues is very similar to wood residues, consisting of cellulose (40–50%), hemicellulose (25–35%), lignin (15–20%), and various extractives (2–8%) (Garlapati et al. 2020). The generation of these waste originates, above all, in the pulp mills, paper mills, and wood manufacturing industries, including sawmills, pellet plants, and other wood processing facilities (Andrade et al. 2017).

Biomass (such as wood and forest residues) is a common renewable energy source. The breakdown of these main polymers results in sugars that can be transformed into attractive chemicals. In this case, the conversion of lignocellulosic sugars through biochemical fermentation or chemical conversion may result in the generation of biofuels, organic acids, sugar alcohols, or furans (Ajao et al. 2018). Today, the pulp and paper industry is considered a major user and producer of energy and biomass materials from woody residues. However, this industrial sector faces an economic stalemate due to new market constraints (low sales prices, heightened competition, and fuel expenses) along with global attention focused on a circular and bio-based economy. The pulp and paper industry must, therefore, change the business model to increase profits and, at the same time, collaborate to mitigate climate change. In this sense, the production of new value-added chemicals from residual biomass represents an unprecedented opportunity for revenue diversification (Bajpai 2018; Brunnhofer et al. 2019).

6.3.3 Municipal Wastes

With about 70% of the world's population living in cities by 2050, the concentration of consumption in urban areas will pose challenges not only for the supply of energy and materials but also for the management of waste (United Nations 2014). The waste law of December 2012, defines municipal waste as that generated in homes or any waste of resources generated by a community (Mesjasz-Lech 2014). According to the European Commission Department (2017) responsible for EU policy on the environment, in 2010 alone, a total of 2.5 billion tons of waste was produced. Of these, only 40% has been reused or recycled, while some countries send 80% of their waste to landfills.

Improper and indiscriminate disposal of municipal waste deteriorates soil and water quality and can cause toxic, carcinogenic, and mutagenic effects on aquatic and terrestrial organisms, including humans (Ifeoluwa 2019). However, its judicious use opens many avenues for use as a sustainable source of resources that allows the generation of diverse products through the approach of a waste biorefinery (Saini et al. 2021).

Waste identification is the first step in defining possible options via waste processing optimization. It has been argued that the largest flow of urban waste comes from wastewater (domestic and pharmaceutical products), food waste, gardens, waste paper, and plastic materials, among others. For these most of the technologies used are anaerobic digestion, composting, recycled or incinerated with energy recovery (Satchatippavarn et al. 2015).

Despite crucial, levels of municipal waste generation and treatment remain scarce, as it is not systematically monitored or reported in many countries. Although some biogas and biomethane companies are based on sewage sludge, gas, and waste, the potential for improvement in this field is still high (Sánchez et al. 2019).

6.3.4 *Industrial Wastes*

The management of industrial waste is one of the most prodigious challenges of today's society. The waste management process includes several stages (production, collection, storage, transport, and processing). The industrial waste can result from human activities within the industry or from contaminants through the production steps, which are classified according to their composition: (i) biodegradable waste, which includes food waste, paper waste, and agricultural waste (slaughter and brewery industries); (ii) recyclable waste, which includes paper, glass, cans, aluminum foil, plastics, fabrics, metal tire waste; and (iii) composite waste, which includes clothes and tetra packaging (Kumar et al. 2016; Rabbani et al. 2020).

Within the industrial waste biorefinery, there are many optimization ideas and perspectives and this has attracted significant interest because they can provide environmentally benign waste management solutions (Rehan et al. 2019). Fortunately, several industries are involved in audits that aim to assess their environmental performance and these are re-evaluating their waste management plans for use in biorefinery approaches (Sakai et al. 2017). In sum, it is still necessary for most industries to carry out a meticulous audit of their waste management plans throughout their production chain. Those that properly analyze their own waste stream and see gaps for recovery and resource savings discover environmental and economic advantages.

6.3.5 *Aquatic Organisms*

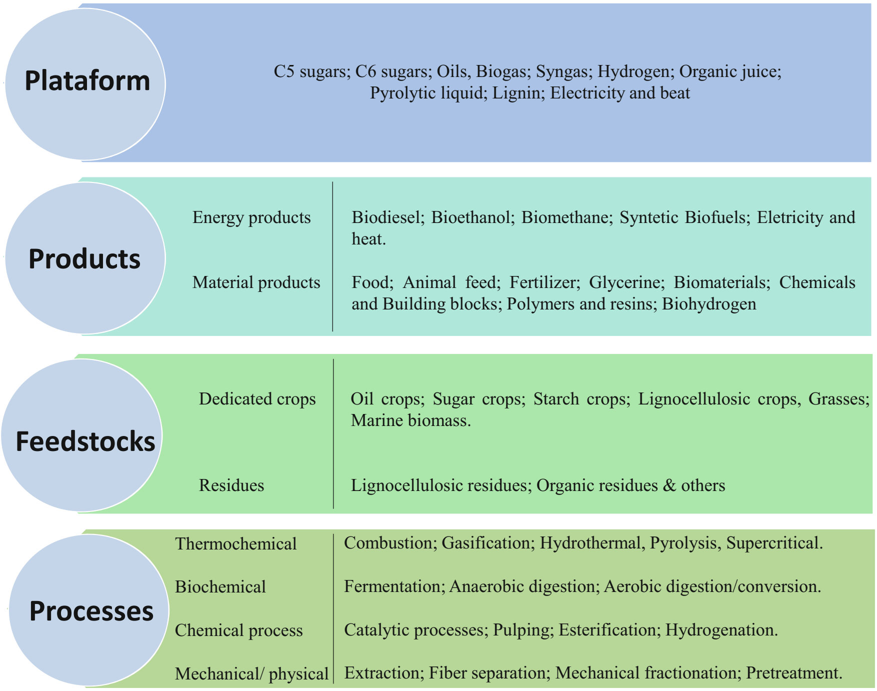
The interest in the concept of microalgae-based biorefineries has gained strength in recent years, as these microorganisms produce a wide variety of products, capable of replacing oil refineries. Besides biofuels, microalgae can supply valuable components, such as proteins, pigments, among other products suitable for different sectors (energy, food, pharmaceutical industry, nutraceutical, etc.) (Fozer et al. 2017).

Although most consolidated biorefineries are derived from conventional raw materials (such as soy, palm, rapeseed, sunflower, sugar cane, and corn), the use of bio-based matrices, such as microalgae biomass, has gained much attention due to the minimization of competition for energy resources and areas destined for food production (Brasil et al. 2017; Koyande et al. 2019). Another advantage of these microorganisms is that they can grow in habitats considered unfavorable such as brackish water and wastewater. They also have the potential to capture GHGs, especially atmospheric CO_2, and bioconvert them into various bioproducts (Severo et al. 2019). In addition, their cultivation and processing can occur in the same location, an ideal characteristic in the sequencing, integration, and intensification production of several microalgae products, which favors the approach of biorefineries (Severo et al. 2021).

6.4 Steps for the Application of Biorefinery

Biorefineries are classified based on some common characteristics, such as raw material, platforms, processes, and products, as shown in Fig. 6.2. This representation uses each of these characteristics as structural elements, providing a basic standardization that lists the main criteria that are expected to be achieved (study of environmental, social, and economic impacts) (Jungmeier et al. 2015; VDI 2016).

After defining the raw material and what type of waste will be used, technologies and operations apply to biorefinery are varied and involve the stages of transport and pre-treatment of biomass, conversion (chemical, biological), output, and application of the final product (FitzPatrick et al. 2010). The valorization of the residue can occur through the total use of the residue or by the use of fractions of the residue. However,



Plataform		C5 sugars; C6 sugars; Oils, Biogas; Syngas; Hydrogen; Organic juice; Pyrolytic liquid; Lignin; Electricity and beat
Products	Energy products	Biodiesel; Bioethanol; Biomethane; Syntetic Biofuels; Eletricity and heat.
	Material products	Food; Animal feed; Fertilizer; Glycerine; Biomaterials; Chemicals and Building blocks; Polymers and resins; Biohydrogen
Feedstocks	Dedicated crops	Oil crops; Sugar crops; Starch crops; Lignocellulosic crops, Grasses; Marine biomass.
	Residues	Lignocellulosic residues; Organic residues & others
Processes	Thermochemical	Combustion; Gasification; Hydrothermal, Pyrolysis, Supercritical.
	Biochemical	Fermentation; Anaerobic digestion; Aerobic digestion/conversion.
	Chemical process	Catalytic processes; Pulping; Esterification; Hydrogenation.
	Mechanical/ physical	Extraction; Fiber separation; Mechanical fractionation; Pretreatment.

Fig. 6.2 Different classifications of biorefinery-based systems. Modified from Lindorfer et al. (2019)

using the fractionation approach, the main challenge is separating its components (Romaní et al. 2018).

The pre-treatment of the raw material is fundamental for the total use; after this process is carried out, the raw material has the potential to be satisfactorily dried and increase the yield. The applied methods are divided into five categories such as physical, physical-chemical, chemical, biological, and electrical, it can also be done by a combination of both (Kumar et al. 2009).

Physical pre-treatment involves crushing, seeking to reduce the particle size, this reduction will determine the quality and efficiency of this process (Wyman et al. 2005). Pre-treatments involving physicochemical and chemical methods are effective but involve large investments. The most used are alkaline and acid hydrolysis, although they do not have an excellent performance or a low cost, for some raw materials such as lignocellulosic, they maintain a relatively effective reaction rate. A negative aspect of the use of these methods is related to the environment, as many products used are toxic and difficult to remove, making the pre-treatment more costly, due to the intensive input of energy (Vu et al. 2020).

Biological pre-treatments are economically viable and environmentally friendly. They have a higher cost compared to acidic and alkaline hydrolysis, but a lower energy input. A negative aspect is when hydrolysis is very slow, but which can be pre-assessed, if it contains the main requirements for a good rate of development, such as an accessible surface, polymerization, enzymatic efficiency (Lugani et al. 2020).

Regarding conversion, they can be produced out chemically or biologically. Chemical conversion is divided into pyrolysis, hydrothermal carbonization, liquefaction, incineration, gasification, direct combustion, neutralization, oxidation, transesterification, and polymerization. Among these, pyrolysis is the least explored method, but it has been applied since the 70s, mainly converting algae into fuel. Liquefaction and gasification transform biomass into liquid and gaseous fuels respectively, and these can be burnt directly or applied later to car engines. In coal-fired industries, direct combustion may be an alternative, as coal combustion can increase energy efficiency (Brennan and Owende 2010; Chew et al. 2017).

Some subcategories involve biological conversions, such as composting, fermentation, landfills, anaerobic digestion, electrolysis, and bioelectrochemical. When you have a high level of organic waste, anaerobic digestion is usually applied, a great method for converting these solid wastes into biogas. Enzymes are capable of converting some raw materials such as straw, sugars, lignocellulose into ethanol through a fermentation process. A microbial fuel cell becomes a bioelectrochemical, capable of producing electricity using electrochemical processes (Uçkun Kiran et al. 2018).

Techno-economic assessments are essential for evaluating the economic performance of the process. These studies investigate and optimize the production processes of a biorefinery and include thorough descriptions of equipment and energy and material flows. The system limits of these studies are usually limited to the production process and, therefore, it is noteworthy that they ignore the other aspects that concern the production chain. The methods utilized to model the performance of a biorefinery depend on technology and technical maturity and generally address three issues: (i) economic analysis; (ii) environmental assessment; and (iii) life cycle assessment (Zetterholm et al. 2020).

The economic analysis is one of the steps of great importance, which helps to assess the quality of these systems, through the identification of processes that are promising, analyzing their investments in order to guarantee finance. In order to obtain a very detailed evaluation, the factor related to the cost of production must be provided for each step of the system, but in cases of confidential data, it is recommended to apply the values that are related to the entry and exit of the biorefinery, but the evaluation will have a less granularity. Thus, the total costs that are determined for each product end up helping to determine the economic potential and the feasibility of marketing these bioproducts (VDI 2016; Lindorfer et al. 2019).

The environmental assessment is also an extremely important item to be assessed, it is based on the useful life of every product or process to be investigated. However, the environmental impacts that can be caused by biorefineries require a more detailed assessment of this systematic. The focus of these assessments is the accumulated demand for energy and greenhouse gas emissions, but there are other categories that are generally excluded from this type of assessment, as the models are very variable, examples of these categories are eutrophication and destruction of the ozone layer (Soh et al. 2014).

Life cycle assessment is the most used method to assess these indicators, it is based on ISO 14040, where the steps for the development of the methodology are: definition of objective and scope, inventory analysis, impact assessment, interpretation. This process requires that all flows are collected for the inventory, the lack of data results in a retroactive reset involving the limits of this system, and when applied to the sensitivity analysis, it may happen that a reset of the limits related to this system may be needed (Gonzalez-Garcia et al. 2018).

Evaluating all the criteria and steps followed, residues are considered a promising source for a biorefinery approach, in which biomass has multiproduct potential because it has a varied composition. However, the integration of biomass conversion technologies remains a challenge. More research must be carried out to increase the sustainability and economics of the waste biorefinery, to be easily produced at a commercial level (Khoo et al. 2019).

6.5 Bottlenecks of Waste Biorefineries: Current Status and New Accomplishments

The environmental problems of the twenty-first century inspire research efforts toward the development of sustainable resources for the production of food, materials, and energy. The bottlenecks present in biorefinery development are found in many types of operating units and processes. Researchers face problems with the development of simple techniques applicable to the exclusive production of a product, through the hyperaccumulation process, which becomes immature due to the high production cost, not justifying the large-scale implementation of waste biorefineries (Brasil et al. 2017).

From a technical and economic point of view, the fundamental challenges of biorefineries appear to be related to (i) reducing impacts that fluctuations in the composition and characteristics of waste can have in the processes assumed in a biorefinery; (ii) organize an integrated set of waste suitable as raw material to maximize the yield and quality of the final product; (iii) determine the optimal system size ranging from high-performance facilities with multiple raw materials to decentralized and more specialized systems with a reduced number of platforms; (iv) system integration with other industries to allow better circulation of materials and energy; and (v) keep up with fluctuating market demands and volatility in product prices (Duan et al. 2020; Alibardi et al. 2020).

Firstly, alternative/current biomass waste management (i.e., the reference system) is generally not taken into account, which assumes that biomass is freely available without any other cost or implementation challenges (Tonini et al. 2015; Lindorfer et al. 2019; Leceta et al. 2014). Second, mass and energy balances are often incomplete and may not be linked to the substrate composition itself (Hedegaard et al. 2008). Despite the overall mass flows of co-products generated in waste biorefinery solutions are usually treated at LCA, ignoring their compositional changes lead to misleading conclusions about their potential to be substituted by conventional biorefineries (Tonini et al. 2015). In addition, organic waste represents a plurality of substrates with distinct characteristics and whose availability changes significantly, for example, they can be impacted by seasonal availability (Cristóbal et al. 2018). In this case, biorefineries can be designed to take turns between raw materials whose availability is seasonal or use mixed supplies.

The waste biorefinery compared to conventional ones involves greater complexity due to heterogeneity and low purity of waste materials (Duan et al. 2020; Ubando et al. 2020). The alternative of utilizing adequate organic waste without processing should always be considered, as the application of non-putrescible crop residues to the soil or the utilize of clean food or residues such as animal feed (Caldeira et al. 2020). In addition, the increase of the output products should impact the level of waste recovery achieved, as streams that are deflected from the landfill would necessity to meet specific technical and quality standards to be used in a biorefinery (Alibardi et al. 2020). In this sense, the importance of choosing the functional unit for comparison and interpretation of results is indisputable.

Biorefineries that produce multiple outputs increase the difficulty of identifying a major function (Ahlgren et al. 2013). Multifunctionality is leading to a common problem of allocating environmental impacts to multiple outcomes. Different outputs may actually have multiple functional units and different physical characters, leading to a central issue in LCA for biorefineries (Lindorfer et al. 2019). In general, the assumptions made significantly influence the results of the evaluation of a waste biorefinery. For example, in the LCA, the selection of allocation is one of the very discussed issues. Transport of residual raw materials to the biorefinery is also another major logistical issue. Although it is generally given more attention to the choice of value recovery processes, a feasibility analysis should also include supply chain management (Caldeira et al. 2020).

According to Cristóbal et al. (2018), few large factories would be the more lucrative in the scenario, as it allows for concentrated production, enjoys economies of scale, and simplifies transport logistics. A strategy based on several smaller plants co-located with the processing plants would minimize transport costs for raw material. Barriers such as high capital costs and low-cost sustainable biomass distribution are limiting the realization of these large-scale biorefineries, which can be circumvented by small-scale biorefineries, which require a smaller complementary investment. However, there are still many technological and strategic challenges that hinder the commercial development of waste biorefineries (IEA 2019).

6.6 Perspective on Business and Commercialization

The urgent need to transition from the linear economy (economy based on fossil fuels) to the circular economy requires sustainable resources for the production of materials and chemicals. In this context, waste biorefineries constitute a sustainable business ecosystem by presenting a clear and objective value proposition where the connected units exchange cheap raw material for value intermediate products. The potentials of producing a spectrum of products from residual biomass can guarantee the sustainability of productions, which is the central idea of the circular bioeconomy, as well as solve the problems of environmental concern (Tsegaye et al. 2021).

The market for value-added products is huge and is expanding rapidly with the strengthening of the business system. The production and consumption of biofuels over the years is an excellent example of how the use of biomass and product formation can fuel a country's economy. For example, the biofuels industry is expected to reach a market value of USD 153.8 billion by 2024 of which the bioethanol market alone is expected to grow by more than USD 60 billion in 2025 (Sodhi et al. 2022). Countries are formulating and implementing policies to establish different environmentally sustainable economic models. Various industries, biotechnology, and agrotechnology companies are exploring these opportunities and leading innovations to produce value-added products such as pigments, biofuels, novel foods, intermediates, and bioactive compounds on a large scale for commercial purposes. On a global scale, the volume of renewable biochemicals (except biofuels) is about 50 billion kilograms per year (Chandel et al. 2018). Furthermore, the bioeconomy sector is transforming markets by providing new horizons, investment, and job opportunities.

Currently, the operation of biorefineries on an industrial scale is not economically viable compared to fossil fuel equivalents. Despite its promising alternatives, the current scenario of waste biorefineries has not yet become significantly attractive to investors. There exist several reasons for this trend, such as high and operating capital expenses (CAPEX and OPEX), uncertainty process, low growth, and product yield (Zetterholm et al. 2020). Availability of biomass for biorefineries also varies according to seasonal availability, region, and area, which can also include acquisition cost, loss during storage, storage, and transport cost to the biorefinery (Chandel et al. 2010). Also, in terms of processing, pre-treatment is the main capital-intensive factor, accounting for 30–50% of the total operating cost (Junqueira et al. 2017).

Many studies based on technical-economic and profitability analysis of waste biorefineries were carried out. For example, sorghum bagasse biorefinery for bioethanol production was considered expensive compared to the equivalent price of gasoline (Van Rijn et al. 2018). The economic analysis of wood-based biorefineries was also considered unprofitable for the production of ethylene (100 kg), biomethane (130 Nm^3), and lignin (0.45 ton) when operated on the basis of 400 tons of beechwood per day (Nitzsche et al. 2016). According to Cristóbal et al. (2018), the food waste biorefineries for production of lycopene and carotene would only be profitable to have up to 56 factories installed across Europe. However, the turnaround time period should be carefully considered as for most biorefineries in the real world, implementation can vary between 3 and 15 years. Potato residue biorefineries for the production of pharmacologically active compounds would also only be profitable if 28 plants were implemented with the price of the compound fixed at more than USD 300/kg (Sánchez Maldonado et al. 2014; Alibardi et al. 2020).

However, the demand for some specialty chemicals could satisfy the needs of high-value pharmaceutical markets (Padi and Chimphango 2021). Expanding the size of the market, the polymer industries are able to support many installations and are crucial to solving the problem between market volume and high-value products. The total cost of producing polyhydroxyalkanoate (PHA) from slaughter residues can vary around USD 2/kg with biodiesel as a co-product at an average recovery time of 3 years (Tsegaye et al. 2021). Chemical-based products such as ethylene, isobutanol, farnesene, 5-HMF, and others can also play a key role in bioeconomy. Some of these chemicals are considered to be base or platform chemicals, intermediate chemicals for development plus various household chemicals (Chandel et al. 2018).

Finally, the implementation of large-scale biorefineries is associated with several risk factors and barriers such as price, policy, market, and technological barriers. The social acceptance of final products is also fundamental for their diffusion and market penetration and for their integration into the economic system (Zetterholm et al. 2020). Biorefineries offered several promising opportunities in terms of reducing greenhouse gas (GHG) emissions and several important surveys result and positive interest of the main chemical agents in investing in biorefinery projects (IEA 2014). However, more public/private investments are needed to move beyond the ongoing initial stage to the next viable technology maturity level in industrial operations (Valdivia et al. 2016). Figure 6.3 highlights the main results found in the content analysis by a SWOT exam (Strengths, Weaknesses, Opportunities, and Threats) for the context of a waste biorefinery. This analysis assesses four important parameters, namely, internal factors such as strengths and weaknesses and external factors as

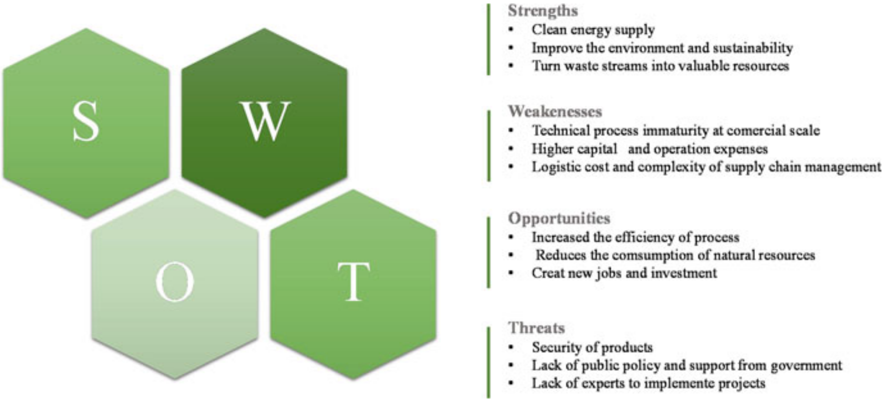


Fig. 6.3 SWOT (Strength, weakness, opportunities, and threats) analysis of waste biorefineries. Modified from Chandel et al. (2018)

opportunities and threats of a key commercial and strategic point for the implementation and desired success of a waste biorefinery (Paes et al. 2019).

6.7 Conclusions and Outlook

The integrated waste recovery approach through biorefineries has opened a new paradigm in waste management in which the full potential of the raw material can be tapped and useful products can be obtained. Global commercial production and many patents issued for new methodologies have allowed greater investment opportunities, which clearly define the promising future potential for valuing residual biomass and its contribution to strengthening the bioeconomy, transforming existing markets.

Even with the countless technological advances achieved today, the establishment of a waste biorefinery presents many bottlenecks, which are further intensified by the persistence of low prices for fossil fuels. Furthermore, the full development of these facilities often depends on the prior success of cutting-edge research and development efforts, which rely on the application of incentives to drive the progress of new technologies. In terms of process and product development, methods for forming stable products must be designed for best applicability. Efforts should also be directed toward developing simple approaches and better processing pathways for high product yields along with cost-effectiveness.

Perhaps the biggest challenge is to learn to scale up and integrate technologies, not just within the confines of the biorefinery but to expand the horizons to scale up and integrate systems and processes on a large scale. As a result, it is expected that production expenses within the biorefinery vision will decrease and that the products will become economically competitive with their counterparts. However, while this is not achieved, the development of the biorefinery seems to continue to depend on the encouragement of regulations and public policies. And it is noteworthy that there will be no progress without the optimization of previously established technological bottlenecks.

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Part II
Feedstocks

Chapter 7
Strategies for Municipal Solid Waste: Functional Elements, Integrated Management, and Legislative Aspects

Hamidi Abdul Aziz and Salem S. Abu Amr

Abstract Solid waste production has increased as a result of population growth, industrial development, and urbanisation. Solid waste complications can be traced all the way back to ancient times. Municipal solid waste (MSW) is the waste produced and collected in a city, and it is primarily associated with waste generated in the residential, manufacturing, commercial, and institutional sectors. The amount and type of waste generated vary by region. New and effective strategies for designing urbanisation models are needed, as are policies for effective solid waste management. Solid waste management encompasses all forms of waste treatment, processing, transportation, sorting, disposal, and related management. It does not end by collection; it needs to be done with the wastes is an important part of the overall management procedure. This chapter contains basic waste information. They differ in terms of form, source, quantity, and composition. The functional elements of the waste management system are then addressed, which include storage, collection, transportation, recovery and processing, composting, thermal treatment, and final disposal, among other things. There is also a discussion of waste legislation, accompanied by examples of integrated solid waste management.

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Acronyms

APCr	Air Pollution Control Residues
ASME	American Society of Mechanical Engineers
C&I	Commercial and industrial
C&D	Construction and demolition
CBA	Cost-Benefit Analysis
BFR	Brominated flame retardants
CFC	Chlorofluorocarbons
HCFC	Hydrochlorofluorocarbons,
EPA	Environmental Protection Agency
EIA	Environmental Impact Assessment
EU	European Union
HFA	Humic and fulvic acids
ISWM	Integrated solid waste management
LCA	Life Cycle Assessment
MSW	Municipal solid waste
MFA	Material Flow Analysis
RCRA	Resource Conservation and Recovery Act
RA	Risk Assessment
RMA	Rubber Modified Asphalt
SEA	Strategic Environmental Assessment
SoEA	Socioeconomic Assessment
SA	Sustainable Assessment
S/S	Solidification/stabilisation
TDA	Tyre Derived Aggregate
UNEP	United Nations Environment Programme
US	United States
UK	United Kingdom
VFA	Volatile fatty acids

Nomenclature

%	Percentage
$	American dollar
Capita	head/person or individual

7.1 Introduction

Solid waste production has increased as a result of population growth, industrial development, and urbanisation. Residential areas, marketing locations, restaurants and food areas, public and industrial installations, waterworks and sanitation services, building and agricultural sites all generate solid waste as a result of activities (USEPA-US Environmental Protection Agency 2013). Solid waste is still a major problem in many countries. Solid waste complications can be traced all the way back to ancient times. Waste has changed quantitatively and qualitatively over time as a result of new inventions, technologies, and services (USEPA-US Environmental Protection Agency 2013, 2021). The generation rates and structure vary depending on the country and lifestyle. The classification of waste is influenced by a number of factors, including economic circumstances, waste disposal strategies, institutional environment, lifestyle changes and living standards, community, and geography. One of the key reasons for rising solid waste generation due to the urban population is urbanisation. New and effective strategies for designing urbanisation models are needed, as are policies for effective solid waste management (USEPA-US Environmental Protection Agency 2021). Nearly everything that we do generates waste in some way (USEPA-US Environmental Protection Agency 2021). Solid waste disposal has become a major issue worldwide, especially in developing countries. The waste generation rate is generally proportional to the rate of economic growth and the urban population's age. Despite this expansion, waste management is still a difficult challenge. In most cases, only a small portion of the raw materials consumed is used to produce a product; the rest is discarded.

Strong waste management encompasses all forms of waste treatment, processing, distribution, sorting, recycling, and related management. It usually entails a holistic approach that encompasses all of the above practices. It does not end with collection; what has to be achieved with the wastes is a vital part of the overall management procedure. Without careful treatment and storage, an excess of solid waste can cause significant problems in a community, such as the proliferation of pathogens, foul odours, and environmental contamination. As a result, an effective solid waste management system is needed.

7.1.1 Definition of Solid Waste

Solid waste is any unwanted/unused and/or unvalued material that is dumped or discharged for recycling in a solid form. MSW is characterised by the Environmental Protection Agency (EPA) as any volume of waste produced from homes, hospitals, schools, and institutions that includes any objects thrown away after use, such as packaging materials, plastic bags and papers, plastic bottles and containers, and batteries (USEPA-US Environmental Protection Agency 2013). Solid waste is defined as garbage or refuse, sludge from a wastewater treatment plant, water supply treatment plant, or air pollution control facility, and other discarded material resulting from industrial, industrial, mining, and agricultural operations, as well as community activities, according to the Resource Conservation and Recovery Act (RCRA) of the USA, which was enacted in 1976. Municipal waste is classified as materials that include commercial and residential wastes that are produced from municipal, agricultural, and other sources, according to the Indian Rules for

Management and Handling of Solid Waste published in 1999. Municipal solid waste (MSW) refers to the waste produced and processed in a city and is primarily concerned with waste generated in the residential, manufacturing, commercial, and institutional sectors. Waste or trash is the term used in the USA, while rubbish is used in the UK. It is a form of waste made up of everyday items that have been discarded by the general population. Except for scheduled wastes such as sewage and nuclear wastes, municipal solid waste (MSW) in Malaysia is defined as any scrap materials, other unwanted surplus substances, or rejected products that occur as a result of human activity, as defined by the Solid Waste and Public Cleansing Management Act 2007 (Act 672).

7.1.2 Sources of Solid Waste

Solid waste is made up of a variety of different materials that people discard. MSW, or rubbish, is made up of a wide range of items that people throw out. These items include packaging, food, clothing, hardware, yard trimmings, tyres, and appliances.

There are many ways to categorise waste sources, but the following are the most common: Domestic or private, commercial (restaurants, retail shops, and other businesses), administrative (such as offices, classrooms, and domestic hospital wastes), non-hazardous industrial (such as offices, cafeterias, and packing, but not process waste), building and demolition (C&D), agricultural and municipal activities. Household waste accounts for 85–90 percent of overall MSW content for the bulk of local governments in many countries. MSW contains biodegradable organic matter and is one of the most complex fractions to sort when mixed with other fractions.

7.2 Waste Generation and Quantity

The design and implementation of the technical elements involved with solid waste management include an understanding of the origins and forms of solid wastes. Data on the composition and rates of waste generation are both crucial.

The quantity and composition of collected MSW are important for proper waste management. Both solid waste management activities at the local, provincial, and subregional levels, as well as at the state and federal levels, revolve around the management of these waste materials. As a consequence, it is important to understand everything you can about MSW. The amount and kind of waste generated vary by region. Any of the information is presented in the table below.

A collection of statistics on waste disposal in the USA have been published by the US Environmental Protection Agency (USEPA-US Environmental Protection Agency 2021). Between 1960 and 2018, the per person urban solid waste production per day was seen in Fig. 7.1 (3). The amount of MSW produced per person increased

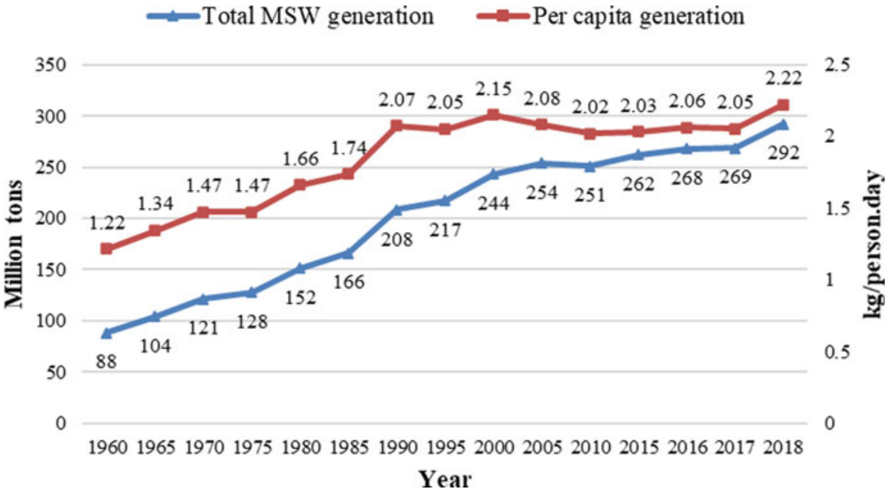


Fig. 7.1 MSW generation rates in the USA from 1960 to 2018 (USEPA-US Environmental Protection Agency 2020)

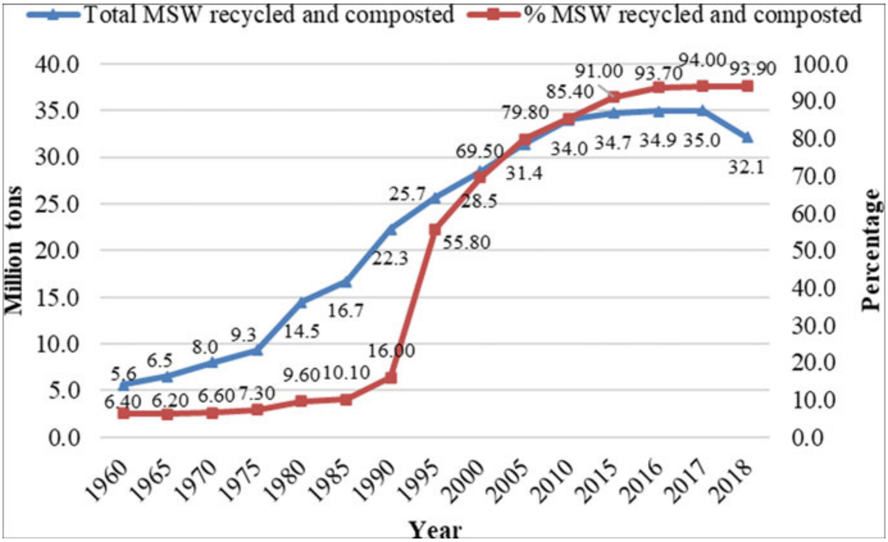


Fig. 7.2 Total municipal solid waste (MSW) recycled and composted in the USA from 1960 to 2018 (USEPA-US Environmental Protection Agency 2020)

from about 1.22 kg per day in 1960 to 2.3 kg per day in 2018. In 2018, approximately 292 million tons of MSW were produced (Fig. 7.1). A total of 94 million tons of waste was recycled or composted, resulting in a 32.1 percent recycling and composting record (Fig. 7.2). In comparison, 18 million tons of food (6.1 percent)

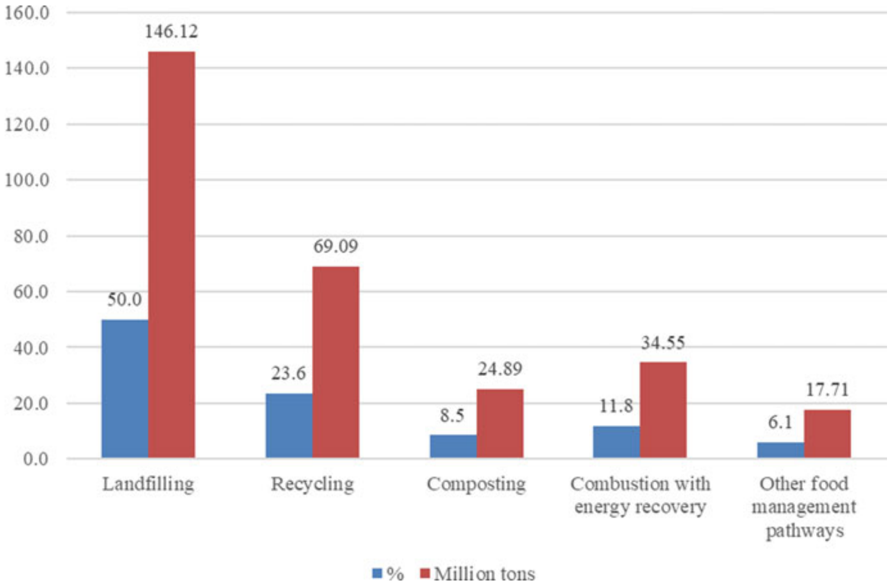


Fig. 7.3 Management of municipal solid waste (MSW) in the USA in 2018 (USEPA-US Environmental Protection Agency 2020)

is processed by other food management pathways (Fig. 7.3). About 34 million tons of MSW (11.8 percent) is combusted thanks to energy recovery. About 146 million tons (50.0 percent) were eventually poured on the land (Fig. 7.3).

Over the past few decades, MSW generation, recycling, composting, combustion with energy recovery, and landfilling have all improved radically (2). The combined recycling and composting rate have risen from less than 10% of generated MSW in 1980 to 35.0 percent in 2017 (Fig. 7.2). Recycling alone (not including composting) has grown from 14.5 million tons (9.6% of MSW) in 1980 to 69 million tons (23.6%) in 2018. Despite recycling more tons of waste than ever before in 2018, the recycling rate fell to its lowest level since 2006. In 1980, composting was almost non-existent, but by 2018, it had increased to 24.9 million tons (8.5 percent).

In 2018, the Environmental Protection Agency (EPA) updated its food measurement approach to help capture surplus and excess food flows in the food system (USEPA-US Environmental Protection Agency 2020). Such food management mechanisms accounted for 17.7 million tons (6.1 percent) of the total, as seen in Fig. 7.3. In 1980, combustion with energy recovery accounted for just 2.8 million tons, or less than 2% of total generation. In 2018, 34.6 million tons of MSW were generated. Energy-recovery-burned MSW accounted for 118 percent of the total MSW made.

In 2019, around 3700 tons of putrescible waste will be dumped in landfills in Hong Kong (HKEPD-Hong Kong Environmental Protection Department 2020). Putrescible waste accounted for the majority of MSW produced in Hong Kong. Five point seven one million tonnes of hazardous waste are disposed of at strategic

Table 7.1 Hong Kong's total solid waste at a landfill in 2019 (HKEPD-Hong Kong Environmental Protection Department 2020)

Waste category		Average daily quantity (tonnes per day)	Year-on-year growth rate
1	Municipal Solid Waste (MSW)	11,057	−3.2
	(i) Domestic	6554	−2.4
	(ii) Commercial and industrial	4503	−4.5
2	Construction waste	3946	−3.3
3	Special waste[a]	635	−8.1
4	Total waste received at landfill	15,637	−2.8

[a] Does not include special waste not disposed of at landfill

landfills in 2019. The estimated daily quantity was 15,637 tonnes per day (tpd), a decrease of 2.8 percent over the previous year (Table 7.1). MSW includes domestic, rural, commercial, and industrial C&I waste. In 2019, 11,057 tpd (4.04 million tonnes) of MSW was disposed of, down 3.2 percent from 2018. Local civil strife, which wreaked havoc on culture and forced the local economy to contract in the second half of 2019, can be blamed in part for the move. When population density is taken out of the calculation, the MSW disposal average in 2019 was 1.47 kg/person/day, compared to 1.53 kg/person/day in 2018. The majority of MSW is made up of household waste. It disposed of 6554 tpd (2.39 million tonnes) in 2019, a 2.4 percent decline from 2018. In 2019, 4503 tpd (1.64 million tonnes) of C&I waste was disposed of, down 4.5 percent from 2018. The amount of C&I waste produced is generally proportional to the rate of consumption. The contraction of the local economy may have contributed to the decrease in C&I waste disposal in 2019.

Table 7.2 shows the improvements in per capita urban solid waste (MSW) generation in the EU from 1995 to 2018 (IPCC 2019). The rate of MSW generation in Europe is seen in Table 7.3 (OECD-Organisation for Economic Co-operation and Development 2021). In addition, according to Eurostat figures, the EU provided 1.38 kg of municipal waste per capita per day in 2019, with 48 percent of municipal waste being recycled (material recycling and composting) (Eurostat 2021).

The World Bank (Silpa et al. 2018) estimates that the world produces 2.01 billion tonnes of municipal solid waste per year, with at least 33% not being handled in an environmentally sustainable way. The average volume of waste produced per person per day is 0.74 kg, but it ranges from 0.11 to 4.54 kg. High-income countries generate about 34 percent of the world's waste, or 683 million tonnes, despite having just 16 percent of the world's population. The overall amount of waste produced in low-income countries is expected to more than triple by 2050 (Fig. 7.4).

ASEAN countries have a combined population of 625 million inhabitants, accounting for 8.8% of the world population, according to the United Nations Environment Programme (UNEP). The population is expected to exceed 650 million people by 2020, with urban areas accounting for more than half of the total population in this country. Asian cities will contain the most waste in 2025,

Table 7.2 Waste generation rate based on region (IPCC 2019)

Region	MSW generation rate (kg/capita·day)	Region	MSW generation rate (kg/capita·day)
Asia		**Oceania**	
Central	0.93	Australia and New Zealand	1.64
Eastern	1.32	Melanesia	3.23
South Eastern	1.26	Polynesia	3.70
Southern	1.37	**Africa**	
Western	1.89	Northern	1.12
Europe		Eastern	0.79
Eastern	1.01	Middle	0.52
Northern	1.32	Southern	0.90
Southern	1.29	Western	0.49
Western	1.62		
America			
Caribbean	2.14		
Central	1.59		
South	1.18		
Northern	2.63		

according to estimates, with 1.8 billion tonnes (up from 0.28 billion tonnes in 2012) (UNEP 2017). The MSW generation rate in ASEAN is 1.14 kg/capita/day (Table 7.4). The following is a list of the cumulative annual MSW generation in order: With 64 million tonnes per year, Indonesia produces the most urban waste, followed by Thailand (26.77 million tonnes per year), Vietnam (22 million tonnes per year), the Philippines (14.66 million tonnes per year), and Malaysia (14.66 million tonnes per year) (12.84 million tonnes per year), Singapore (7.5 million tonnes per year), Myanmar (0.84 million tonnes per year), and Lao PDR (0.84 million tonnes per year) are the top three exporters (0.07 million tonnes per year). With the exception of Singapore, where organic waste accounts for just 10.5 percent of total MSW, organic waste accounts for the bulk of MSW in all ASEAN countries (about or more than 50%). Other types of waste often found in MSW dumps include plastics, metals, and paper. Aside from MSW, hospital waste, E-waste, agricultural waste, and building waste are all emerging waste sources in ASEAN countries.

Looking forward, global waste is expected to hit 3.40 billion tonnes by 2050, which is more than double the rate of population growth over that period (Silpa et al. 2018). Overall, there is a positive relationship between waste generation and earnings. By 2050, daily waste production per person in high-income countries is projected to increase by 19%, compared to 40% or more in low- and middle-income countries.

Table 7.3 MSW generation rate in Europe (OECD 2021)

Country	Toons per year
Austria	61,225
Belgium	63,152
Czech Republic	25,381
Denmark	20,982
Estonia	24,278
Finland	122,869
France	323,474
Germany	400,072
Hungary	15,908
Iceland	1067
Italy	163,995
Korea	180,367
Latvia	2533
Lithuania	6644
Luxembourg	10,130
Netherlands	141,024
Norway	11,197
Poland	182,006
Portugal	14,739
Slovak Republic	10,607
Slovenia	5517
Spain	128,959
Sweden	141,626
Turkey	75,535
United Kingdom	277,281

7.3 Types and Composition of Solid Waste

7.3.1 Types of Solid Wastes

Miezah et al. (2015) discovered that the majority of urban solid waste generated in developed countries comes from households (55–80 percent), followed by markets or commercial areas (10–30 percent). The above is made up of a wide range of variable quantities provided by factories, highways, establishments, and other sources. Solid waste from such sources is usually high in volume and heterogeneous in composition. Waste characteristics vary based on the source of the waste. The characterisation of these wastes is critical for any successful care or disposal practices. Separating produced solid wastes is one of the most critical and reliable methods of solid waste management because it provides valuable knowledge about the condition of the segregated wastes for any future use. The most important sources and forms of solid waste are mentioned in Table 7.5.

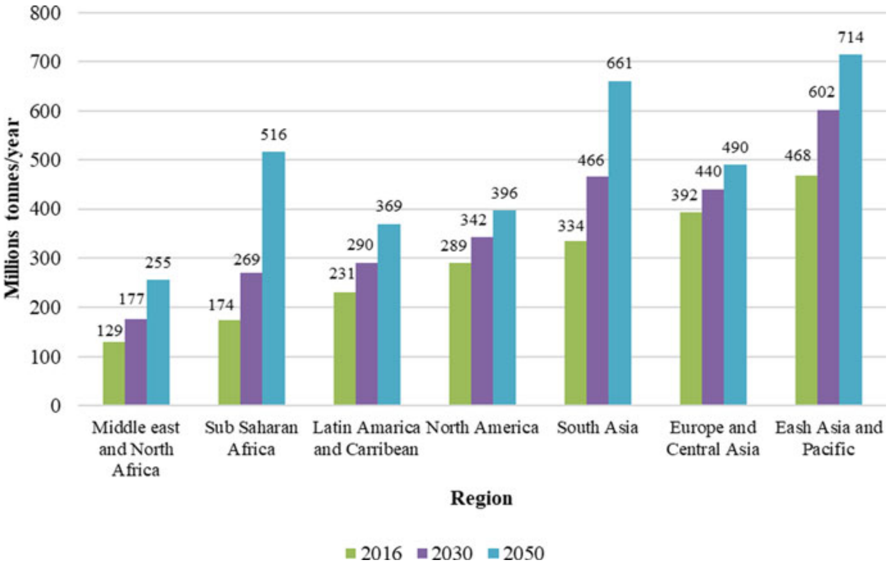


Fig. 7.4 Generation municipal solid waste by region (Silpa et al. 2018)

Table 7.4 MSW generation in ASEAN countries (UNEP 2017)

No	Country	MSW generation		
		kg/capita·day in 2009	Annual MSW in 2009 (metric tons)	Projected MSW in 2025 (kg/capita·day)
1	Brunei Darussalam	1.40	210,480	–
2	Cambodia	0.55	1,089,429	–
3	Indonesia	0.77	64,000,000	1.0
4	Lao PDR	0.69	77,380	0.80
5	Malaysia	1.17	12,840,000	1.40
6	Myanmar	0.47	12,840,000	0.60
7	Philippines	0.53	14,660,000	0.80
8	Singapore	1.10	7,514,500	1.10
9	Thailand	1.10	26,770,000	1.50
10	Vietnam	0.57	22,020,000	0.70

7.3.2 Composition of Solid Waste

Population development, market growth, improvements in eating patterns, and waste management system technical advancements are both social and economic influences that have had a direct effect on the waste aspect (Buttol et al. 2007). The composition of waste varies by location and by income level, suggesting various consumption patterns (Fig. 7.5) (Silpa et al. 2018). High-income countries contain

Table 7.5 Sources of solid wastes within a community

Source	Typical activities or locations where waste is produced	Types of wastes
Residential	From various types of houses with different income groups	Food wastes/organics, paper, cardboard, plastics, textiles, leather, yard wastes, wood, glass, bottles, tin cans, drink cartons, aluminium, other metals, ashes, garden waste, special wastes (including bulky items like discarded furniture, domestic E-waste, household hazardous wastes, batteries, oil, and used tyres
Commercial	Restaurants, supermarket, mini market, grocery shops, hotels, motels, shops, service stations, automobile workshops, laundrette, etc.	Paper, plastics, cardboard, wood, food waste, glass, metals, special wastes (see above), hazardous wastes, etc.
Institutional	Schools, higher leaning institutions, prisons and government detention centres, hospitals, governmental offices, training centres, etc.	As above in commercial
Construction and demolition	New construction sites, road repair and renovation sites, broken pavement, demolition of buildings	Concrete, wood, steel, tar, glass, dirt, etc.
Municipal services (excluding treatment facilities)	Landscaping wastes, street cleaning, grass cutting, tree trimming, drain cleaning, dead animal wastes, parks and beaches, other recreational areas	Street rubbish, sidewalks, vacant lots, tree branches, debris, grass, general wastes from parks, beaches, and recreational areas, etc.
Treatment plant sites; municipal incinerators	Treatment systems for water, wastewater, and industrial waste, etc.	Wastes from treatment plants, mostly sludges, bottom and fly ashes, and slag
Municipal solid waste	All of the above	All of the above
Industrial	Construction, manufacturing- light and heavy, fabrication, chemical plants, refineries, power plants, process waste, etc.	Wastes from industrial processes, scrap materials, etc. Non-industrial wastes-rubbish, food wastes, ashes, special wastes (see commercial), hazardous wastes
Agricultural	Dairies, feedlots, farms, field and row crops, orchards, vineyards, etc.	Spoiled food wastes, agricultural wastes, rubbish, used packaging from fertiliser, etc., hazardous wastes

less food and renewable waste (32 percent of total waste) and more dry waste that can be recycled (51 percent of total waste), such as plastic, paper, cardboard, metal, and glass. Food and green waste are generated in 53 percent of middle-income countries and 57 percent of low-income countries, respectively, with the proportion of organic waste increasing as economic growth levels fall. Just 20% of the materials used in construction in low-income countries are recyclable. There is no difference

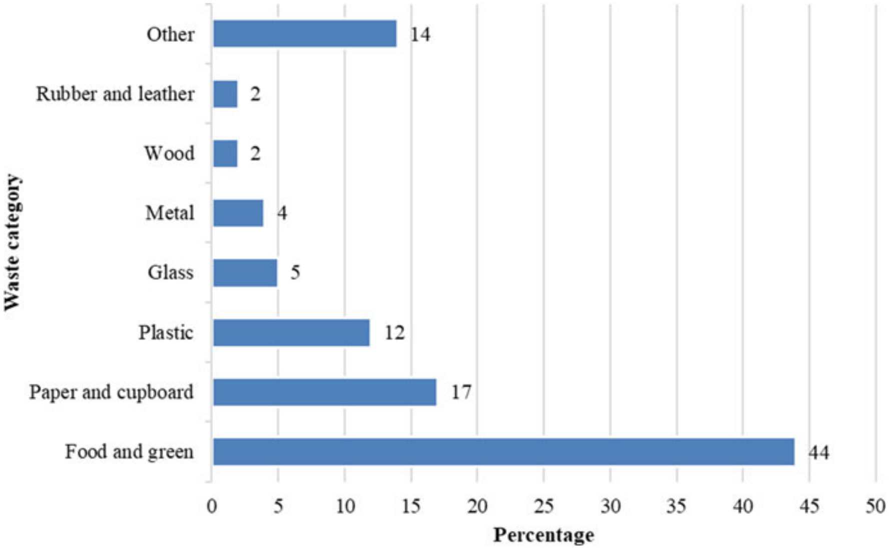


Fig. 7.5 Global waste composition (Silpa et al. 2018)

in waste streams across countries, with the exception of waste streams linked to incomes. All regions contain around 50% or more organic waste on average, with the exception of Europe, Central Asia, and North America, which generate more dry waste. Food debris accounts for 55.9% of urban solid waste in China, 8.5 percent of paper, 11.2 percent of plastics, 3.2 percent of textiles, 2.9 percent of wood waste, 0.8 percent of rubber, and 18.4 percent of non-combustibles (Hui et al. 2014).

Textiles, rubber, and leather materials made up 8.9% of total MSW produced in the USA in 2018 (Fig. 7.6) (USEPA-US Environmental Protection Agency 2020). Figure 7.7 depicts the average daily MSW (by composition) at Hong Kong landfills in 2019.

Table 7.6 shows the MSW compositions in ASEAN countries. With the exception of Myanmar, all ASEAN countries have between 45 and 60 percent food waste/organics (73 percent). Except in Singapore, they are often disposed of in landfills or dumpsites. MSW may be categorised into many categories, including food waste, cloth, plastic, textiles, glass, wood, metal, metal containers, rubber, leather, scraps, and bulky waste, among the several variations.

7.4 Functional Elements of the Waste Management System

There is no single waste management system that can be applied to all waste sources; however, in many countries, the application of a hierarchy ranking methodology for solid waste management is the most widely adopted management strategy.

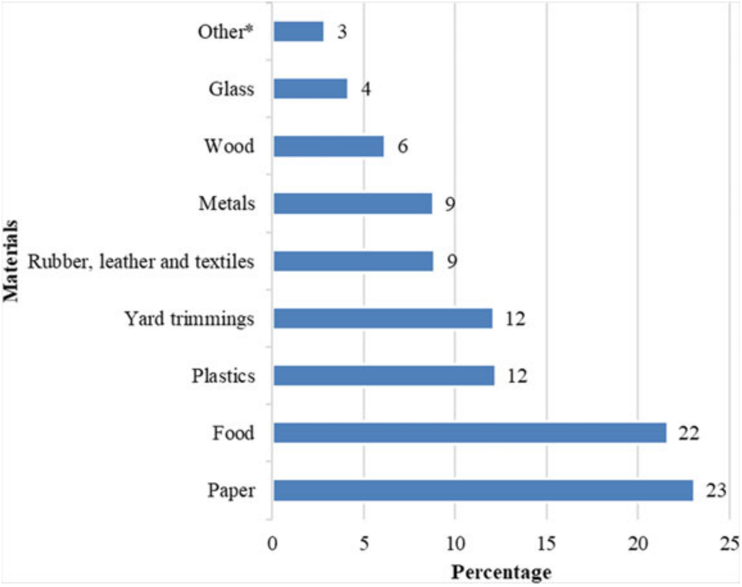


Fig. 7.6 By material distribution of MSW stream generated in the USA in 2018 (USEPA-US Environmental Protection Agency 2020)

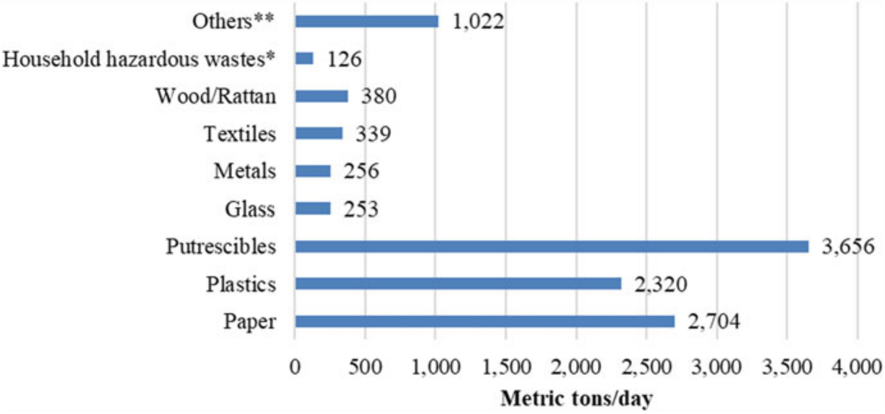


Fig. 7.7 Average daily MSW (by composition) at landfills in Hong Kong in 2019 (HKEPD 2020)

The public and local governments face a significant challenge in managing the waste caused. MSW management is a waste management system that follows the waste management hierarchy, which includes planning, administration, organisation, generation, storage and collection, transportation, sorting and recovery, and disposal methods (Fig. 7.8).

According to UNEP, open dumping and waste burning are popular in the majority of ASEAN countries (Silpa et al. 2018). Composting and anaerobic digestion of

Table 7.6 MSW composition in ASEAN countries (UNEP 2017)

No	Country	MSW composition (%)									
		Food/organics	Paper	Plastic	Metal	Glass	Textile	Rubber	Grass/wood/etc.	C&D[a]	Others
1	Brunei Darussalam	36	18	16	4	3					
2	Cambodia	60	9	15		3	1	1			
3	Indonesia	60	9	14	4.3	1.7	3.5	5.5			2.4
4	Lao PDR	64	7	12	1	7	5	3			
5	Malaysia	45	8.2	13.2		3.3					27.3
6	Myanmar	73	2.24	17.8		0.5	1.1				5.2
7	Philippines	52	8.7	10.6	4.2	2.3	1.6				
8	Singapore	10.5	16.5	11.6	20.8	1.1	2.1		8.6	16.9	11.9
9	Thailand	64	8	17.6	2	3	1.4	1	1		
10	Vietnam	55	5	10	5	3		4			

[a] C&D-Construction and demolition

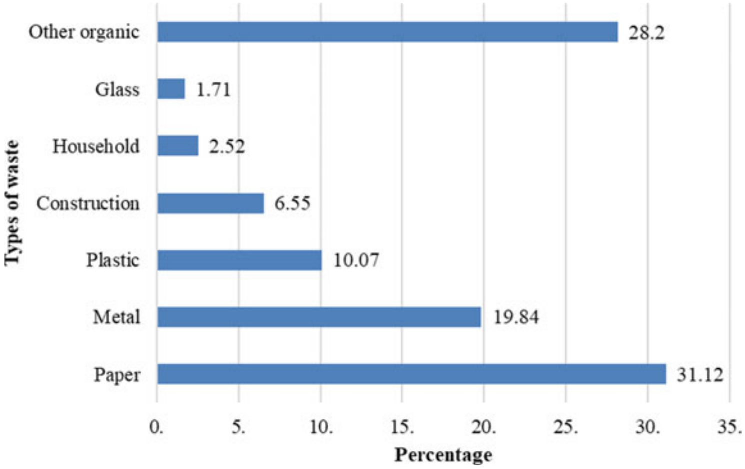


Fig. 7.8 In 2014, the following materials made up the majority of waste produced by mining, quarrying, and oil/gas extraction in the USA (Eurostat 2021)

organic wastes are popular in ASEAN, as is the recycling of valuable recyclables such as paper, plastic, and metal. On the other hand, the informal economy is more environmentally conscious. Singapore, on the other hand, stands out from the rest of ASEAN because it has a sound and well-organised waste management scheme. Singapore chooses waste to energy (WTE) through incineration as its primary waste management option due to its limited land resources.

7.4.1 Onsite Handling and Storage

Every nation and region have its own waste management strategy. MSW that is handled improperly will pollute water and soil, as well as have a negative impact on public health. Waste is typically deposited after it is generated at its source before being processed and transported to a landfill site.

When onsite storage of solid wastes, the type of container, the location of the container, the effect on public health, and the waste management methods should all be considered. The attributes of processed solid waste, the pace of recycling, and the container's available capacity define the capacities and sizes of containers used for onsite waste disposal. There are two types of waste storage in many countries: commingled waste storage and isolated waste storage. Commingled waste is a term that refers to initial or mixed waste. The most popular way of waste disposal was commingled waste storage, with 84 percent of households doing so and the rest separating organic waste from other wastes. A communal bin has been developed for a group of houses or a specific neighbourhood. In general, the primary operation of the field determines the type of waste container used. To gather waste directly from a residential household, a waste bin or a wheelie is widely used. Meanwhile, communal bins are provided for low- and medium-sized houses, and occupants can either deposit their trash in the communal bins themselves or use the services of the building maintenance staff. Spiral waste bins (SWB) are used in Malaysian apartments and condominiums where large quantities of waste are produced. SWB allows for a larger storage capacity due to its ability to compress waste (Tinmaz 2002). This would provide a more sanitary and efficient climate, but it would be expensive to implement. The Kuala Lumpur International Airport (KLIA), Complex, Kastam Kelana Jaya, and Kompleks Maju Junction in Malaysia all use these networks (Recyclingbin.com 2021). In the commercial and wet industry, a rolled-on/rolled-off (RORO) bin, a 12 m^3 bin that can be rolled on and off the trailer, is commonly used by local governments or private businesses.

Curbside collection using conventional and specially constructed trucks, incidental curbside collection by a volunteer group, and people carrying the separated waste to drop-off and recycling centres are the three types of collection systems used in Malaysia for waste segregated at source. As a result, residents would use their own containers and sort their garbage at the point of origin. Figure 7.9 depicts some of the most often used containers.

Fig. 7.9 Some of the typical storage bins

7.4.2 Waste Collection

A phase in the waste management process is waste processing. The proper collection of solid waste is essential for the protection of public health, environmental sustainability, and safety. That is the movement of solid waste from a source to a materials processing facility, dump station, or landfill disposal site. Waste recycling also includes the curbside storage of recyclable products that are technically not waste as part of a local landfill diversion scheme. The collection activity accounts for approximately half to seventy percent of the overall amount required for solid waste management (collection, transportation, sorting, recycling, and disposal) (Tchobanoglous et al. 1993).

Strong waste disposal, for example, accounts for almost half of the local authority's (municipal) operational budget in Malaysia, with waste generation responsible for the other half.

Waste disposal is an important aspect of waste control, but rates vary greatly depending on income levels, with almost uniform waste collection in upper-middle- and high-income countries. Low-income countries produce over 48 percent of waste in cities, but this figure falls to just 26 percent outside of cities. About 44% of waste is collected in Sub-Saharan Africa, while at least 90% of waste is collected in Europe, Central Asia, and North America (Fig. 7.10) (Silpa et al. 2018).

The nature and source of waste have an effect on the collection Scheme. A door-to-door recycling scheme is commonly used for domestic waste, in which waste is collected from the home (Fig. 7.11). A typical bin is usually given for areas not completely accessible to collection vehicles, and it is shared by several people or streets. A shared bin is used by a high-rise building or apartments, and selection is usually undertaken every day.

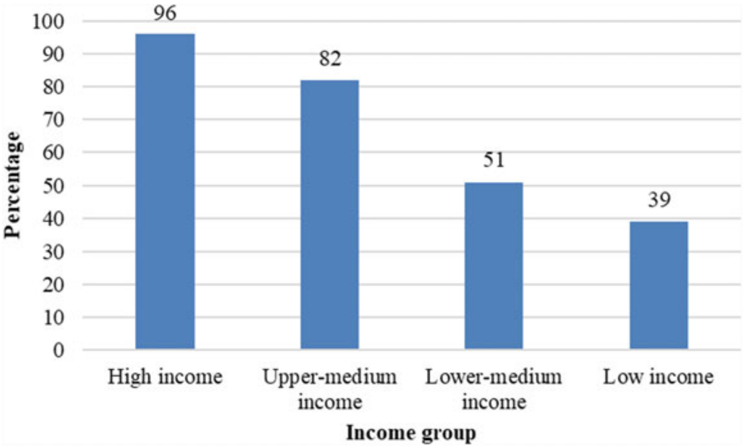


Fig. 7.10 Waste collection rates by income level (%) (Silpa et al. 2018)

Fig. 7.11 Example of the house-to-house collection

Dumpsters from an industrial bin are typically used to store commercial and non-hazardous waste. The recyclable material processing method is used to gather recyclable materials that have been removed at the point of generation. The selection method is often influenced by a number of influences, including but not limited to:

- The served area
- Types and tonnage/volume of waste generated
- Presence or absence of waste recycling facility
- Types of waste treatment system-landfill, composting, anaerobic digester, incineration, etc.
- Economic constraints
- Types of the collection vehicle

A hauled container system or a stationary container system is used to store commercial and non-hazardous industrial waste. A hauled container scheme entails transporting a waste storage container to a landfill site, draining it, and returning it. The truck, on the other hand, usually swaps empty and filled containers onsite. (ii) A stationary container arrangement is one in which, after being emptied, waste storage containers sit at the point of generation.

Waste disposal is a time-consuming process that accounts for almost three-quarters of solid waste treatment costs. Although city employees are often assigned to the task, it is often more cost-effective for the municipality to contract out collection services to private corporations. A driver and two to three collection personnel are normally assigned to each collection car. These are normally enclosed, compacting trucks with 10 to 30 cubic metre capacities. The truck will come to a complete stop at each home where the bin is kept (front or back of the street). The routing of this collection system should be configured to save time and power. The truck's capacity will be compressed to less than half of its original size.

Fig. 7.12 Example of compactor truck

Fig. 7.13 Ro-ro bin

Choosing the best collection route is difficult, particularly in densely populated cities. An optimum route is one that makes the most effective use of labour and equipment, and choosing one requires computer simulations that take into consideration all of the various construction variables in a vast and complex network. Variables include collection frequency, haulage distance, operation level, and setting. Due to low population densities and high unit costs, waste collection in rural areas can be especially difficult.

Due to the ease at which food waste decomposes, refuse disposal is normally done at least once a week. However, in a hot world, the collection is usually conducted 3–4 days/week. Daily collections are made at commercial properties such as hypermarkets and wet markets.

Many communities already have source isolation and recycling schemes in place, where residents and companies remove recyclables from garbage and place them in separate bins for processing. Residents in some cities will also bring recyclables to drop-off centres. The collection is normally handled by a dedication collection scheme assigned by the municipality. Collection automobiles come in a variety of shapes and sizes. The following are the most common:

(i) Tractor with a compactor (Fig. 7.12). It collects trash from both small (household) and large (communal) containers. (ii) Ro-Ro (roll-on-roll-off) (Fig. 7.13). The trucks transport huge containers (Ro-Ro bins) to landfills. (iii) Open-top vans (Fig. 7.14). Open vehicles were used to transport landscaping and

Fig. 7.14 Open truck

grass to the dump, as well as cutting garbage. A net is also placed on top of the load to keep waste from falling. However, some private contractors continue to extract and transport domestic waste using open vehicles.

The waste disposal scheme may also be divided into main and secondary systems. Table 7.7 lists both of them (16).

7.4.3 *Pneumatic Waste Conveyance System (PWCS)*

The PWCS is an automatic waste management system that gathers household waste and transfers it to a sealed container using a vacuum-type underground pipe network. Trucks gather the garbage on a regular basis and transport it to a landfill. The entire waste is stored in an automated manner, which reduces personnel needs while increasing production. The PWCS (Fig. 7.15) reduces the environmental and sanitary issues associated with open refuse collection systems (Waste Collection Report 2007). There are many benefits of the PWCS programme. Here are a few examples:

- The whole garbage disposal system is computerised.
- Manpower is small, as is the need for manual labour.
- Workplace conditions have improved.
- Eliminates noxious odours from garbage chutes.
- Reduces leaks during garbage disposal, making the environment more sanitary and cleaner.
- Aesthetically pleasing.
- Lessens the need to vacuum the chute.

Table 7.7 Options for primary and secondary waste collection (Wilson et al. 2014)

Vehicle	Comments
Primary	
Wheelbarrow	Recommended for waste collection from households located in narrow streets to a communal collection point. Required maintained street surface.
Hand cart	Stable for waste transfer in long-distance, especially on the road with bad surfaces. It is recommended for the door-to-door waste collections in crowded areas.
Cycle cart	Can move up to 3 m^3 of waste to a communal bin or a transfer station.
Tractor	Higher costs than all other options; however, it recommended transferring a large volume of waste for long distances.
Secondary	
Truck bin lifter	Suitable for collecting and transferring communal bins from residential and commercial areas.
Enclosed light truck	Suitable for waste collection from narrower streets
Flatbed crane truck	It is recommended for waste collection from transfer stations, markets and industrial areas.
Compactor	Expensive method for waste collection and transfer. Not suitable for high-density wastes. It required high skills for maintenance. It is recommended for low-density waste with large volumes.

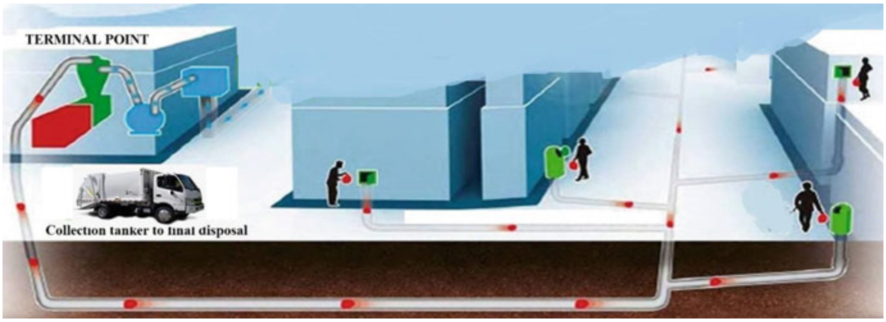


Fig. 7.15 Basic layout of a waste pneumatic collection system (Waste Collection Report 2007)

- There is a reduction in pest infestation.
- Waste decomposition is kept to a minimum.
- At the disposal site encourages waste separation for recycling.

7.4.4 Transfer Station

At least one transfer station will be required if the waste's final destination is not close to where it was produced. A waste transfer is a way of lowering the cost of recycling waste management while increasing the amount of recyclable waste. A transfer station is a single location where garbage from different collection vehicles is combined into a larger truck, such as a tractor-trailer. The waste is then delivered, normally over long distances, to a recycle or storage facility. Non-compacted waste can be transported in open-top trucks up to 76 cubic metres (100 cubic yards) to a centralised collection or storage site (Recycling magazine 2020). Occasionally, enclosed compactor trailers with ejector systems are used. At a direct discharge facility, many collection trucks spill directly into the transport vehicle. Trash is then emptied into a storage pit or onto a platform at a storage dump facility, and then the solid waste is hoisted or forced onto the transport truck using machinery. Large transfer stations can typically accommodate more than 500 tons of garbage every day. At least one transfer station will be required if the waste's final destination is not close to where it was produced. A waste transfer is a way of lowering the cost of recycling waste management while increasing the amount of recyclable waste. There are a few options in the transferring activities of waste. The common transfer activities that take place at transfer stations are reloading (transferring from smaller truck to larger truck), compaction or separation of the waste (Fig. 7.16) (Recycling magazine, 2020).

7.4.5 Waste Processing and Recovery

A multitude of technologies is used in solid waste disposal. The process of removing the economic value of goods and materials from waste that would otherwise be recycled is known as recycling. It entails collecting and converting recycled materials into new forms that can be used as raw materials for new products. While most people equate the term with urban waste, it may also apply to industrial or other forms of waste. The functional part of recycling includes all of the procedures, equipment, technologies, and facilities used to improve the efficiency of the other functional elements, as well as the reuse of recycled products and energy conversion from solid waste.

There are three basic approaches that can be used to recycle recyclable materials from MSW:

- Separation at the source by the building's, company's, or organisation's holders. This is the simplest and most effective strategy. Additional processing may not be needed.
- Collecting and treating mixed recyclables at consolidated materials recycling facilities (MRFs).
- Hybrid MSW storage of recycling items extracted from the waste stream at mixed waste disposal or front-end processing plants.

Recycling has two major benefits: it conserves renewable resources and landfill space, improving landfill life. Recycling provides additional work openings because it entails the storage and transportation of goods, which requires a significant number

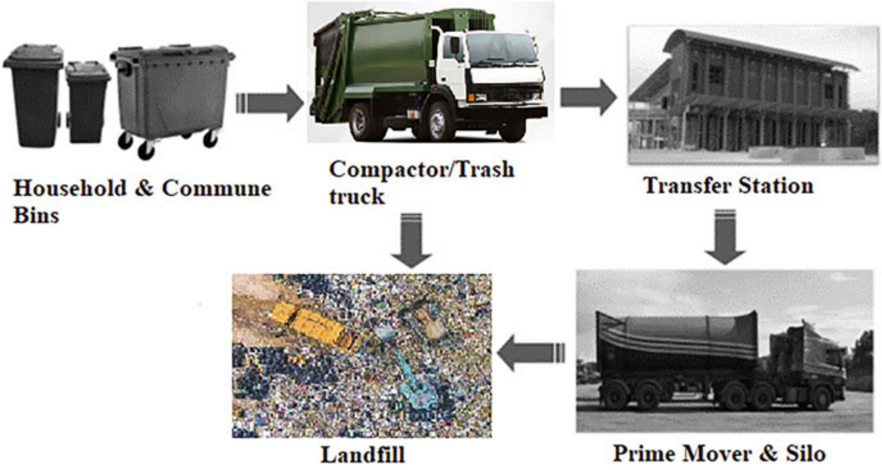


Fig. 7.16 A typical transfer station (Recycling magazine, 2020)

of resources and labour. Recycling serves to provide a supply of raw content and monetary benefit by discouraging the recycling of materials that can be reused or transformed into anything useful. The selling of aluminium, newspapers, packaging, glass, rubber, and other recycled products, for example, will help a city save money on waste management. Inevitably, recycling contributes to the protection of natural resources in every way. For every ton of paper recycled, 17 mature trees, 7000 gallons of water, 3 cubic yards of landfill area, and two barrels of oil are saved (recyclingbin.com). By selling recyclables, saving electricity, and reducing waste volume, a proper materials recovery system will lower waste management operating costs. Based on national waste management laws, the rate of recycling varies greatly across the world. Singapore and South Korea had the highest rates of municipal solid waste recycling, with a combined average of 59 percent. Figures 7.17 (OECD.stat 2021) and 7.18 (USEPA-US 2020) show MSW solid waste recycling rates by area in 2017 and the number of products recycled in the USA from 1960 to 2018. Since then, the amount of MSW that has been recovered and recycled has increased, reaching 69 million tons in 2018.

A materials recovery facility (MRF) (Fig. 7.19) handles the majority of waste management and recycling (USEPA-US 2020). Based on content, Fig. 7.20 depicts a figure for the total amount of materials obtained from municipal waste sources in the USA in 2018. This year, 1.67 million metric tons of rubber and leather goods were collected from urban waste (USEPA-US 2020).

It is a dedicated plant that takes commingled goods and, using a mixture of machines and/or manual labour, removes and densities them for sale to end-user manufacturers. This are carried out mechanically, using differences in physical characteristics of the waste, such as height, density, and magnetic properties. Shredding or pulverising waste items reduces their bulk, resulting in a uniform mass of

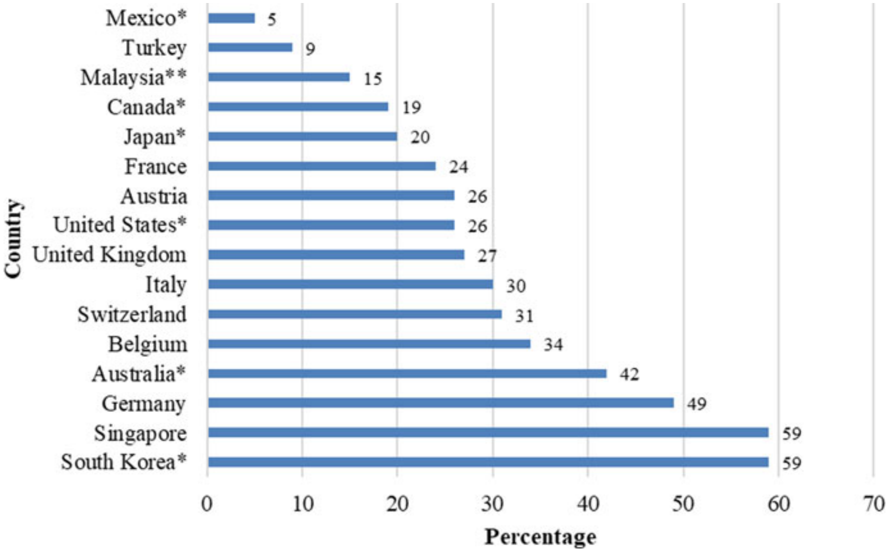


Fig. 7.17 Recycling rates of municipal solid waste in 2017 by country (**Estimated) (recyclingbin.com)

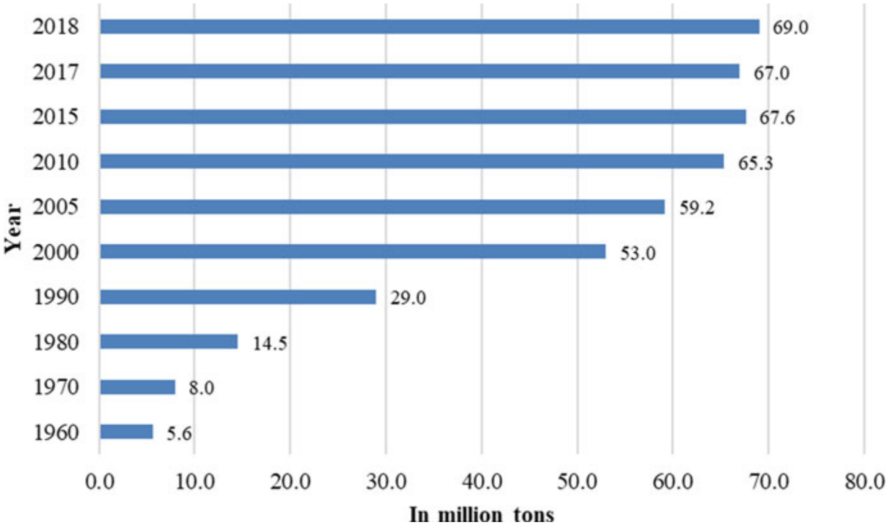
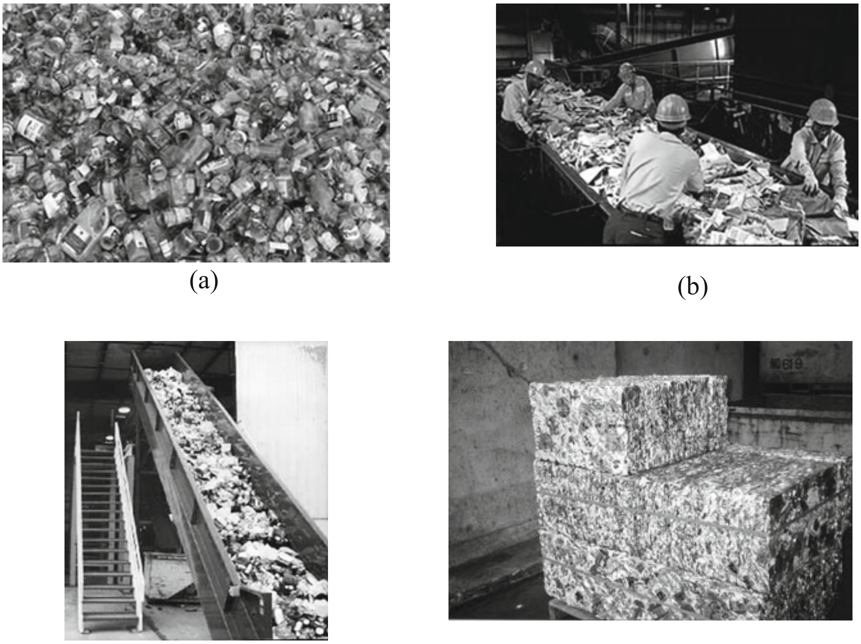


Fig. 7.18 The number of materials recycled in municipal solid waste in the USA between 1960 and 2018 (USEPA-US 2020)

material. This is done with hammer mills and rotary shredders. MSW constituents can be isolated and recycled in various ways. Paper, plastics (PET and HDPE), glass, aluminium, ferrous metals, and non-ferrous metals are the most common. MRFs are divided into two types: clean and dirty. Clean MRFs deal with the contents of mixed



(a) (b)

(c) (d)

Fig. 7.19 An example of a typical MRF facility. (**a**) Commingle waste. (**b**) Manual or automatic sorting process. (**c**) Pulverised and conveyed to next process. (**d**) A baled product

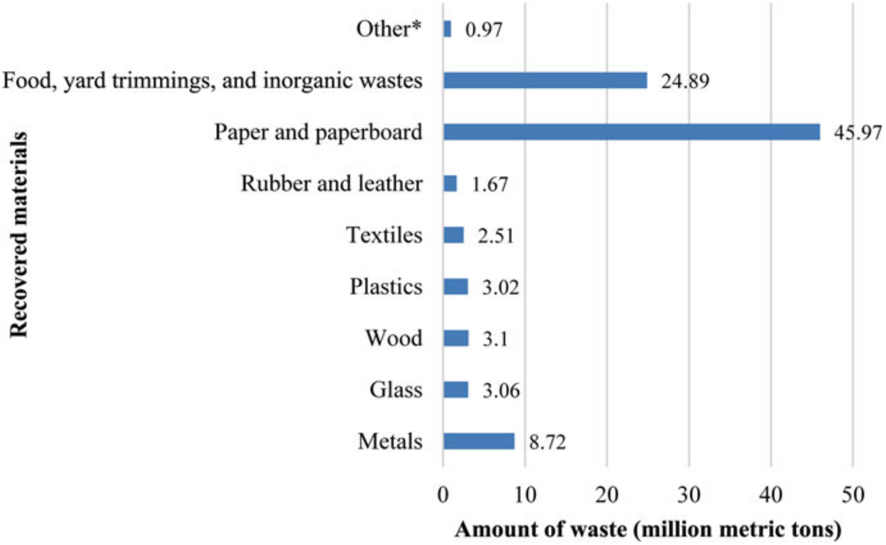


Fig. 7.20 Shows the number of materials recovered from industrial waste in the USA in 2018, based on content (USEPA-US 2020)

recycling bins that are all recyclable, while dirty MRFs deal with solid waste that includes some salvageable recyclable materials (Table 7.8).

7.4.6 Final Disposal by Landfilling

There are several disposal options for solid waste based on their composition and sources. This includes:

- Direct burning of solid waste and dumping in the sea is not advisable.
- Dumping on land in landfills or dumpsites.
- Heat treatment-incineration, pyrolysis, gasification.
- Composting and reuse process in agricultural activities.
- Biological fermentation and digestion.

7.4.6.1 Introduction

The most common choice for final waste disposal, particularly in developed countries, is a sanitary landfill. It is the simplest, cheapest, and most cost-effective method of waste disposal. Landfills are now considered the oldest and most practical means of disposing of solid waste in many countries. Owing to the rise in waste volume emitted daily, many landfill sites are quickly filling up, and many do not have a sufficient 3'R facility. Land acquisition for landfilling is becoming more difficult, particularly in urban areas, due to land scarcity and land prices.

Modern urban waste disposal sites are well-engineered and equipped with waste disposal systems. However, if the dumping site is not well handled, this approach will lead to significant environmental issues. Mass dumping of waste into a given area, usually a pit or a sidehill, is the most common form of land dumping. Since the waste has been dumped, large machines compress it. When the dumping cell is out, it is "sealed" with a plastic sheet or dirt. Solid waste can decompose in a landfill before being converted into a comparatively inert and stable substance. Landfilling is, in effect, an important part of waste management. The recycling process, on the other hand, produces non-recyclable materials and residuals that must be disposed of in a landfill. However, proper landfill construction and control after their closing remain critical concerns for effective and safer solid waste disposal and maintenance. This covers leachate storage and disposal systems as well as landfill gas control systems.

7.4.6.2 Landfills in the World

Nearly half of the world's population, according to Worldatlas (2019), lacks access to basic waste storage and recycling facilities. More than 70% of MSW is disposed of in landfills around the world, with landfills accounting for the bulk of waste

Table 7.8 The available technologies used for solid waste processing, treatment and disposal (Parvez et al. 2019)

Types of waste and technology available	The processing	Key issues
Paper	Paper recycling	High capital investment is required
	Waste to Energy	– No auxiliary fuel needed – High capital investment is required
Plastic	Incineration	– High calorific value, no auxiliary fuel needed – Efficiency is high. – High capital cost
	Recycling	– Expand landfill life span – Needs to identify buyers
Construction waste	Reuse and recycling	– Substitute for new products. – Non-recyclables/residuals sent to landfill
Organic and Garden	Composting	– Improves nutrient quality, thus destroying pathogens and acting as a soil conditioner. – Time-consuming and requiring a substantial amount of land
	Anaerobic digestion and methanation	– Generates anaerobic/gaseous fuel – Reduction in greenhouse gas emission. – Capital intensive method – Less effective for lower biodegradable
Inorganic	Sanitary landfills and landfill gas recovery	– It-Cheaper if the land is available – Potential for energy recovery of landfill gas – May cause air and water pollution if not designed and maintained properly – Land requirement is high
	Refused Derived Fuel (RDF) Production	– A burner made of RDF pellets. – Trained staff are needed. – A large initial capital expenditure is required.
Chemical/hazardous	Recycling	– Recycled into new products – Killed personal required
	Incineration, waste to energy	– Reduced air pollutants in modern design – Involves high capital investment – Requires good air pollution control systems
	Hazardous waste landfill	– Secured landfill with extra pollution control – High capital investment – Expert requirement
Medical/hospital	Off-site	– Proper handling and expert requirements – Mainly incinerated
E-waste	Recycling	– E-waste recycling centres must be devoted. – Electronic devices contain potentially dangerous materials, such as poisonous chemicals.
Metal	Recycling	– Metal recycling saves landfill space and requires a large initial investment. – Ample space is needed.

collected in low- and middle-income developed countries. These unregulated landfills are often found in urban areas. Pollution from open burning and groundwater pollution are two other widespread concerns from unregulated sites.

This graph depicts a ranking of some of the world's biggest dumpsites as of 2019 (Fig. 7.21). This year, the Apex Regional Landfill in Las Vegas, Nevada, occupied approximately 2200 acres of soil. It is the largest landfill in the USA, with a life expectancy of 250 years and a waste capacity of up to 50 million tons (Worldatlas 2019).

The world's largest landfill in 2019 is depicted in Fig. 7.21. Table 7.9 shows the waste generation, number of landfills in the EU, and other disposals/treatment methods (23). The waste disposal approaches used in ASEAN are mentioned in Table 7.10.

A vast amount of garbage is recycled or dumped in landfills all around the world (Fig. 7.22) (Worldatlas 2019). A landfill is used to dispose of some 37% of garbage, with 8% of it going to sanitary landfills with gas disposal systems. About 31% of waste is publicly discarded, while 19% is recovered by recycling and composting, and 11% is incinerated for final disposal. Waste disposal and storage, such as controlled landfills or more stringently operated services, are almost exclusively the responsibility of high- and upper-middle-income countries. Open dumping is common in low-income countries; 93 percent of waste is discarded in these countries, compared to just 2% in high-income countries. The three areas that publicly dump more than half of their waste are the Middle East and North Africa, Sub-Saharan Africa, and South Asia. Upper-middle-income countries have the largest proportion of waste in landfills (54 percent). This figure fell to 39% in

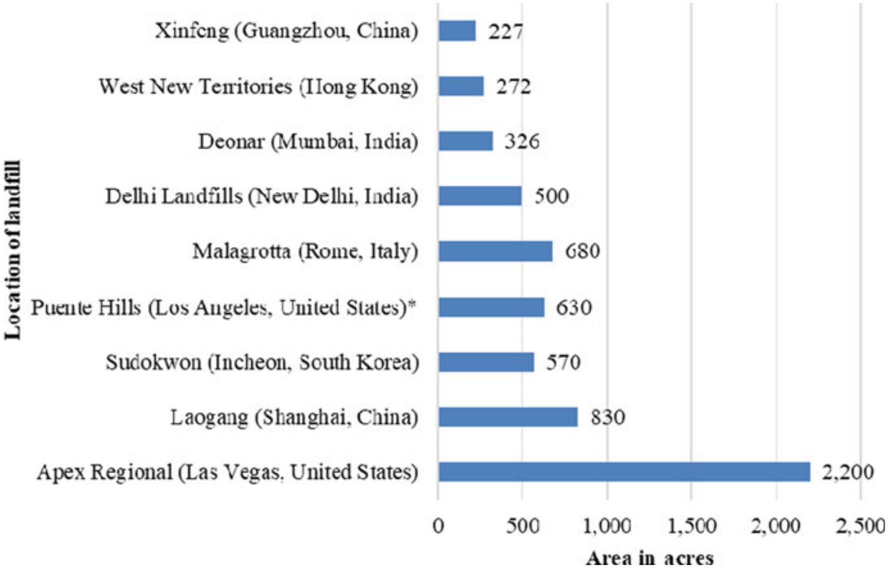


Fig. 7.21 Size of largest landfills globally as of 2019 (Worldatlas 2019)

high-income countries, with 36% of waste allocated to recycling and composting and 22% to incineration. Incineration is most often used in countries with a lot of electricity, a lot of money, and a lot of lands.

7.4.6.3 Categories of Landfill

Landfill sites are classified into five groups, as practised in Malaysia and many other countries. Table 7.11 explains its functions in detail. Anaerobic landfills, anaerobic sanitary landfills, modified anaerobic landfills, semi-aerobic landfills, and aerobic landfills are among the various types of landfills.

7.4.6.4 Landfill Leachate and Its Treatment

The collected urban solid waste in landfill sites is subjected to a variety of physico-chemical processes, which result in the production of leachate, a heavily polluted, dark-black liquid with a foul odour. Leachate is a solvent that disintegrates solid waste. It is made up of natural moisture and water in organic matter debris (a by-product of chemically decayed organic matter), as well as rainwater that percolates through the landfill's interior layers, increasing the solubility of suspended products (Fig. 7.23).

The composition of MSW, site topography, area hydrogeological state, age of solid waste, temperature variations, humidity, and landfill site activity are all important factors in the production of leachate in landfill sites. As a result, it is critical to safeguard the ecosystem's long-term viability by investigating environmentally sustainable and reliable recovery processes that can handle leachate to the point that it is safe to discharge into surface water supplies (Fig. 7.24). Table 7.12 shows a standard feature and description of landfill leachate (24–27). The benefits and drawbacks of each physical and chemical treatment process are clearly displayed in Table 7.13.

Biological treatment is also limited to young and intermediate leachates with a high biodegradable organic matter content (BOD5/COD>0.5). High contaminant landfill leachate with a poor biodegradability index of less than 0.1 and a high concentration of ammoniacal nitrogen is better treated with physical-chemical approaches. In the treatment of old or stabilised leachate, which is difficult to degrade, both physical and chemical therapies have shown to be highly successful (Costa et al. 2019).

Table 7.9 Waste Generation and Treatment facilities (kg/capita) (Eunomia 2021)

Country	Year	Source	Population (000s)	Waste generated	Landfill	Incineration	Other recovery	Material recycling	Composting and digestion	Recycling rate
1. Germany	2015	OECD	81,202	628.6	59.3	196.7		300.7	114.6	66.10%
2. Wales	2016/ 2017	Welsh Government	3100	512.8	48.7	125.8	0.3	327.2		63.80%
3. Singapore	2016	Singapore Government	5607	1394.6	543.1			850.5		61.00%
4. South Korea	2014	OECD	50,424	361.3	60.9	91.5		209.9	3.3	59.00%
5. Taiwan	2016	Taiwan EPA	23,492	317.6	3.9	127.4	2.6	159.7	24.5	58.00%
6. Netherlands	2016	Netherlands Government	16,981	560.6	12.5	209.7		171.5	145.7	56.60%
7. Austria	2015	OECD	8538	566.4	16.8	214.6		145.3	177	55.90%
8. Slovenia	2015	OECD	2067	448.1	101.7	76.5	14.3	208.1	34.3	53.90%
9. Belgium	2015	OECD	11,369	414.1	78.4	179.7		142.1	79.2	53.50%
10. Switzerland	2015	OECD	8129	741.8		350.6		236.7	154.5	52.70%
11. Italy	2016	Italy EPA (ISPRA)	60,656	496.2	122.5	96.7		153.4	107.4	52.60%
12. Luxembourg	2015	OECD	563	632.7	111.5	215.7		180.4	125.1	48.30%
13. Sweden	2015	OECD	9799	446.6	3.6	228.7		144.6	69.8	48.10%
Country										
14. Denmark	2015	OECD	5611	799.3	9.1	420.4		217.9	151.8	46.30%
15. Scotland	2015	SEPA	5400	457.2	213.1	41.9		202.1		44.20%
16. United Kingdom	2015	UK Gov—Defra	64,532	489.2	115	153.5		133.3	79.4	43.50%
17. Norway	2015	OECD	4904	446	15.1	233.5	6.3	116.5	74.4	42.80%
18. England	2016/ 17	UK Gov—Defra	55,268	476.2	74.8	184	13.8	127.1	76.5	42.80%
19. Poland	2015	OECD	38,016	285.7	129.7	37.9		75.4	46	42.30%

20. Northern Ireland	2015/16	NI Gov—Daera	1900	510.1	205.4	90	1.4	122.3	91.1	41.80%
21. Australia	2015	OECD	23,941	557.2	260.6	64.9		231.7		41.60%
22. Finland	2015	OECD	5493	498.5	57.3	238.9		140.2	62.1	40.60%
23. France	2015	OECD	66,498	502.3	134.8	174.4		111.8	86.7	39.60%
24. Hong Kong	2014	Hong Kong Government	7240	776.2	492.7			283.6		36.50%
25. United States	2014	OECD	318,857	735.3	386.7	94.3		188.9	65.5	34.60%

Table 7.10 MSW management and disposal in Asean (UNEP 2017)

No	Country	Segregation at source (%)	Collection rate (Urban) (%)	Recycling rate (%)	Management/treatment/disposal method				
					Composting	Incineration	Sanitary landfill	Open dumps	Open burning
1	Brunei Darussalam	<50	90	15			√	√	
2	Cambodia	<50	80	<50	√		√	√	√
3	Indonesia	<50	56–75	<50	√	√	√	√	√
4	Lao PDR	<50	40–70	<50					
5	Malaysia	<50	>70	50–60 (Metal, paper, plastic) <50 (Others)	√		√	√	√
6	Myanmar	<50		70 (Plastic, paper, metal)		√	√	√	
7	Philippines	50–70	40–90	20–23 (Paper) 30–70 (Al) 20–58 (Other metals) 23–42 (Plastic) 28–60 (Glass)	√		√	√	
8	Singapore	70	>90	50–60 (Paper, horticulture) >90 (Fe, CanD, used slag) >80 (Scrap tyre) >80 (Wood) >50 (Others) 60 (Overall)		√	√	√	

9	Thailand	<50	>80	>90 (Metal) 50–60 (Paper, construction) <50 (Others)	√	√	√	√	
10	Vietnam	<50	80–82	>90 (Metal) >70 (Plastic, E-waste) 50 (Paper) <50 (Others)	√			√	

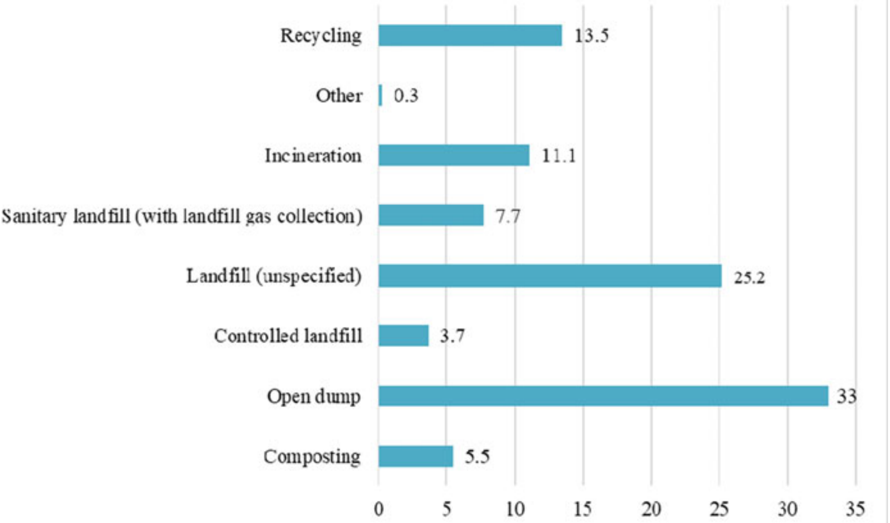


Fig. 7.22 Global treatment and disposal of waste (%) (Silpa et al. 2018)

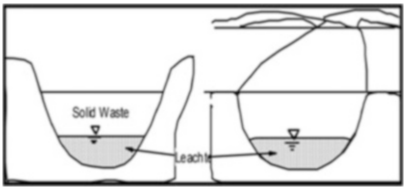
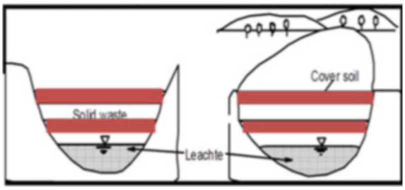
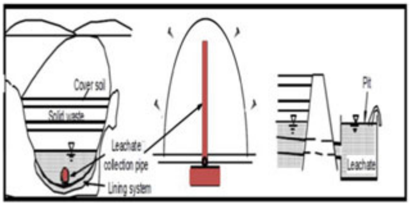
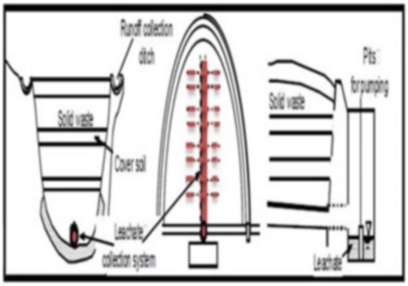
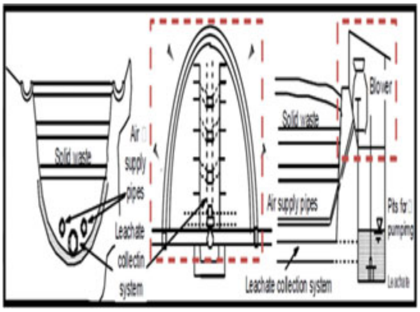
7.4.6.5 Design, Operation, and Challenges for Landfilling

Landfill Siting Due to the difficulties of finding an appropriate spot, one of the key problems facing the local authority for waste management is site selection for landfill development. One of the most difficult obstacles is neighbourhood opposition, which will usually object to the landfill being located near their homes.

Landfill Design According to technical principles and environmental codes of practice, the landfill should be appropriately designed to account for all different features, such as a sufficient baselining system, leachate disposal system, regular soil covering and final top liner, surface run-off collection and discharge system, gas pollution system, and adequate access facilities to the landfill. The materials used in landfill construction and lining systems should have no negative impact on the environment, particularly groundwater. The landfill baseliner is made up of two upper and lower liners that compacted the soil. Furthermore, the primary aim of a baseliner is to reduce the risk of groundwater contamination due to leachate infiltration.

Gas Emission The natural decomposition of waste in the landfill involving microorganisms to break down the waste usually happens. The rate of degradation and decomposition of waste depends on the amount of water in and the temperature of the waste. During this process, the organic fraction of the wastes turns into CH_4 and CO_2. Moreover, some organics can be directly transformed into gas, such as cleaning

Table 7.11 Types and characteristics of conventional landfills

Types	Characteristics	Illustrations
Anaerobic landfill	Solid waste is dumped into a dug area or a valley, and water is merged to allow for the anaerobic process to take place. This basic landfill has caused many serious environmental and human health problems by producing hazardous leachate.	
Anaerobic sanitary landfill	This method layers solid waste with soil (sandwich form). Other characteristics are similar to those of anaerobic landfills.	
Improved anaerobic landfill	Improvement was made to this design by adding a leachate collection system at the bottom of the pond. Other characteristics are similar to that of anaerobic landfills, except for the moisture content that is notably low.	
Semi-aerobic landfill	In this model (Fukuoka method), O_2 is supplied spontaneously through the collection pipe to stabilise the solid waste. Therefore, the collection pipe is designed to be bigger than the previous model so that it can function to collect leachate and provide O_2. The aerobic process occurs here and increases the decomposition rate of solid waste.	
Aerobic landfill	This method is designed to enhance the aerobic process of landfill systems since semi-aerobic landfills have performed well in terms of biodegradation and stabilisation of landfills. Air and re-circulation leachate systems are also installed in order to increase and maintain the humidity as well as to supply nutrients for the microorganisms present in the water sample.	

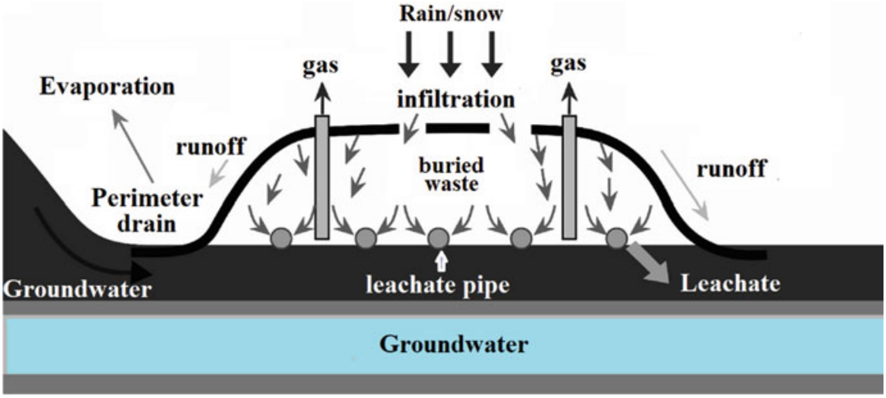


Fig. 7.23 Leachate formation in landfill

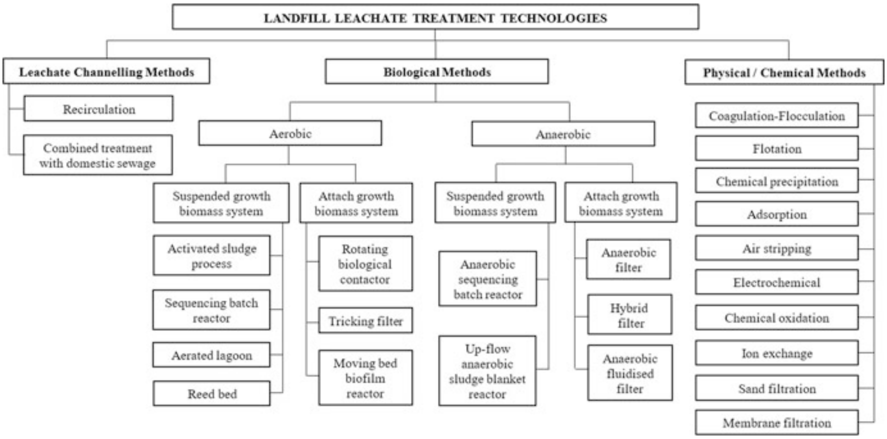


Fig. 7.24 Schematic diagram of landfill leachate treatment technologies

materials waste. Typical constituents in the gas produced by municipal solid waste landfill are given in Table 7.14 (WHO 2014).

Landfill operation and maintenance: For the purposes of public and environmental protection, the landfill should be designed to meet safety standards. The following aspects of service and repair should be well-managed:

(1) The waste in the landfill should be marked by the operators as non-hazardous, clean, and suitable for disposal, (2) the waste in the landfill should be covered regularly, (3) surface drainage should be controlled to keep the waste decomposition in the landfill and not increase leachate usage, and (4) the machinery used in the landfill should be preventive and introduce safety operations to the site staff.

Table 7.12 Typical characteristics and classification of landfill leachate

No.	Parameter	Unit	Category of landfill leachate		
			Young	Intermediate	Stabilised
1	Age	Year	<5	5–10	>10
2	pH	–	<6.5	6.5–7.5	>7.5
3	COD	mg/L	>10,000	5000–10,000	<5000
4	BOD_5/COD	–	>0.5	0.5–0.1	<0.1
5	Organic	–	80% (VFA)	5–30% (VFA + HFA)	HFA
6	NH_3–N	mg/L	<400	–	>400
7	Colour	PtCo	<1000	–	1500–7000
8	TOC/COD	–	<0.3	0.3–0.05	>0.5
9	Conductivity	μs/cm	15,000–41,500	6000–14,000	–
10	Heavy metal	mg/L	Low	Low	Low
11	Biodegradability	–	Important	Medium	Low

Note: VFA (Volatile fatty acids) and HFA (Humic and fulvic acids)
Source: Shehzad et al. (2015), Aziz and Ramli (2018), Costa et al. (2019), Pasalari et al. (2019)

Table 7.13 Comparison of the physical and chemical methods in leachate treatment (Eunomia 2021)

No.	Method	Leachate			Cost	Remark
		Y	M	O		
1	Coagulant-flocculation	Poor	Fair	Fair	Low	High sludge production
2	Air stripping	Poor	Fair	Fair	High	Air pollution
3	Chemical precipitation	Poor	Fair	Poor	Low	Disposal of hazardous waste
4	Adsorption	Poor	Fair	Good	Low	Carbon fouling
5	Chemical oxidation	Poor	Fair	Fair	High	Toxic by-product
6	Electrochemical	Poor	Fair	Fair	High	High energy usage
7	Membrane filtration	Good	Good	Good	High	Membrane clogging
8	Ion exchange	Poor	Fair	Fair	High	High anion/cation
9	Flotation	Poor	Fair	Fair	High	High capital cost

7.5 Integrated Solid Waste Management

Integrated solid waste management (ISWM) is a comprehensive approach to waste management that encompasses waste control, diversion, recycling, reuse, treatment, and disposal. Management refers to how waste is treated from source to source (a cradle to grave approach). It also considers the waste management hierarchy, accounting for both primary and indirect waste collection, sorting, treatment, and recycling impacts. Solid waste disposal must be sustainable from planning to construction, commissioning, and operation. ISWM may be used to develop a long-term solid waste management scheme that is both environmentally and economically viable, as well as socially appropriate.

The ISWM approach is currently the most appropriate scheme for solid waste treatment. ISWM encourages waste minimisation by waste collection, reuse, and recycling, as well as waste disposal using traditional or innovative technologies, by improving the efficiency of the total management system for all forms of wastes, composting, incineration, and landfilling.

A hierarchy (a system of order of importance) may be used in waste management to prioritise actions for executing group policies. The ISWM hierarchy usually includes source removal, recycling, waste transformation/processing, and landfilling. As seen in Fig. 7.14, a greater focus on source reduction and the least on final disposal should be put. The most common solid waste management strategies are prevention, minimisation, reuse, recycling, energy recovery, and landfill disposal.

Source Reduction (Reduce): At the very top of the ISWM ladder, source reduction (reduce) means reducing the amount and/or contamination of existing wastes. Designing, manufacturing, and shipping materials with a low toxic content, a small supply of material, or a longer usable life may help reduce waste. In the home, company, or industry, selective buying practices and the reuse of products and services may also help to minimise waste.

The second-highest level of the hierarchy is reuse and recycling, which includes (1) waste separation and collection; (2) waste material preparation for reuse, reprocessing, and remanufacture; and (3) waste material reuse, reprocessing, and remanufacture. Recycling is an important aspect of reducing water consumption and pollution that must be disposed of in landfills.

You can get a lot of recyclables back if you build a Materials Recovery Plant (MRF). Both recyclable materials will be sorted in a structured fashion at this site, allowing them to be recycled and turned into new items. The landfill's productive life will be extended as a result of this.

A properly designed waste segregation system is intended to improve the overall recycling process while also extending the life of the landfill. A 3Rs (recover, reuse, recycle) campaign should be prioritised at the same time. Residents should be reminded of the importance of sorting garbage at a collection point. A proper

Table 7.14 Typical parameters found in landfill gas (WHO 2014)

Component	Percentage (dry volume basis)
Methane	45–60
Carbon dioxide	40–60
Carbon monoxide	0–0.2
Nitrogen	2–5
Oxygen	0.1–1.0
Sulphides	0–1.0
Ammonia	0.1–1.0
Hydrogen	0–0.2
Trace constituents	0.01–0.6
Non-methane organic compounds	0.01–0.6

recycling scheme must be devised as quickly as possible. Training is critically necessary for the long term. The 3Rs movement is important, and it is a daunting task that can only be met by education. This could take a long time, but it should start right away. Residents will have to sort their garbage at the recycling centre. The provision of facilities is needed. It would be important to evaluate success and loss. The recycling rate is expected to rise significantly in the near future if these two approaches (recycling at the point of use by MRFs and recycling by education) are combined.

Waste Processing/Transformation: The physical, chemical, or biological transformation of wastes is the third step in the ISWM hierarchy. MSW is typically transformed physically, chemically, and biologically to (1) improve the efficiency of solid waste management activities and processes, (2) recover reusable and recyclable materials, and (3) recover conversion products (e.g., compost) as well as energy in the form of heat and combustible biogas. Waste transformation, in most situations, results in less garbage capacity being used. The reduction of waste volume by incinerator heat treatment is a well-known example.

Landfilling: By the end of the day, something has to be achieved for (1) non-recyclables that are no longer useful; (2) residuals after solid wastes have been removed at a materials recycling plant; and (3) residuals after a waste to energy facility. The supervised dumping of wastes on or in the earth's mantle, which is ranked fourth in the ISWM hierarchy, is referred to as landfill, and it is by far the most typical method of final disposal for waste residuals.

However, different aspects must be investigated in order to incorporate a successful comprehensive solid waste management scheme. This involves estimating the amount of waste to be produced and conducting numerous studies such as Environmental Impact Assessment (EIA) and Socioeconomic Assessment (SoEIA), Sustainable Assessment (SA), Risk Assessment, and Life Cycle Assessment (LCA). On top of that, a Cost-Benefit Analysis and a feasibility study are also necessary.

7.6 Legislative Aspects of Solid Waste

Transportation, handling, collection, and recycling of various types of waste are also governed by waste management rules. Waste regulations are generally applied to deter pollution by limiting or prohibiting the uncontrolled release of waste products into the atmosphere. They also have regulations aimed at lowering waste production and encouraging waste recovery and recycling. The waste designation is the process of classifying a product as a "waste" subject to legislation. Non-hazardous municipal solid waste, for example, may be disposed of in landfills in the USA and many other countries, while other metal scrap is considered hazardous and must be processed, collected, cleaned, and disposed of instead.

The choices for disposing of a given waste are determined by disposal criteria. In many countries, littering is the most common and widespread of these principles.

Before being disposed of at a landfill site, some waste must be treated in a certain manner. For example, the Land Disposal Restrictions under the Resource Conservation and Recovery Act Subtitle C hazardous waste management policy of the US Environmental Protection Agency ban hazardous waste from being disposed of on land (primarily in landfills) without prior permission.

Specific standards for the design and operation of a landfill can be followed, especially in regard to the need to adhere to site limits in order to prevent pollution of surface and ground water. It also oversees operational strategies aimed at reducing dust and other annoyances (leachate and gases), as well as environmental enforcement schemes.

There is also environmental legislation, which requires arrangements on the transportation and handling of hazardous waste across international borders. Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal, 1989; Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal, 1989; Basel Convention on the Control of Transbound AND (Agreement on the International Carriage of Dangerous Goods through Inland Waterways) was signed in Geneva in 2000; Convention to Ban the Importation of Hazardous and Radioactive Wastes into Forum Island Countries and to Control the Transboundary Transport and Management of Hazardous and Radioactive Wastes, Geneva, 2000; Convention to Ban the Importation of Hazardous and Radioactive Wastes into Forum Island Countries and to Control the Transboundary Transport and Management of Hazardous and Radioactive Wastes, Geneva, 2000; Convention to Ban the Importation of Hazardous and Radioactive Wastes into Forum Island Countries and to Control the Transboundary Transport and Management.

The Resource Conservation and Recovery Act (RCRA), enacted in 1976, is the principal federal law governing solid waste and hazardous waste disposal in the USA. The Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA), which is administered by the US EPA, established the federal Superfund programme in the USA Environmental Protection Agency (EPA). The programme's goal is to monitor and clean-up sites that have been polluted with toxic substances. Hazardous waste production and storage are regulated by the US Environmental Protection Agency (EPA), hazardous waste transportation is regulated by the US Department of Transportation (DOT), and radioactive waste is regulated by the Nuclear Regulatory Commission (NRC).

In the UK, waste legislation is largely derived from EU governance and then transposed into UK law by Statutory Instruments. In October 1996, the government imposed a Landfill Tax on some types of waste stored in landfills in response to the increasing volume of waste discarded in landfills. Landfill operators, for example, who were approved under the Environmental Protection Act (EPA) or the Pollution Control & Local Government Order 1978, had until 31 August 1996 to register their tax liability. The tax is seen as a key tool in the UK's efforts to meet the Landfill Directive's goals for landfilling biodegradable waste. By raising the expense of landfill, some modern waste disposal schemes with higher tipping fees are more financially appealing. The Landfill Directive, also known as Council Directive 1999/31/EC, is a European Union directive that controls landfill waste management in the EU. It was adopted on 26 April 1999. By 16 July 2001, it had been ratified by all of the organisation's member nations. The Directive's overarching aim is to "avoid or reduce as much as possible the harmful environmental effects of waste landfilling, as well as any resulting threat to human health". The implications of this act for waste control and disposal are far-reaching. Following that, waste quotas for England and Wales were introduced in 2000 and 2002, with an emphasis on recycling, composting, and energy from waste (EFW) technologies for MSW recovery (Buttol et al. 2007; Emery et al. 2007).

The Landfill Directive (European Commission 2018), the Waste Incineration Directive, and the Packaging and Waste Packaging Directive are the foundations of the current European waste policy (European Commission 2018). The EU Landfill Directive, which was adopted on 26 April 1999, and went into force on 16 July 1999, set mandatory quotas for the UK and other EU countries to reduce the biodegradable portion of urban waste discarded to landfill to 75% by 2010. In the same way, by 2013, this will have to be reduced to 50%, and by 2020, it will have to be reduced to 35%. The Welsh Assembly Government launched the "Wise About Waste" National Waste Strategy for Wales in 2002, with the aim of ensuring that the country complies with European waste management directives. By 2003/2004, a minimum of 15% of MSW must be recycled or composted, with a 5% target for each category, according to the targets. By 2006/2007, the target had been raised to 25%, with a minimum of 10% for each party. The total target is set to be 40% by 2009/2010, with a minimum goal of 15% for each category, Emery and his associates (30). Environmental regulations, as well as other green growth, economic development, and climate change programmes, regulatory mechanisms, and initiatives, have also been adopted in the majority of ASEAN countries. In Indonesia, Malaysia, the Philippines, and Thailand, waste management law remains. Waste management strategy is primarily under the control of the Ministry of the Environment. Other relevant ministries are in charge of specific waste sources as well (for instance, the Ministry of Health for hospital waste, Ministry of Local Government for domestic waste). At the local level, municipalities and federal or local governments are directly responsible for waste collection schemes.

The four subsidiary laws that govern solid waste management in Malaysia are the Local Government Act of 1976, the Environmental Quality Act of 1974, the Town and Country Planning Act of 1976, and the Streets, Drainage, and Construction Act of 1976. Local municipalities are the most powerful agency involved in solid waste management at the moment. As a result, in 1988, the Malaysian Ministry of Housing and Local Government's Technical Section presented a National Solid Waste Management Action Plan, also known as the Action Plan for a Beautiful and Clean Malaysia (ABC). This year, the Gazette issued the Solid Waste and Public Cleansing Management Act 672 and the Solid Waste and Public Cleansing Management Corporation Act 673.

7.7 Concluding Remarks

The aim of this chapter was to provide a broad picture of the essence of the solid waste problem, both qualitatively and quantitatively, as well as the problems concerning its management. Among the numerous environmental issues of waste management are the exponential rise in waste volumes and a complex waste mix of recent and existing waste sources. Proper solid waste disposal is critical for public health and the environment in both developed and developing countries. For centralised urban solid waste management, full compliance with waste management hierarchy structures is needed. Successful municipal solid waste disposal necessitates waste minimisation and reduction. Recycling and reusing waste are seen as a viable choice for boosting the economy and lowering the volume of final waste disposal. Despite the many recycling methods available, landfilling is widely accepted as a feasible alternative for disposing of municipal solid waste around the world. Increasing waste collection volumes and the need to satisfy more stringent regulatory standards of disposal operations are forcing many municipal councils to raise capital and operational revenue reserves.

Both short- and long-term options are critical in the overall management structure. Infrastructure, technology, funding, policy, and stakeholder engagement are all big issues in many countries. On the other hand, if we change our mindset about waste as a resource, these challenges might become opportunities. Front-end solutions, such as mechanisms for waste reduction/prevention by sustainable use and resource utilisation, must be considered in addition to enhancing waste collection rates and waste to energy (WTE) technologies and practices. Both countries should promote discrimination at the source in order to provide a sustainable recovery mechanism. To inspire citizens to recycle, such benefits, such as a recycle for life card that pays people that give recyclables to recycling centres, may be invented. A successful model So that waste can be turned into income and the current digital economy loop can be improved, a proper value chain in the entire solid waste management system (including waste generation, segregation, processing, transfer, care, and disposal, as well as resource recovery through the 3Rs) should be planned. Furthermore, every nation should investigate developing waste-related co-benefits, such as lower greenhouse gas (GHG) emissions, which aids in the achievement of sustainable development goals (SDGs), and so on. Greater collaboration between public and private agencies in waste value chains will help pool capital and collect common waste management obligations, especially in terms of selecting and applying environmentally sound technologies (ESTs) that are appropriate for the local waste characteristics.

Furthermore, the right balance of regulatory, fiscal, and social tools, as well as mechanisms for effective compliance oversight from all related stakeholders, must be designed and implemented. Improving organisational efficiency and fostering inter-departmental/agency co-operation is also essential. Alternative and innovative finance mechanisms, such as public-private partnerships (PPPs), public funding projects (PFIs), and the use of the polluter pays principle, would supplement current revenue sources. Companies that recycle waste in a “safe” manner should be granted tax cuts.

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Chapter 8
Sewage Sludge Biochar

**Cícero Célio de Figueiredo, Joisman Fachini, Alyson Silva de Araujo,
Jhon Kenedy Moura Chagas, and Jorge Paz-Ferreiro**

Abstract The global production of sewage sludge (SS) has accompanied population growth and the expansion of global sewage treatment rates. Sewage sludge is a solid waste rich in nutrients, mainly N, P, Ca, Mg, and Zn. However, SS can also have high contaminating potential. Pyrolysis is an effective technological alternative to transform SS into an agricultural input. The solid product of SS pyrolysis is called SS biochar. In this chapter, we present the state of the-art of SS use in agriculture, highlighting benefits, limitations, and perspectives. Furthermore, we review innovative approaches to render SS biochar production and applicability more efficient and socially acceptable. Such approaches include: (a) SS biochar enrichment technologies; (b) SS biochar for plant disease control; and, (c) SS biochar for soil carbon sequestration. The risks of contamination with heavy metals from SS biochar were also discussed. Finally, recommendations were elaborated for improving the multiple uses of SS biochar in agriculture.

8.1 Introduction

Sewage sludge (SS) is an urban waste generated during wastewater treatment. Globally an estimated 9.5 million m^3 of human sewage and 900 million m^3 of municipal wastewater are produced every day (Mateo-Sagasta et al. 2015). Several alternatives have been used to transform SS into a suitable product to be applied in agriculture. Among them, thermal treatments such as incineration, gasification, hydrothermal carbonation, and pyrolysis belong among the suitable solutions of SS disposal (Racek et al. 2020).

Thermal processing of SS by pyrolysis represents an important alternative to allow for agricultural use of this residue and presents advantages such as reduction of

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volume and transport costs in addition to the elimination of undesirable microorganisms (Paz-Ferreiro et al. 2018). Biochar is a solid, carbon rich product obtained by heating biomass under limited oxygenation conditions, in a process known as pyrolysis (Sohi 2012). Despite increasing the concentration of total heavy metals in relation to the raw material, pyrolysis reduces the bioavailability of several metals (Figueiredo et al. 2019a, b; Chagas et al. 2021a). In addition, the application of biochar to the soil has an alkalinizing effect (Hossain et al. 2011), increases the accumulation of total carbon (C) and soil organic matter pools (Chagas et al. 2022), and can reduce phosphorus (P) adsorption (Cui et al. 2011).

Although few studies have been performed in tropical regions (Sousa and Figueiredo 2016; Faria et al. 2018; Figueiredo et al. 2018a, b, 2020), the benefits of SS biochar are already clear with regard to the supply of multiple plant nutrients for several crops (Sousa and Figueiredo 2016; Faria et al. 2018). Recently, studies have shown positive effects of SS biochar on the control of plant pathogens (de Araujo et al. 2019a) and in increasing the use efficiency of N from mineral fertilizers (Figueiredo et al. 2020).

There is still a significant shortage of information on the advantages and limitations of using biochar from sewage sludge on agricultural land. Therefore, this chapter summarizes the main approaches applied to the SS biochar as a soil amendment, including advantages, limitations, and perspectives.

8.2 State of the Art

8.2.1 Sewage Sludge in Agriculture: Benefits and Limitations

As biomass rich in carbon and nutrients, SS can be used for different purposes, emphasizing disposal in agricultural areas, land reclamation, landscaping, forestry, industrial processes, power generation, civil construction, and biochar production. Furthermore, SS may be destined for incineration or landfill (Fig. 8.1). In agriculture,

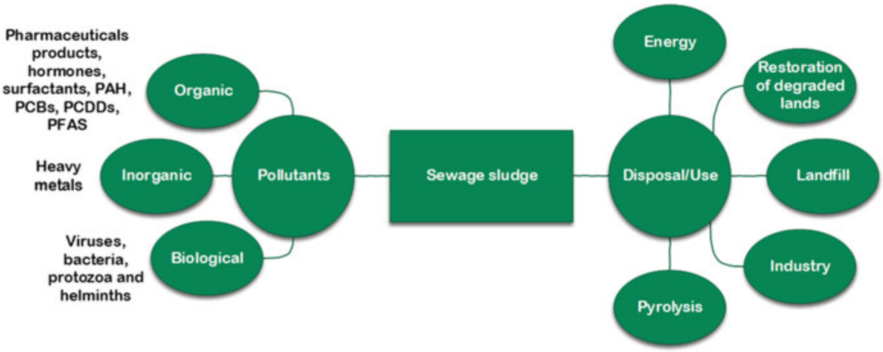

Fig. 8.1 Disposal alternatives and major contaminants present in the sewage sludge

SS can be used as a fertilizer or as a soil conditioner. It is estimated that the municipal wastewater produced globally contains enough nutrients to replace 25% of the nitrogen currently used to fertilize agricultural land in the form of synthetic fertilizers, and 15% of the phosphorus (Andersson et al. 2016). Alternatives such as prolonged alkaline stabilization, adopted in the state of Paraná, Brazil, have been successful among farmers, despite a limited adoption (Souza et al. 2008). In this process, the pH of the sludge is raised to 12 by adding large amounts of lime. The monitoring of pollutants in the sludge and in the soil is required, in addition to complications which include logistics of transporting the sludge, uneven demand over the year (concentrated in two growing seasons), and the high number of rainy days, which present challenges for practical application.

Despite the advances in research and government actions in recent decades, the use of SS worldwide is still very limited, particularly in developing countries that lack efficient sewage treatment systems (Andersson et al. 2016). As a result of the precautionary principle, legislation dealing with the use of SS imposes several restrictions on the agricultural use of this waste. Figure 8.1 shows the main pollutants present in SS, such as organic compounds, inorganic and biological components. Several types of organic chemicals, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and perfluoroalkyl substances (PFAS) may be found in treated SS (Paz-Ferreiro et al. 2018).

The presence of these contaminants with values above the limits established in specific legislation makes SS unfit for use in agricultural areas because of its high potential for contamination of the environment and the food chain (Collivignarelli et al. 2019). As a consequence of restrictions for their use, large amounts of SS accumulate in drying yards or are disposed of in dumps and water courses. With the lack of planning for the sustainable use of SS, major sanitary and environmental problems have been witnessed in many cities around the world.

Among the alternatives to make use of SS in agriculture feasible, thermal processing by pyrolysis has received much attention from researchers in the last decade (Paz-Ferreiro et al. 2018; Patel et al. 2020; Chagas et al. 2021a). Pyrolysis produces a solid material called biochar that can be used in agriculture, as well as biogas and bio-oil that can be used as an alternative energy source (Patel et al. 2020). In the specific case of SS the pyrolysis transformation eliminates pathogens and degrades potentially damaging organic compounds (Devi and Saroha 2013), thus permitting that SS be used for nutrient cycling and C accumulation in the soil.

8.2.2 Pyrolysis as a Sustainable Alternative to Enable the Disposal of Sewage Sludge on Agricultural Soil

8.2.2.1 Chemical Characteristics of Sewage Sludge Biochar

Compared with other urban wastes, SS biochars present high levels of nutrients such as P, N, Ca, and Mg (Figueiredo et al. 2018b), and when applied to tropical soils they are able to substitute soluble chemical fertilizers used in the production of different crops (Sousa and Figueiredo 2016; Faria et al. 2018; Fachini et al. 2021a, b; Chagas et al. 2021b).

The concentration of nutrients in the SS biochar is dependent on factors such as the type of treatment applied to the sewage and pyrolysis conditions such as temperature and residence time. Sludge that undergoes tertiary treatment, using methods for precipitation of N and P, is rich in these nutrients and poor in those that are removed together with water, such as potassium.

Figure 8.2 shows the macronutrient contents of sewage sludges and biochars produced at 300 and 500 °C. Overall, the pyrolysis of SS enriches the macronutrients in the biochars. The significant increase in phosphorus content with the pyrolysis temperature is a good characteristic considering that soils from tropical regions usually have a very low content of this nutrient. Despite increasing nitrogen contents up to 300 °C with decreases at higher temperatures, generally pyrolysis reduced the concentrations of nitrate and ammonium from the feedstock (Figueiredo et al.

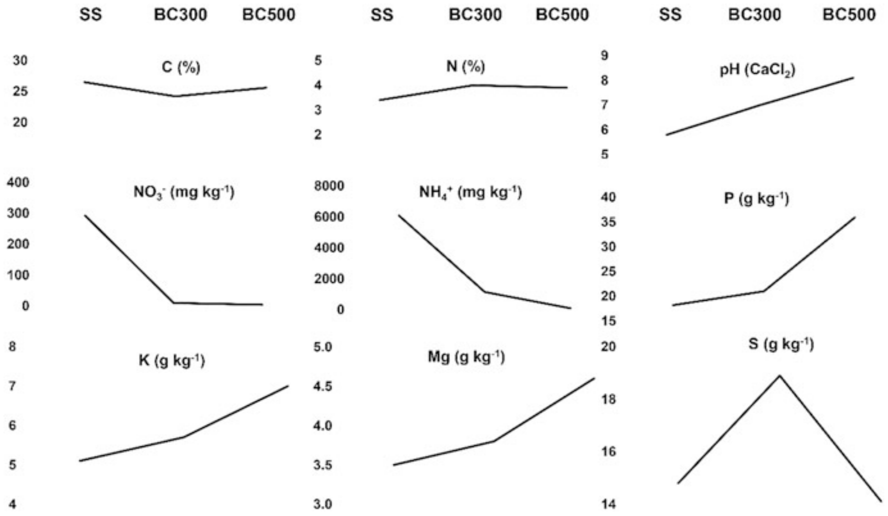

Fig. 8.2 Characteristics of sewage sludge (SS) and biochars produced at 300 °C (BC300) and 500 °C (BC500). Mean values estimated from Mierzwa-Hersztek et al. (2018); Chagas et al. (2021b), Tian et al. (2019); Gonzaga et al. (2018); Jafari Tarf et al. (2021); Khanmohammadi et al. (2015); Khan et al. (2015); Yuan et al. (2013); Zhang et al. (2015); Figueiredo et al. (2018a); Yuan et al. (2015); Méndez et al. (2012)

2018b). This decrease may be a result of nitrogen transformation to pyridine and pyrrols during pyrolysis, especially above 300 °C. Nevertheless, the concentration of ammonium in BC300 is 30 times higher than those normally found in acid soils from tropical regions (Nascente et al. 2012). As the pyrolysis temperature increases the biochar becomes more alkaline highlighting its function to act as a soil acidic neutralizer.

8.2.2.2 Sewage Sludge Biochar as Soil Amendment

Sewage sludge biochar can act as a soil amendment improving the chemical, physical, and biological properties (Fig. 8.3). Among the nutrients provided by SS biochar obtained after tertiary treatment, P was highlighted by its great availability in the soil and high absorption by the crops (Faria et al. 2018; Figueiredo et al. 2021). It is currently well known that SS biochar is a source of P, potentially replacing soluble mineral fertilizers. However, studies on the dynamics of P and the microbiota related to its cycling in the soil under application of SS biochar are incipient (Figueiredo et al. 2019b) and this represents an important scientific gap, since the efficiency of phosphate fertilization in tropical soils with high capacity of P adsorption is very low.

Sewage sludge biochar may also indirectly improve nutrient use efficiency by plants. For example, the beneficial effect of the interaction of biochar with plant growth-promoting microorganisms such as mycorrhizal fungi has been demonstrated. Hammer et al. (2014) concluded that hyphae of arbuscular mycorrhizal fungi can access biochar micropores that are too small for the penetration of most plant roots (<10 μm) and may therefore mediate plant uptake of P present in the

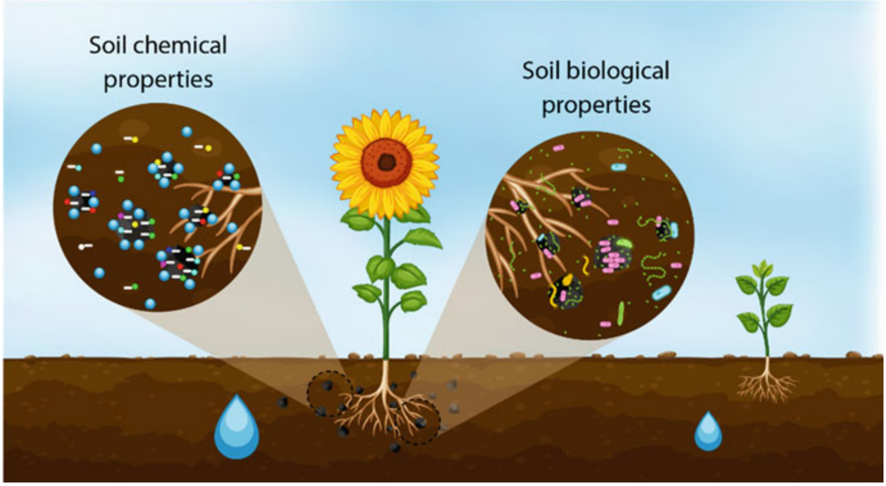

Fig. 8.3 Schematic of the action of sewage sludge biochar on the soil chemical and biological properties

biochar. Thus, the functions of arbuscular mycorrhizal fungi and biochar can contribute to the sustainability of weathered soils, deficient in available P under natural conditions, such as those that predominate in tropical soils.

The exclusive application of SS biochar or combined application with chemical fertilizer (NPK) increased corn productivity for two consecutive harvests in tropical soils (Faria et al. 2018). According to these authors, with the exception of potassium, the 15 Mg ha^{-1} dose of biochar was able to provide all nutrients in sufficient quantity to promote corn yields of 10 Mg ha^{-1} in tropical acid soil from the central region of Brazil. Residual effects of SS biochar on soil nutrient contents remained up to 3 years after stopping biochar application (Chagas et al. 2021b).

8.2.2.3 Sewage Sludge Biochar for Plant Disease Control

Studies on the use of biochar to control plant diseases have grown in recent years (Kumar et al. 2018; Liu et al. 2019; de Araujo et al. 2019a; Jaiswal et al. 2020). Biochars are able to control plant diseases caused by fungi, bacteria, or viruses (Jaiswal et al. 2020; Zhang et al. 2017a, b; Wang et al. 2018). However, most studies have focused on the effects of biochar on the control of fungal diseases (Wu et al. 2020; Wang et al. 2019; Kolton et al. 2017). Among the phytopathogenic fungi evaluated, the genus *Fusarium* stands out (Jaiswal et al. 2020; Wu et al. 2020; Liu et al. 2019). The diseases caused by this genus were the most suppressed by biochar application (Jaiswal et al. 2018; Rogovska et al. 2017).

Biochar has direct and indirect effects on the pathogen or disease. The most often reported effects are: reduced disease rate (Wang et al. 2020); inhibition of mycelial growth (Wu et al. 2020); reduced pathogen virulence (Wu et al. 2020); delay in the spread of the disease (Sabes et al. 2020); pathogen suppression (Wang et al. 2019); reduced plant susceptibility to disease (Kolton et al. 2017); greater plant resistance to the disease (Dai et al. 2017); reduction of root infection rate; and reduced disease severity (Rogovska et al. 2017).

Feedstocks commonly used to produce biochar suitable for plant diseases control are: wood and its derivatives (wood chips/barks, sawdust) (Jaiswal et al. 2019; Heck et al. 2019), vegetable residues used in the greenhouse (Jaiswal et al. 2020), and rice straw/husk (Wu et al. 2020; Sabes et al. 2020). A wide range of pyrolysis temperatures can be used for this purpose (300–1000 °C) (Marra et al. 2018; Atucha and Litus 2015). However, the highest plant disease control rates were obtained with biochar produced at pyrolysis temperatures ranging from 350 to 600 °C (Jaiswal et al. 2018; Lu et al. 2016a, b).

The dose of biochar is also an important factor for effective disease control. The best results were obtained when biochars were applied at doses ranging from 0 to 5% (de Araujo et al. 2019a). Furthermore, there is a certain specificity between the type and dose of biochar and the type of pathogen. Thus, each material can have an optimal dose with greater impact on the disease (Liu et al. 2019).

Recent studies have indicated that biochar from SS is also capable of controlling soilborne pathogenic fungi that infect various types of crops (de Araujo et al. 2019a, b). As a consequence of disease control, SS biochar promoted higher productivity of crops such as beans (de Araujo et al. 2019a) and soybeans (de Araujo et al. 2019b). These studies also indicated a synergistic effect between SS biochar and beneficial microorganisms such as *Trichoderma* spp. to control pathogenic fungi and increase crop productivity. Despite this potential, the use of SS biochar to control pathogens still needs to be better studied under field conditions and with a wide variety of pathogens and host plants.

8.2.2.4 Biochar Enrichment

Biochar enrichment techniques have allowed to obtain biochar-based fertilizers, with great potential to improve soil fertility (Lustosa Filho et al. 2020). According to Ndoung et al. (2021), there are three methods to enrich biochar with nutrients: (i) direct treatment method, (ii) pre-treatment method, and (iii) post-treatment method. In the direct treatment method, nutrient-rich feedstocks are submitted to slow pyrolysis (Ndoung et al. 2021). In the pre-treatment method, the feedstock is treated with nutrient-rich materials before undergoing pyrolysis. In this method, feedstocks may be enriched with chemical fertilizers, organic wastes, or agro-industrial residues. In the post-treatment method, several products can be used to composite enriched biochar after the pyrolysis process. In this process, biochars are mixed with a nutrient-rich source, including chemical fertilizers, clays, ground rock, composts, wastewater, etc.

Biochar enrichment may be produced from a wide variety of possibilities and combinations (Ndoung et al. 2021). Significant success has been obtained by enriching biochar with nutrients such as P (Lustosa Filho et al. 2020; Carneiro et al. 2021), N from urea (Shi et al. 2020), sulfur (Zhang et al. 2017a, b), and iron (Dad et al. 2021). Among the post-treatment (post-pyrolysis) methods, the granulation and pelleting processes of biochar are the most commonly used for nutrient enrichment (Ndoung et al. 2021). They have been used to minimize the risk of dust and respiratory problems caused by the application of biochar in powder form (Vincevica-Gaile et al. 2019). Specific characteristics of feedstock should be considered in biochar enrichment. For sewage sludge biochar, for example, an interesting strategy is enrichment with potassium, since this nutrient is present in low concentration in SS and, consequently, in the biochar. Furthermore, the high adsorptive capacity of biochar can retain K (Fachini et al. 2021b), acting as a slow-release fertilizer, thus reducing the loss of this nutrient through leaching. Figure 8.4 shows an alternative technological process to produce K-enriched SS biochar in the form of granules and pellets.

Enriched biochars can improve soil chemical and biological properties, nutrient use efficiency and increase crop productivity compared to mineral fertilizers and

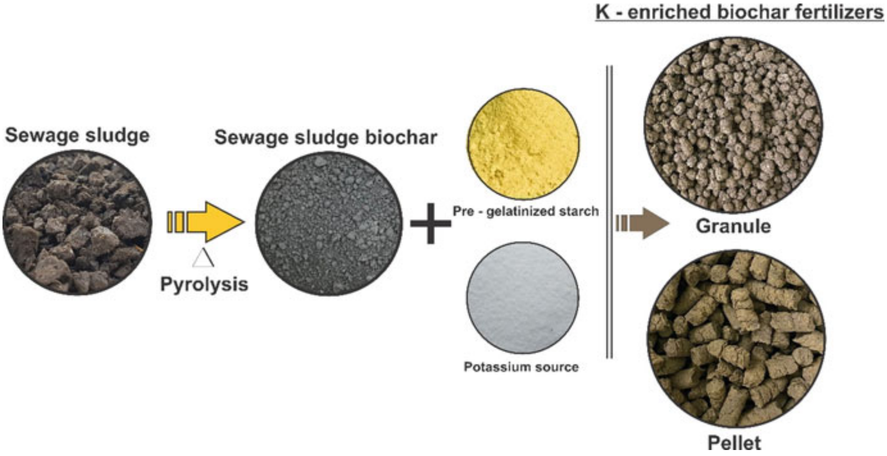

Fig. 8.4 Steps to produce enriched fertilizers from sewage sludge biochar

biochars applied separately (Ndoung et al. 2021). According to these authors, the application of a P-enriched biochar increased soil P and N contents. In addition to increasing the concentration of P, the application of P-enriched biochar also increased soil chemical properties such as pH and CEC (Carneiro et al. 2021). The main mechanism that explains the greater efficiency of a biochar-based fertilizer is the way in which the enriched nutrient is released. Biochar-based fertilizers differ from other fertilizers in their ability to gradually release nutrients into the soil, acting as a slow-release fertilizer (Lustosa Filho et al. 2020), increasing efficiency by reducing losses due to leaching or volatilization (Gwenzi et al. 2016).

8.2.2.5 Sewage Sludge Biochar and Carbon Sequestration in the Soil

The nutritional performance of biochar produced from several feedstocks is widely known. According to Zimmerman et al. (2011), biochar is also capable of increasing soil C stocks mainly in stable forms of organic compounds. This is possible since pyrolysis alters the feedstock promoting C buildup in the final biochar (Novotny et al. 2015). Therefore, when used as a soil amendment, biochar can sequester C in the soil (Figueiredo et al. 2018a; Chagas et al. 2022) and reduce greenhouse gas emissions from agricultural activities (Chagas et al. 2022; Plaza et al. 2016). According to Woolf et al. (2010), adopting biochar technology could compensate up to 12% of global CO_2 emissions into the atmosphere.

In general, biochars obtained at lower temperatures around 300 °C have fewer aromatic structures than those obtained at higher temperatures ($\geq$500 °C) (Al-Wabel et al. 2013; Figueiredo et al. 2018a). This difference in the organic matrix of the biochars exerts a strong influence on the nutrient mineralization rate and on the long-term accumulation of C (Al-Wabel et al. 2013). Recently, Chagas et al. (2022), using results from a global meta-analysis, concluded that biochar increases several types of SOM fractions. Among these fractions, the most labile and active fractions such as microbial biomass, labile C, and easily oxidizable C are most sensitive to the changes promoted by crops (Cambardella and Elliott 1992). On the other hand, the stable fractions such as humic substances represent more recalcitrant forms of SOM, whose changes occur over a longer period of time (Figueiredo et al. 2018b).

Despite substantial advances in biochar knowledge in recent years, there are still many questions regarding its real short- and long-term impacts and how it acts on the soil (Cernansky 2015). Of the few works performed under field conditions with SS biochar application for consecutive years, Figueiredo et al. (2018a) concluded that the pyrolysis temperature is the driving factor in the function of biochar to increase organic C in the soil. In general, biochar produced at lower temperatures (around 300 °C) can increase labile fractions. On the other hand, when made at higher temperatures ($\geq$500 °C), biochars increase recalcitrant SOM pools.

8.2.2.6 Sewage Sludge Biochar and the Risks of Contamination with Heavy Metals

Sewage sludge has heavy metal (HM) contents that vary depending on the origin (industrial, urban, or mixed) and the treatment that the sewage receives (Fytili and Zabaniotou 2008). Wang et al. (2008) reported that the application of SS from mixed-source sewage treatment (urban, commercial, and industrial) in China increased the concentration of heavy metals in the soil at all doses utilized (15–150 Mg ha^{-1}).

Chemical composition of the biomass used in pyrolysis is directly related to the HM concentration in the biochar obtained. Biochar produced from several feedstocks (e.g., wood, rice straw, animal manure) generally shows low levels of heavy metals, since these are not part of their natural composition (Park et al. 2011; Bian et al. 2014; Lucchini et al. 2014). However, in the case of SS the presence of HMs in the biochar is dependent on the type of sewage that makes up the sludge (domestic, industrial, or mixed). This dependence results in SS biochars with distinct HMs concentrations (Chagas et al. 2021a, b). For example, the municipal SS biochar submitted to secondary treatment showed a HM content suitable for agricultural use according to the local regulations of Guiyang, China (Liu et al. 2014). However, Van Wesenbeeck et al. (2014) observed that even on Oahu, a small island located in Hawaii, the HM contents in SS varied significantly between communities and over the years.

During pyrolysis, most metals including Pb, Ni, Cu, Zn, and Cr are retained in the biochar (solid fraction), since they present boiling points higher than the temperature normally used in pyrolysis (Van Wesenbeeck et al. 2014; Lu et al. 2016a, b). Thus, pyrolysis concentrates total HMs in the biochar (Lu et al. 2016a, b; Kameyama et al. 2017; Figueiredo et al. 2019a, b), and depending on the HM contents present in the

SS may make its use unviable for agricultural purposes (Chagas et al. 2021a, b). The higher the pyrolysis temperature used, the higher the concentration of total HMs in the biochar (Yuan et al. 2015; Lu et al. 2016a, b). However, when using temperatures >600 °C, some heavy metals such as Cd volatilize and leave the reactor together with the produced gases. Below 600 °C the small heavy metal losses observed are mainly due to the escape of charged fine metal particles carried in the gas outflow (Kistler et al. 1987).

Even when there is an increase in the concentration of HMs during pyrolysis, it is observed that when applied to the soil, biochar affects the behavior of these metals, reducing their solubility, availability, transport, and spatial distribution (Zhou et al. 2017). Thus, with the application of SS biochar there is a reduction of the HM levels available in the soil, with values lower than those present with the use of sewage sludge (Figueiredo et al. 2019a, b; Chagas et al. 2021a, b).

Table 8.1 summarizes the effects of SS biochar on total and available HM in the soil and plant. Even when applying SS biochar with total HM contents below the local regulated limits, all studies shown in Table 8.1 that assessed the HM content in soils after SS biochar application reported accumulation of at least one of the analyzed HMs in the soil. In general, SS biochar increases the total HM content but decreases the available HM in the soil and the rate of HM uptake by plants.

In the specific case of SS biochar of predominantly domestic origin, in the central region of Brazil, Figueiredo et al. (2019a, b) concluded that with the increase in pyrolysis temperature there is reduced availability of these HMs, with values below 5.2% in relation to the total contents. Even with the application of 15 Mg ha^{-1} of SS biochar, the total and available contents in the soil were similar to the control treatment, without biochar application, 1 year after its application. Recently, Chagas et al. (2021a, b) proved that this low HM contents in soil amended with SS biochar may remain for at least 5 years.

8.3 Recommendations

Despite the potential benefits of SS biochar as an agricultural input, some aspects still need to be considered in future studies. Further information from long-term experiments is crucial. Production or co-production of biochar in combination with other feedstocks/materials such as soil remineralizers and organomineral fertilizers should be studied. Furthermore, identify additional benefits of biochar (plant disease and pest management/control) should be improved. Finally, studies on the energy efficiency of the SS pyrolysis process need to be broad.

Table 8.1 Sewage sludge/biosolids effects on total and available heavy metal (HM) in soil and plant

Reference	Crop	Pyrolysis temperature (°C)	Dose of biochar	Soil texture	Soil pH	Total HM								Available HM								Leaf content/HM uptake							
						As	Cd	Cr	Cu	Mn	Ni	Pb	Zn	As	Cd	Cr	Cu	Mn	Ni	Pb	Zn	As	Cd	Cr	Cu	Mn	Ni	Pb	Zn
[1]	Rice	550	5%	S	4.9									↓	↑	↓	↑		↓	↓	↑	↓	↑	↓	–		↓	↓	↑
	Rice	550	10%	S	5.4									↓	↑	↓	↑		↓	↓	↑	↓	↑	↓	–		↓	↓	↑
[2]	Corn	350	7.3 t ha^{-1}	M	7.5–7.6												–	–		↓	↑				–	–		↓	–
	Corn	350	14.5 t ha^{-1}	M	7.5–7.6												–	–		↓	↑				↓	–		↓	–
	Corn	350	29 t ha^{-1}	M	7.5–7.6												–	–		↓	↑				↓	↓		↓	↓
[3]	Rice	800	20 t ha^{-1}	M	7.9		↑		–			↑	↑		↓		–			↓	–		–		–			–	–
	Wheat	800	20 t ha^{-1}	M	7.7		↑		–			↑	↑		–		↑			–	↓		–		–			↓	–
[4]	Grass	300	5%	M	8.6	↑	↑	–	↑	↑		↑	↑										↓	–	↓	↓		↓	↓
[5]	Cucumber	550	2%	S	7.3–7.6									↓	–		–			↓	–	↓	↑		–			↓	↓
	Cucumber	550	5%	S	7.4–7.5									↓	–		–			↓	–	↓	↑		–			↓	↓
	Cucumber	550	10%	S	7.4–7.6									↓	–		↓			↓	–	↓	↑		↓			↓	↓
[6]	Grass	500	5%	M	8.6	↑	↑	↑	↑			↑	↑									–	↓	↓	↓			↓	↓
[7]	–	500	4%	M	7.8										–		↑		↑	–	–								
	–	500	8%	M	7.8										–		↑		↑	–	–								
[8]	Corn	300	15 t ha^{-1}	C	4.8			–	–	↑		–	–			–	–	–		–	↑								
	Corn	500	15 t ha^{-1}	C	5.1			–	–	–		–	–			–	–	–		–	↑								
[9][a]	Beans	550	4%	–	5.7									↓	↓	↓			↓	↓	↑	↓	↓	↓			↓	↓	↑
[10]	Corn	350	0.5%	–	6.2																		↑				–	↓	–
[11]	Corn	300–500	15 t ha^{-1}	C	6.7				–		–	↑	–												↑		–	↑	↑
[12]	Corn	300	15 t ha^{-1}	C	4.8																				↑	↑			↑
	Corn	500	15 t ha^{-1}	C	5.1																				↑	↑			↑

(↑), (—), and (↓) mean that biochar application increases, maintains, or decreases, respectively, compared to the control (with no biochar)

[a] Contaminated soil by HM

S sandy; *M* medium; *C* clayey

(continued)

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Chapter 9
Recovery of Value-Added Products from Industrial Wastewaters: A Review to Potential Feedstocks

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Abstract Biorefineries process biodegradable wastes into a range of bio-based products. Several wastes can be used as feedstocks for biorefineries, but liquid effluents, called wastewaters, stand out due their large production flow and pollution potential of water bodies. Noteworthy wastewaters suitable for biorefineries include (i) vinasse, also called sugarcane stillage; (ii) cheese whey; (iii) glycerin; and (iv) cassava wastewater.

Vinasse is the main residue of the sugar and ethanol industry and 10–15 L of vinasse are generated per liter of produced ethanol. It has a high organic content (20–25 g $COD{\cdot}L^{-1}$), low pH, high temperature, and high ash content. Cheese whey is the watery part of milk that is separated from the curd in the cheese-making process. It is the major by-product of dairy industries and it presents high organic load (70–80 g $COD{\cdot}L^{-1}$), low alkalinity content, high nitrogen content, and very high biodegradability. Glycerol is the major by-product of the biodiesel industry. Crude glycerol (925–1500 g $COD{\cdot}L^{-1}$), generated by homogeneous base-catalyzed transesterification, contains glycerol, alkalis, methyl esters, and methanol. Cassava wastewater (10–20 g $COD{\cdot}L^{-1}$) is composed by root cleaning water, cassava milling

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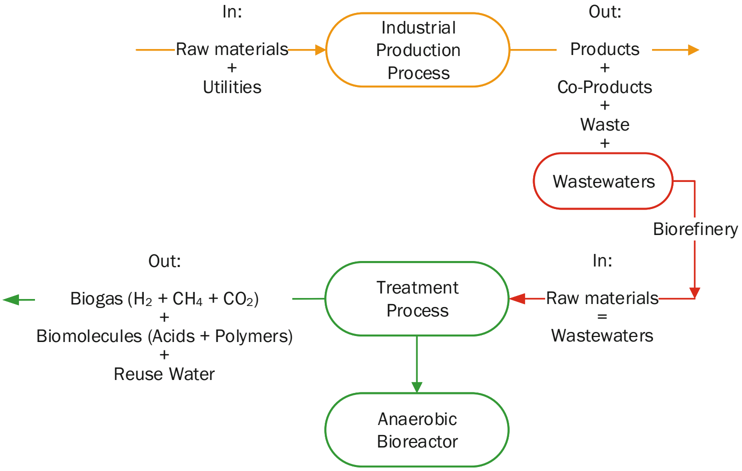
wastewater, and cassava starch wastewater. It is a milky yellowish liquid with large quantities of nutrients.

These effluents production combined was over 3.5 trillion kilos in 2019 and, therefore, pose a huge threat to the environment, but also a great opportunity for biofuels (over 7 × 10^{11} Nm^3 of biogas per year—hydrogen and methane) and biochemicals production.

Thus, the aim of this chapter is to review the production process of these wastewaters and their potential as feedstocks for anaerobic digestion, a wastewater treatment process capable of generating energy (hydrogen and methane) and biomolecules (acids and polymers).

Graphical Abstract



9.1 Introduction

Industrial wastewater is the aqueous discard that results from substances that have been dissolved or suspended in water, typically during the use of water in an industrial process or because of the cleaning activities that take place along with that process (Woodard and Curran 2006). The objective of industrial wastewater treatment is to remove these substances, and several treatment methods are currently available in order to ensure good quality effluent before disposal into the municipal sewer systems (Woodard and Curran 2006). The disposal of such effluents in the environment will lead to surface and groundwater contamination, causing ecosystem imbalance and human health risks. Moreover, the ever-stringent regulatory norms make wastewater treatment a necessity (Drogui et al. 2008).

Nowadays, however, wastewater treatment is not only seen as an obligation to merely comply with federal and state legislations, but also as an opportunity to bring the world closer to a sustainable future. The application of circular economy in wastewater treatment is a great example of today's approach to this subject: the water and the substances contained in these effluents are considered as a resource, and a great deal of research is focused on the possibility of nutrients, energy, biomolecules, metals, organic and inorganic compounds recovery (Guerra-Rodríguez et al. 2020). This intersection between bioprocessing and wastewater treatment can be termed as a "wastewater biorefinery." The implementation of a wastewater biorefinery moves industrial activity toward closing resource cycles, by capturing those components of wastewaters which have value, and re-inserting them into economic circulation through elemental cycling while at the same time remediating wastes and recovering clean water (Pott et al. 2018).

Anaerobic digestion (AD) is one of the most promising biotechnologies for the wastewater biorefinery. It is a cascade of biochemical reactions performed by microorganisms in the absence of oxygen which convert organic matter into acids and biogas. According to Lettinga et al. (1999), this complex process is formed by four major biochemical steps:

I. Hydrolysis: breaking down complex molecules (carbohydrates, proteins, and lipids) into simpler molecules (fermentable sugars, amino acids, and fatty acids);
II. Acidogenesis: soluble products from hydrolysis are converted into soluble metabolites (alcohols, volatile organic acids, hydrogen);
III. Acetogenesis: acetate, hydrogen, and carbon dioxide production from the consumption of acidogenic products;
IV. Methanogenesis: production of methane from acetate (acetoclastic methanogenesis) or hydrogen and carbon dioxide (hydrogenotrophic methanogenesis).

Anaerobic digestion is recognized as a promising technology for economically viable and environmentally sustainable production of biofuels. Although AD technology had primarily been developed and adopted for waste stabilization, in recent years, AD process has been widely adopted for bioenergy production. Over 14,000 commercial AD plants are already in operation in Europe, while Germany alone has more than 8000 plants. The produced biogas is used for combined heat and power (CHP) generation, and/or upgraded to biomethane to be used as transportation fuels, or injected into natural gas grid (Sawatdeenarunat et al. 2016).

Currently, it is possible to produce a few biofuels from AD of organic wastes: ethanol, methane, and hydrogen, the last being considered the fuel of the future for only producing water when burned in fuel cells. While methane production is thermodynamically favorable, biological hydrogen production by anaerobiosis, usually referred to as "dark fermentation," is obtained by "breakdown" of the AD process, in which only hydrolysis, acidogenesis, and acetogenesis (partially) occur, making the process thermodynamically unfavorable and difficult to control. This interruption is mainly achieved by low pH (4.0–5.5) and high organic loading rates;

however, the choice of a proper inoculum (and its possible pretreatment) and reactor start-up strategy are also vital for biohydrogen production (Lovato et al. 2020).

In anaerobic digestion, in addition to having bioenergy as a product of the fermentation phase, different soluble metabolites are generated such as the following solvents and organic acids: Acetic (HAc); Butyric (HBu); Propionic (HPr); Lactic (HLa); Formic (HFo); Succinic (HSuc); Citric (HCi); Caproic (HCa); Valeric (HVa) and Malic Acids (HMa); Methanol (MetOH); Ethanol (EtOH); Butanol (BuOH), among others.

These products have a high value in the market, as they can be used in various sectors as raw materials for chemical, pharmaceutical, food and cosmetic industries, antimicrobial agent, additive in animal feed and flavoring, and biofuel production (de Cavalcante et al. 2017; Veras et al. 2020). There is a growing demand for studies that intend to use organic waste to generate value-added products, aiming within the biorefinery concept to generate a wide range of products. The production of these compounds depends on the medium operating conditions, the composition of the substrate, and the microbiological cultures that will be used. This way, different metabolic pathways can be favored, generating some organic acids in greater amounts than others.

The generation of HLa, for example, in these biological processes is interesting, as this acid is a chemical commodity, used mainly by the food industry, as an antimicrobial agent and flavor adjuvant. Furthermore, this acid can be used as a solvent, stabilizer, humectant, emulsifier, plasticizer. The chemical industry is interested in HLa, with the intention of using it as a raw material for the production of biodegradable plastics. There are also applications in the pharmaceutical, cosmetic, textile and leather industries. HAc, on the other hand, is widely used by the pharmaceutical, tanning, and leather dyeing industries. HBu can be used in the manufacture of plastics; leather tanning processes; and production of medicines. HPr is generally used by food industries, chemicals and in manufacturing (Zhou et al. 2018).

A requirement for AD viability is that the wastewater needs to be biodegradable, due to anaerobic microorganisms' metabolism, and produced in large volumetric flows for the process economic feasibility. Therefore, wastewaters from agro-industries stand out as promising candidates for AD and wastewater biorefinery. Noteworthy wastewaters suitable for this process are (i) vinasse, also called sugarcane stillage; (ii) cheese whey; (iii) glycerin; and (iv) cassava wastewater.

Vinasse is the main residue of the sugar and ethanol industry and 10–15 L of vinasse are generated per liter of produced ethanol. It has a high organic content (20–25 g $COD{\cdot}L^{-1}$), low pH, high temperature, and high ash content. Cheese whey is the watery part of milk that is separated from the curd in the cheese-making process. It is the major by-product of dairy industries (9–10 L of whey are generated for every kg of cheese produced) and it presents high organic load (70–80 g $COD{\cdot}L^{-1}$), low alkalinity content, high nitrogen content, and very high biodegradability. Glycerol is the major by-product of the biodiesel industry. In general, for every 100 kg of biodiesel produced, approximately 10 kg of crude glycerol are generated. Crude glycerol (925–1500 g $COD{\cdot}L^{-1}$), generated by homogeneous base-catalyzed transesterification, contains glycerol, alkalis, methyl esters, and methanol. Cassava wastewater (10–20 g COD·L^{-1}) is composed by root cleaning water, cassava milling wastewater, and cassava starch wastewater. On an average 6 L of cassava wastewater are produced for every kilo of cassava processed. It is a milky yellowish liquid with large quantities of nutrients and different physical-chemical characteristics due to the harvest seasonality.

These effluents production combined was over 3.5 trillion kilos in 2019: 1700 billion of vinasse, 95 billion of cheese whey, 4 billion of glycerin, and 1800 billion of cassava. Therefore, they pose a huge threat to the environment, but also a great opportunity for biofuels (over 7×10^{11} Nm^3 of biogas per year—hydrogen and methane) and biochemicals production. Thus, the aim of this chapter is to review the production process of these wastewaters and their potential as feedstocks for anaerobic digestion, a wastewater treatment process capable of generating energy (hydrogen and methane) and biomolecules (acids and polymers).

9.2 Sugar and Ethanol Production Process and Its Wastewaters

The sugar and ethanol production process from sugarcane makes the Alcohol Industry one of the most important in the world (de Menezes and Silva 2019). The countries that stand out the most in sugarcane processing are Brazil, India, Thailand, the USA, and China. Brazil is the world's leading sugarcane producer, representing 21% of the total global production, followed by India (17%), European Union countries (8.5%), and Thailand (6%). Sugar production is expected to expand mostly due to the flexibility of sugar mills to switch between sugar and ethanol production, which reduces investment risks. Thus, sugarcane production is expected to grow by 1.1% per year, slightly higher than in the last decade. Changes in the global production volume will occur mainly from the contributions of productions from Brazil (49%), India (18%), and Thailand (6%) (OECD-FAO 2020).

Mainly in tropical countries, sugarcane has potential to be a replacement for fossil fuels, which have a known high energy demand (Grassi and Pereira 2019). In Brazil, a favorable situation for the ethanol production from sugarcane led to the creation of the "*Programa Nacional do Álcool (Proálcool)*" (National Alcohol Program) in 1975, in order to minimize the effects of market fluctuations in sugar prices and the oil crisis (Ferreira et al. 2019). In this context, the sugarcane processing for sugar and ethanol production is consolidated as a biorefinery model. In addition to sugar and ethanol, sugarcane can also be used for the production of derivatives such as press mud, raw sugar, bagasse (Moraes et al. 2015), sugarcane juice (de Menezes and Silva 2019), vinasse (Rego et al. 2020), molasses (Freitas et al. 2020), electricity (through the bagasse excess), and bioplastics (OECD-FAO 2020).

The main stages of sugarcane processing are presented in Fig. 9.1. The first steps consist primarily of harvesting, washing, and milling the raw material. At this stage, 70% of sugarcane juice and 30% of bagasse are produced from the original product. The juice and bagasse are separated by crushing and pressing the sugarcane. Bagasse can be burned to produce steam and electricity, used in composting and fertilizing

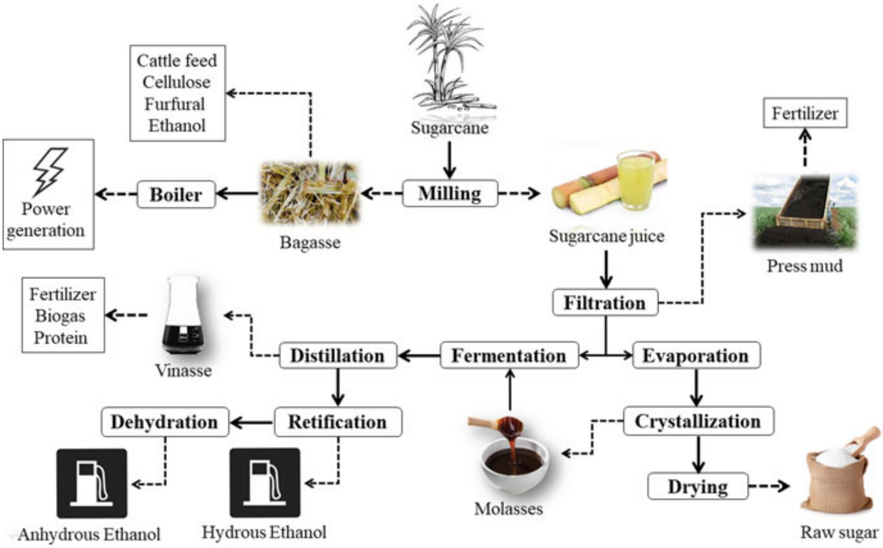


Fig. 9.1 Flow diagram of sugarcane processing

sugarcane itself, animal feed, manufacturing fiber boards for constructions, manufacturing plastic materials, cellulose, and paper, among others (Manochio et al. 2017).

The sugarcane juice is treated by filtration and the impurities are removed, producing a by-product called press mud. This press mud can be used as a fertilizer due to its several macro and micronutrients. After filtration, a part of the juice goes through a cooking and evaporation process until it reaches a solids content between 65 and 75%. The molasses is produced in this step. After the evaporation, the product undergoes the crystallization, drying and cooling of the mass, which becomes hard and brittle for the production of sugar.

The portion of juice that does not go through the evaporation step is mixed with yeast in the fermentation step, producing carbon dioxide and a mixture of ethanol and fermented wine. These by-products are separated in distillation columns due to the different boiling points of the mixture components. The mixture is vaporized and condensed into distinct liquids differentiated by their alcohol content. The vinasse produced in this stage has an alcohol content of 0.03%. The steam with 96% alcohol content is converted into hydrated ethanol. Finally, the hydrated ethanol goes through the dehydration process, producing anhydrous ethanol (Manochio et al. 2017).

The by-products generated from sugarcane processing, such as molasses and juice, within the biorefinery concept, can be reused as sources for the production of bioenergy and high value-added products from biological processes (anaerobic digestion). Thus, environmental and energy gains will be generated in the processing of sugarcane. It occurs because these by-products (molasses and juice) are mainly made up of valuable carbohydrates such as sucrose, which can be converted into a range of bioproducts in anaerobic digestion. The reuse of the by-products generated enables the optimization of sugarcane processing, seeking to maximize the use of all elements of this raw material (Ferreira et al. 2019; Freitas et al. 2020). Vinasse, for its part, is a residue from sugarcane processing and can be used in the fertigation of crops. However, the continuous application of vinasse in the soil can cause environmental contamination due to the presence of compounds that are difficult to degrade and the high organic load of this residue. Thus, anaerobic digestion is also an alternative to minimize pollution damage to the environment, generating value-added products and bioenergy from this process (Ramos and Silva 2020).

9.2.1 *Juice, Molasses, and Vinasse*

9.2.1.1 Characterization of Juice and Molasses

Sugarcane production in Brazil in the 2021/2022 harvest was 628.14 million tons (CONAB 2020). In this scenario, 439.70 million tons of juice were produced, considering that around 70% of the sugarcane is converted into juice, while 30% of the solid part is transformed into bagasse. This juice is generated after the sugarcane is harvested, washed on a conveyor belt, and milled by a variety of knives and crushers. The crushing and extraction of juice are carried out in mills, consisting of three to five rollers that will press the cane, separating the juice from the bagasse. The sugarcane juice is sieved and then treated and filtered, generating a press mud, rich in macro and micronutrients. After its treatment, the juice can go through an evaporation, cooking, and crystallization process for the production of molasses and sugar, or go on to the distillation process, generating vinasse and ethanol.

Sugarcane juice is a greenish-yellow viscous liquid, containing 70% water, 15% sugars, 13% fiber, and 2% impurities in its composition. The main sugar present in the sugarcane juice is sucrose (200 $g \cdot L^{-1}$) (Plangklang et al. 2012). The characterization of the sugarcane juice is presented in Table 9.1. The composition of the juice can vary depending on the harvesting period (Fuess et al. 2020). For examples, the 2017/2018 harvest had a pH of 4.54 and the concentrations of organic matter, total

Table 9.1 Physical-chemical parameters of the sugarcane juice (Plangklang et al. 2012; Menezes and Silva 2019; Fuess et al. 2020)

Parameters	Concentration	Parameters	Concentration
COD ($g \cdot L^{-1}$)	205.30 ± 47.10	Sulfate ($g \cdot L^{-1}$)	403 ± 14.0
Sucrose ($g \cdot L^{-1}$)	199.00	Potassium ($mg \cdot L^{-1}$)	1579.0 ± 550.0
Glucose ($g \cdot L^{-1}$)	3.40	Calcium ($mg \cdot L^{-1}$)	317.0 ± 179.0
Fructose ($g \cdot L^{-1}$)	3.20	Magnesium ($mg \cdot L^{-1}$)	288.6 ± 27.0
TSS ($g \cdot L^{-1}$)	12.81 ± 0.21	Copper ($mg \cdot L^{-1}$)	0.4 ± 0.3
VSS ($g \cdot L^{-1}$)	2.43 ± 1.24	Zinc ($mg \cdot L^{-1}$)	2.4 ± 1.0
N-NTK ($g \cdot L^{-1}$)	4.24 ± 0.09	$P\text{-}PO_4^{-3}$ ($mg \cdot L^{-1}$)	245.0 ± 100.0

COD chemical oxygen demand; *TSS* total suspended solids; *VSS* volatile suspended solids; *N-NTK* total nitrogen; $P\text{-}PO_4^{-3}$ phosphates

Table 9.2 Physical-chemical parameters of the sugarcane molasses (Wang et al. 2013; Freitas et al. 2020)

Parameters	Concentration	Parameters	Concentration
COD ($g \cdot L^{-1}$)	844.7 ± 21	Calcium ($g \cdot L^{-1}$)	6.3 ± 80
Total carbohydrate ($g \cdot L^{-1}$)	564.7 ± 62	Magnesium ($g \cdot L^{-1}$)	2.9 ± 224
Sucrose (% $p \cdot p^{-1}$)	28.71	HAc ($g \cdot L^{-1}$)	23.87 ± 3.2
Fructose (% $p \cdot p^{-1}$)	10.35	HPr ($g \cdot L^{-1}$)	27.6 ± 0.5
Glucose (% $p \cdot p^{-1}$)	3.77	HLa ($g \cdot L^{-1}$)	17.9 ± 8.9
TSS ($g \cdot L^{-1}$)	6.21	HSu ($g \cdot L^{-1}$)	30.4 ± 2.9
VSS ($g \cdot L^{-1}$)	1.34	HCi ($g \cdot L^{-1}$)	41.9 ± 2.6
N-NTK ($g \cdot L^{-1}$)	12.9 ± 0.0	HFo ($g \cdot L^{-1}$)	14.2 ± 2.6
Potassium ($g \cdot L^{-1}$)	24.5 ± 2.9		

COD chemical oxygen demand; *TSS* total suspended solids; *VSS* volatile suspended solids; *N-N-NTK* total nitrogen; *HPr* propionic acid; *Hla* lactic acid; *Hsu* succinic acid; *HCi* citric acid; *HFo* formic acid

carbohydrate and sulfate of 129.15 g COD·L^{-1}, 117.37 mg glucose·L^{-1}, 403 mg·L^{-1}, respectively. In the 2018/2019 harvest, the authors observed a pH of 6.14 and concentrations of organic matter, total carbohydrate and sulfate of 149.50 g COD·L^{-1}, 131.50 mg glucose·L^{-1}, 417 mg·L^{-1}, respectively. The authors collected the juice after the treatment steps.

Molasses, another by-product of sugarcane processing, is also called fine honey. It is synthesized in the sugarcane juice crystallization step in the generation of sugar crystals, as described above. Molasses is mainly composed of sugars in the form of sucrose, fructose, and glucose. Molasses is also composed of nutrients such as total nitrogen (2.8% $p \cdot p^{-1}$), ferric oxide (0.020% $p \cdot p^{-1}$), magnesium oxide (0.10% $p \cdot p^{-1}$), diphosphorus pentoxide (0.07% $p \cdot p^{-1}$), and aluminum oxide (0.06% $p \cdot p^{-1}$), essential for the production of bioenergy and soluble metabolites (Wang et al. 2013).

Table 9.2 presents the physicochemical characterization of sugarcane molasses. The high concentration of organic matter in molasses can cause pollution of terrestrial and aquatic environments when this by-product of sugarcane processing is improperly disposed of.

Molasses can be used in off-season periods for ethanol production, generating 12 L of ethanol per ton of processed sugarcane, while juice can generate more than 80 L of ethanol per ton of sugarcane. Thus, juice and molasses can be considered valuable by-products of sugarcane processing, mainly due to the high concentration of fermentable sugars mentioned above. The presence of these sugars in high concentrations in their compositions makes the biodegradable fraction of these substrates higher, facilitating their biodegradation and conversion into a wide range of bioproducts. In this context, considering the concept of biorefinery, the use of a variety of bioproducts generated from the biological process of juice and molasses has become the objective of several studies. These studies aim to optimize the conditions of anaerobic digestion to maximize the production of biofuels such as

Table 9.3 Physical-chemical parameters of the sugarcane vinasse (Ramos and Silva 2020; Rego et al. 2020)

Parameters	Concentration	Parameters	Concentration
COD ($g{\cdot}L^{-1}$)	31.60 ± 5.24	HAc ($mg{\cdot}L^{-1}$)	2882 ± 720
Sucrose ($g{\cdot}L^{-1}$)	11.43 ± 7.03	HLa ($mg{\cdot}L^{-1}$)	2655 ± 266
TSS ($g{\cdot}L^{-1}$)	3.26 ± 0.27	HSu ($mg{\cdot}L^{-1}$)	2648 ± 587
TSV ($g{\cdot}L^{-1}$)	2.66 ± 0.13	EtOH ($mg{\cdot}L^{-1}$)	4593 ± 1378
N-NTK ($mg{\cdot}L^{-1}$)	675 ± 12	HPr ($mg{\cdot}L^{-1}$)	1170 ± 440
P-PO_4^{-3} ($mg{\cdot}L^{-1}$)	113.3 ± 13		

COD chemical oxygen demand; *TSS* total suspended solids; *VSS* volatile suspended solids; *N-NTK* total nitrogen; *HAc* acetic acid; *HPr* propionic acid; *HLa* lactic acid; *HSu* succinic acid; *EtOH* ethanol; *P-PO_4^{-3}* phosphates

ethanol, bioenergy (hydrogen and methane), and value-added products (organic acids).

9.2.1.2 Characterization of Vinasse

Vinasse is the main residue generated from the processing of sugarcane for the production of ethanol, through the fermentation of the juice. An important physico-chemical characteristic of vinasse is its high polluting potential, with compounds that are difficult to degrade. This makes it difficult to dispose of this waste in the environment without prior pretreatment.

For each liter of ethanol produced, around 10 to 15 L of vinasse are generated. Based on estimates of ethanol production in Brazil, in the 2020/2021 harvest (29.8 billion liters) 417.2 billion liters of vinasse will be generated in the country (CONAB 2020). Vinasse temperature when it leaves the distillation column is approximately 90 °C and the pH is acid between 3 and 4. About 75% of the suspended solids in vinasse are organic and biodegradable, providing a high organic load. Vinasse is also composed of glycerol, phenolic compounds, melanoidins, residual sugar, acetic acid, lactic acid, ethanol, and high concentrations of inorganic nutrients (nitrogen, phosphorus, and potassium) (de Barros et al. 2016).

The physical-chemical characterization of sugarcane vinasse is presented in Table 9.3. The presence of melanoidins provides the dark brownish color of this liquid residue, while the high content of organic acids is responsible for the low pH. Vinasse is considered a complex effluent within the same production process due to variations in its composition throughout production. These variations can occur throughout the same harvest, depending on factors such as the milling of a variety of sugarcane, different types of soils with different levels of fertility, and variations in the operations of the fermentation and distillation stages (Moraes et al. 2015).

The characteristics of vinasse are dependent on its production process. The composition varies according to the production stage in which it is generated, whether from sugarcane juice, molasses, or a mixture of both, as shown in Table 9.4.

Table 9.4 Physical-chemical parameters of vinasse from sugarcane juice, molasses, and a mixture of both (Moraes et al. 2015)

	Substrate		
Parameters	Cane molasses	Cane juice	Mixture
pH	4.2–5.0	3.7–4.6	3.9–4.6
COD (g·L^{-1})	22.0–84.9	15.0–33.0	31.5–45.0
Potassium (g·L^{-1})	2.3–12	0.6–2.0	1.2–3.8
Nitrogen (g·L^{-1})	0.07–1.23	0.2–0.7	0.37–0.7
Sulfate (g·L^{-1})	1.2–3.5	0.2–1.4	0.15–1.3
Calcium (g·L^{-1})	0.3–3.6	0.1–0.32	0.46–3.3
Magnesium (g·L^{-1})	0.3–0.9	0.1–0.3	0.29–0.4
Phosphorus (g·L^{-1})	0.04–0.2	0.004–0.25	0.37–0.7
TS (g·L^{-1})	82	21.1–24	53–158
VS (g·L^{-1})	60	15.6–20	13
Phenols (mg·L^{-1})	–	–	1,1
Reduced sugars (g·L^{-1})	9.5	7.9	1.0–8.3

COD chemical oxygen demand; *TS* total solids; *VS* volatile solids

The main organic compounds present in sugarcane vinasse reported in the literature consist of organic acids (mostly lactate and acetate), alcohols (mainly glycerol and ethanol), and carbohydrates, regardless of their origin (Wilkie et al. 2000). The concentration of sugars in the molasses, resulting from the crystallization and evaporation of the juice, increases the content of non-fermentable organics in the vinasse. During sugar processing, higher concentrations of potassium, calcium, magnesium, and phosphorus are observed in molasses vinasse due to the addition of such nutrients. Sugarcane distilleries widely use sulfuric acid in order to minimize the contamination of microorganisms and yeast flocculation in fermentation. The addition of sulfuric acid leads to high concentrations of sulfate in the vinasse (up to 9 g·L^{-1}). Furthermore, toxic metals such as zinc (1.16 mg·L^{-1}), copper (0.35 mg·L^{-1}), barium (0.41 mg·L^{-1}), mercury (0.0019 mg·L^{-1}), and chromium (0.04 mg·L^{-1}) can be found in the composition of vinasse due to tubes lixiviation (Christofoletti et al. 2013; Kiyuna et al. 2017).

With this in mind, the continuous release of vinasse without pretreatment into the environment can cause pollution problems in environmental systems, compromise the structure of the soil and surroundings of water bodies, in addition to reducing crop productivity. This is mainly due to its high organic load (up to 100 g COD·L^{-1}), the presence of sulfates, toxic metals, and organic compounds that are difficult to biodegrade, such as phenols and melanoidins (Ratna et al. 2021). Thus, the use of vinasse as a fertigate can lead to the enrichment of salts in the soil, nitrate leaching, eutrophication of water resources, contamination of terrestrial or aquatic systems by heavy metals and phenolic compounds. Phenolic compounds are toxic to many microorganisms, such as those present in biological wastewater treatment processes (Fuess and Garcia 2014).

The treatment of vinasse has great challenges due to its physicochemical characteristics (low pH, high temperature, dark brown color, high ash content, and high percentage of dissolved organic and inorganic matter). Therefore, it is necessary to determine adequate economic and environmental ways to treat it, in order to minimize its polluting potential. Biological treatment appears as an effective alternative for the disposal of this waste. Anaerobic digestion is capable of converting a significant portion of organic matter into bioenergy and value-added products. Bioenergy can be used in the processing of sugarcane in distilleries, improving the energy efficiency of the process and, consequently, the viability of the anaerobic treatment of vinasse in reactors. Also, anaerobic digestion allows the generation of effluent with a lower organic load, in addition to the removal of sulfate and other compounds present, minimizing environmental pollution problems.

9.2.2 Environmental Compliance and Energy Production

9.2.2.1 Anaerobic Digestion of Vinasse

Table 9.5 presents the removal of organic matter under different operating conditions of anaerobic reactors, treating sugarcane vinasse. In a study using vinasse from sugarcane processing, Albanez et al. (2016a) investigated the digestion of this effluent under anaerobic conditions, in Anaerobic Sequencing Batch Biofilm Reactor (AnSBBR) with liquid phase recirculation. The authors reported that the increase in vinasse concentration increased the methane composition in the medium, the volumetric production, and the removal of organic matter. The increase in vinasse from 1000 mg $\mathrm{COD{\cdot}L^{-1}}$ to 3000 mg $\mathrm{COD{\cdot}L^{-1}}$ increased COD removal from 70% to 84%. COD removal remained between 82% and 84% in vinasse concentrations of 4,000 mg COD $\mathrm{L^{-1}}$ and 5000 mg COD $\mathrm{L^{-1}}$. The increase in vinasse concentration also increased the methane composition (%$\mathrm{CH_4}$) from 49.5% to 77% and the volumetric production from 0.03 L $\mathrm{CH_4{\cdot}day^{-1}{\cdot}L^{-1}}$ to 0.97 L $\mathrm{CH_4{\cdot}day^{-1}{\cdot}L^{-1}}$. From this study, the authors observed that the use of vinasse for anaerobic digestion provided a maximum substrate consumption of 83%, methane content in biogas of 77%, and removed organic load of 4.58 g $\mathrm{COD{\cdot}L^{-1}{\cdot}day^{-1}}$.

Similarly, Cabrera-Díaz et al. (2017) evaluated the variation of the organic loading rate (OLR) in the treatment of sugarcane vinasse in a combined system with two configurations of methanogenic reactors: Upflow Anaerobic Sludge Blanket Reactor (UASB) and Upflow Anaerobic Fixed-Bed Reactor (UAFBR). The authors varied the OLR (2.3 to 24 kg $\mathrm{COD{\cdot}m^{-3}{\cdot}day^{-1}}$) for the UASB and the UAFBR (0.5 and 14.5 kg $\mathrm{COD{\cdot}m^{-3}{\cdot}day^{-1}}$). Cabrera-Díaz et al. (2017) reported that higher OLR caused an increase in the concentrations of volatile organic acids and sulfates, decreasing the efficiency of organic matter removal. The overall organic matter removal was up to 86.7%. In the UASB (OLR of 12.5 kg $\mathrm{COD{\cdot}m^{-3}{\cdot}day^{-1}}$ and HRT of 2 days) the highest removal was 75.1% and a yield of up to 0.289 $\mathrm{m^3}$ $\mathrm{CH_4{\cdot}kg\ COD^{-1}}$. In the UAFBR, the highest efficiency of organic matter removal was 62.5% and a yield of 0.207 $\mathrm{m^3}$ $\mathrm{CH_4{\cdot}kg\ COD^{-1}}$ (OLR of 4.4 kg $\mathrm{COD{\cdot}m^{-3}{\cdot}day^{-1}}$ and HRT of 1.9 days). Therefore, the combination of the two reactors showed satisfactory performance in removing the polluting potential of vinasse.

Table 9.5 Comparison of the biological treatment of sugarcane vinasse under different operating conditions

Anaerobic reactor	Parameters	COD removal efficiency	References
UASB	Temperature—55 °C; HRT—48 h; OLR—2.5–30 kg COD m^{-3}·day^{-1}	62–72%	Souza et al. (1992)
Fixed bed	Temperature—24–33 °C; HRT—48–600 h; OLR—33.97–2.78 kg COD m^{-3}·day^{-1}; 66.06–72.79 mg COD·L^{-1}	61–75.74%	Seth et al. (1995)
UASB	Temperature—55 °C; HRT—100.8–10.8 h; OLR—2.3–24 kg COD m^{-3}·day^{-1}; 10.000 mg COD·L^{-1}	39–67%	Harada et al. (1996)
Two-phase fixed bed	Temperature—30 °C; HRT—25–4 h; OLR—2.75–21.29 kg COD m^{-3}·day^{-1}; 68.660–85.14 mg COD·L^{-1}	67.1–84.5%	Goyal et al. (1996)
Series contact anaerobic filter	HRT—48–96 h; 1.500–19.000 mg COD·L^{-1}	22–98%	Vijayaraghavan and Ramanujam (2000)
AFBR	Temperature—30 °C; HRT—11 h; OLR—1–10 kg COD m^{-3}·day^{-1}; 33.000–66.000 mg COD·L^{-1}	50–90%	Fernández et al. (2001)
UABS + Filter	Temperature—35 °C; HRT—192–96 h; OLR—4.53–11.13 kg COD m^{-3}·day^{-1}; 35.000–45.000 mg COD·L^{-1}	60–79%	Sunil Kumar et al. (2007)
AFBR	Temperature—30 °C; HRT—11 h; TCO—2.0–20.0 kg COD m^{-3}·day^{-1}; 35.000–45.000 mg COD·L^{-1}	65–90%	Fernández et al. (2007)
AnSBBR	Temperature—55 °C; HRT—1–6 day; OLR—1–6.6 kg COD m^{-3}·day^{-1}; 1.000–20.000 mg COD·L^{-1}	55–72%	Ribas et al. (2009)
AnSBBR	Temperature—35–55 °C; OLR—0.85–5.70 kg COD m^{-3}·day^{-1} (55 °C); OLR—2.79–35.94 kg·m^{-3}·day^{-1} (35 °C);	>60%	Döll and Foresti (2010)
AFBR	Temperature—30 °C; HRT—24 h; OLR—3.33–26.19 kg COD m^{-3}·day^{-1}; 2.273–20.073 mg COD·L^{-1}	51–70%	Siqueira et al. (2013)
UASB in two stages	Temperature—55 °C; 1° stage: HRT—10.2 h; OLR—84.2 kg COD m^{-3}·day^{-1}; 2° stage HRT—39–23 h; TCO—15–25 kg·m^{-3}·day^{-1}	74.6–96.1%	Ferraz Júnior et al. (2016)
AnSBBR	Temperature—30 °C; OLR—1.18–5.54 kg COD m^{-3}·day^{-1}; 1.000–5.000 mg COD·L^{-1}	70–84%	Albanez et al. (2016a)
UASB	Temperature—30 °C; HRT—2.8–1.8 day; OLR—0.2–11.5 kg COD m^{-3}·day^{-1}; 1.866–28.543 mg COD·L^{-1}	73–82%	de Barros et al. (2016)

UASB + CSTR	Temperature—25 °C; 1° stage: HRT—1–0.5 day; 2° stage: HRT—4–6 day; OLR—2.5–6 kg COD m^{-3}·day^{-1};16.700 mg COD·L^{-1}	97%	Santos et al. (2017)
Batch in two stages	Temperature—37 °C; 8.500 mg COD·L^{-1}	83.3%	Fu et al. (2017)
AnSBBR	Temperature—30 °C; OLR—1 to 10 kg COD m^{-3}·day^{-1}	88%	Almeida et al. (2017)
UASB in two stages	Temperature—55 °C; 1° stage: HRT—24 a 17 h day; 2° stage: HRT—11–7 h; OLR—5–55 kg COD m^{-3}·day^{-1}; 31.500 mg COD·L^{-1}	60%	de Barros and Duda (2017)
UASB	Temperature—55 °C; HRT—37–18 h; OLR—15–25 kg COD m^{-3}·day^{-1}	70.2%	Fuess et al. (2017b)
Fixed Bed	Temperature—55 °C; HRT—37–18 h; OLR—15–30 kg COD m^{-3}·day^{-1}	83.5%	Fuess et al. (2017a)
ASTBR + APBR	Temperature—30 °C; HRT—60–24 h OLR—2.4–18 kg·m^{-3}·day^{-1}; 6.000–18.000 mg COD·L^{-1}	54–82%	de Aquino et al. (2017)
UASB + APBR	Temperature—35 °C; UASB: HRT—10–1.3 day; OLR—2.3 a 24 kg COD m^{-3}·day^{-1}; APBR: HRT—8–1.2 day; OLR—0.5–14.5 kg COD m^{-3}·day^{-1};	86.7%	Cabrera-Díaz et al. (2017)
Batch	Temperature—55 °C; 24.200 mg COD·L^{-1}	>80%	Kiyuna et al. (2017)
UASB pilot scale	Temperature—22 °C; HRT—33.33–0.86 day; OLR—0.5–32.4 kg·m^{-3}·day^{-1}; 19.220 mg COD·L^{-1}	90%	Del Nery et al. (2018)
Batch, UASB e EGSB	Temperature—37 °C; OLR—12 kg COD m^{-3}·day^{-1}; 4.300–16.200 mg COD·L^{-1}	70%	López et al. (2018)
UASB industrial scale	Temperature—37 °C; OLR—3.7 kg COD m^{-3}·day^{-1}	87%	López et al. (2018)
EGSB	Temperature—26 °C; HRT-7 day; OLR—5.1 kg COD m^{-3}·day^{-1}; 35.762 mg COD·L^{-1}	75%	Vaquerizo et al. (2017)
ABR	Temperature—25 °C; OLR—0.5–2 kg COD m^{-3}·day^{-1}; 18.000 mg COD·L^{-1}	90–95%	Vuitik et al. (2019)
Batch	Temperature—37 °C; 5.000 mg COD·L^{-1}	85.9–95.1%	Santos et al. (2019)
AnSBBR	Temperature—55 °C; OLR—6 to 25 kg COD m^{-3}·day^{-1}	80–88%	Albuquerque et al. (2019)
AFBR in two stages	Temperature—55 °C; 5.000–10.000 mg COD·L^{-1}; 1° stage: HRT—4 h; 2° stage: HRT—24–10 h	70.1–77.3%	Ramos and Silva (2020)

ABR-compartmented anaerobic reactor; AFBR-anaerobic fluidized bed reactor; AnSBBR-anaerobic sequencing bath biofilm reactor; APBR-anaerobic packed-bed reactor; ASTBR-anaerobic structured-bed reactor; CSTR-continuous stirred tank reactor; EGSB-expanded granular sludger-bed reactor; UASB-upflow anaerobic sludge-bed reactor.

de Aquino et al. (2017) reported that the removal of organic matter of 73% and 82% was observed in structured- and packed-bed reactors, respectively, at 15 kg COD m^{-3}·day^{-1} OLR, under mesophilic conditions (30 °C). Vinasse concentrations were evaluated in order to observe the effect of this increase in reactor efficiencies in degrading organic matter and producing methane. Organic matter removal decreased to 54% (structured bed) and 58% (packed bed) with an OLR of 18 kg COD·m^{-3}·day^{-1}. Based on methane yields, the authors observed higher methane results from the OLR of 7.2 kg COD·m^{-3}·day^{-1} in the structured-bed reactors, indicating reactor overload at higher OLR. In the structured-bed reactor, the yields remained between 300 and 310 mL CH_4·kg^{-1} $COD_{removed}$ in all applied OLR.

The presence of sulfate from vinasse production to minimize the contamination of microorganisms can generate competition for substrate between methanogenic archaea (methane-producers) and sulfate-reducing bacteria (sulfide-producers). Sulfide generation can inhibit the microbial communities present and decrease the degradation of organic matter and methane production. In this context, Kiyuna et al. (2017) evaluated the COD/sulfate ratio in the liquid medium on the removal of organic matter and methane production from sugarcane vinasse treatment (55 °C). The batch experiments were carried out in three distinct COD/sulfate ratios: 12.0, 10.0, and 7.5. The authors reported that lower COD/sulfate influences (higher sulfate concentrations) negatively affected the methanogenic activity because part of the electron flow (13.6%) was shifted to sulfetogenesis, minimizing the cumulative production of methane. At a COD/sulfate ratio of 7.5, the methane production (1000 mL of methane) was 35% lower than the production in the reactor with a COD/sulfate ratio of 12.0 (approximately 650 mL). The degradation of organic matter remained above 80%, regardless of the initial COD/sulfate ratio.

The diversification of sugarcane processing for the generation of sugar and/or ethanol allows for variations in the composition of the vinasse generated, also requiring changes in the biodigestion process. Thus, the study by Santos et al. (2019) evaluated the variability of vinasse composition from ethanol, sugar, or brandy production and its effects on anaerobic digestion. The authors observed in batch tests (at 37 °C and COD of 5000 mg·L^{-1}) changes in the treatment of vinasse from three different directions of total sugars (majority production of sugar, ethanol, or brandy). Santos et al. (2019) reported a 6% shift in electron flux for sulfate-reducing bacteria (SRB) from vinasse from ethanol production, at a COD/SO_4^{2-} ratio of 11.85. The SBR activity was responsible for the lowest constant kinetics of organic matter degradation, due to the overcoming of the SBR in the competition for substrate with the methanogenic archaea. Removals of organic matter were 95.1% (brandy production), 87.2% (sugar production), and 85.9% (ethanol production), with the highest concentration of recalcitrant compounds being responsible for the lowest removals.

Vuitik et al. (2019) evaluated the treatment of vinasse (18 g COD·L^{-1}) in compartmented anaerobic reactors (at 25 °C). The authors observed that the removal of organic matter remained between 90 and 95% from the increase of 0.5 to 2.0 kg COD·m^{-3}·day^{-1} of the OLR. Vuitik et al. (2019) indicated that the remaining organic load contained mainly melanoidins and phenols, which are recalcitrant compounds found in vinasse. Furthermore, from kinetic assays, it was possible to observe the inhibition by substrate in vinasse concentrations above 15 g COD·L^{-1}. Fermentative and methanogenic microorganisms work under different optimal conditions for anaerobic digestion. In this way, separating the process into two stages, in different reactors, makes it possible to improve the stages of anaerobic digestion and the performance, stability, and overall control of the process (Sivagurunathan et al. 2018). In this context, Fu et al. (2017) evaluated the anaerobic digestion of vinasse (at 37 °C and 8500 mg COD·L^{-1}) in a two-stage batch system compared to a single-stage system. The authors observed that in the methanogenic stage the removal of organic matter was 83.3% and the methane yield was 10.8% higher in the two-stage system compared to the single stage, proving its efficiency in the treatment of vinasse.

Similarly, Ramos and Silva (2020) verified the treatment of vinasse in anaerobic fluidized bed reactors at 55 °C separated in two stages of digestion. The authors varied vinasse concentrations between 5 and 10 g COD·L^{-1} in a 4-h HRT for the acidogenic reactor, 24 to 10-h HRT for the sequential methanogenic reactor, and 24-h HRT for the single-stage methanogenic reactor. Ramos and Silva (2020) observed organic matter removals of up to 77.3 ± 9.2% in a single stage and up to 69.4 ± 6.9% in two stages. However, in the two-stage biological treatment of vinasse, the energy yield was 52.8% higher than in the single-stage system. In a single stage, the methane yield was 0.30 ± 0.04 L CH_4·g COD^{-1} and the production rate was 3.78 ± 0.40 L CH_4·day^{-1}·L^{-1}, with vinasse concentration of 7.5 g COD·L^{-1}. In the two-stage system, the authors found a maximum methane yield of 0.26 ± 0.06 L CH_4·g COD^{-1}, methane content of 74.5 ± 6.0%, and a production rate of 5.57 ± 0.38 L CH_4·g COD^{-1}, in the vinasse concentration of 10 g COD·L^{-1}. The operation of two-stage systems with acidogenic reactors is an alternative to minimize the negative effects of sulfetogenesis on methane production. Acidogenic reactor conditions aid in sulfate removal. Thus, the greatest production of acids is directed to acetic acid, favoring the activity of methanogens in the subsequent reactor. However, the operation of these reactors must be flexible based on variations in the composition of the vinasse during the season.

The addition of a co-substrate can also dilute inhibitory compounds and increase the efficiency of removing organic matter from the vinasse and producing methane. Volpini et al. (2018) evaluated the removal of organic matter and the production of methane from the co-digestion of vinasse and molasses in AnSBBR (30 °C). The authors used AnSBBR's acidogenic effluent with different concentrations of organic matter (1000 to 4500 mg COD·L^{-1}). Volpini et al. (2018) observed a decrease in organic matter removal from 87% to 71% and an increase in methane production from 0.320 L CH_4·day^{-1}·L^{-1} to 2.974 L CH_4·day^{-1}·L^{-1}, from the increase of OLR from 1.5 to 8.8 kg COD·m^{-3}·day^{-1}. The methane yield increased from 0.193 to

0.340 L $CH_4 \cdot g\ COD^{-1}$ and the methane composition remained between 87% and 91%.

Lovato et al. (2019) evaluated the co-digestion of sugarcane vinasse and glycerin in an AnSBBR under mesophilic conditions (30 and 35 °C) aiming at the production of methane. The authors investigated the effects of adding proportions of glycerin in the anaerobic digestion process (0, 33, 50, 67, and 100% of the influent $g\ COD \cdot L^{-1}$) on the efficiency of organic matter removal and production rate and methane yield. Lovato et al. (2019) reported that the addition of glycerin in the anaerobic digestion process of vinasse had a beneficial effect, causing an increase in methane yield of up to 58.5% with a maximum production rate of 139.32 mol $CH_4 \cdot m^{-3} \cdot day^{-1}$, yield of 15.30 mol CH_4 kg $COD_{removed}$, and organic matter removal of 90 ± 2%, at 10 kg COD $m^{-3} \cdot day^{-1}$, proportion of 50%:50% of vinasse and glycerin at 30 °C. The co-digestion of vinasse makes it possible to increase the stabilization of the digestion process, the concentration of nutrients, the biodegradation of substrates, and the syntrophic relationships between microbial communities.

The choice of an appropriate co-substrate for vinasse, with adequate concentrations and proportions, increases the synergism between the microbial communities and minimizes the adverse effects of the inhibitory compounds present in the residue (Albanez et al. 2016b). Sugarcane molasses is a potential co-substrate for vinasse, as it consists mostly of fermentable sugars and nutrients important to anaerobic populations. A great advantage of using sugarcane molasses as a co-substrate for vinasse is the fact that both are by-products of sugarcane processing for the production of sugar and alcohol. The ease of joining the two residues from the same production process for treatment and the possibility of increase of bioenergy generation, reducing the polluting potential of the residues, makes the processing of sugarcane more economically viable and environmentally appropriate (Albanez et al. 2018).

Different processes that originate different vinasses with varied compositions make it necessary to evaluate the components present in this residue (Wilkie et al. 2000). Based on this assessment, treatment techniques and operating conditions can be analyzed to make them suitable for removing the main pollutant compounds from the waste. Buitrón et al. (2014) reported a 73% organic matter removal and a reduction in methane percentage from 68% to 40% when HRT was reduced from 24 h to 18 h using tequila vinasse (1636 mg $COD \cdot L^{-1}$) in mesophilic AnSBBR (30 °C) (2.3 $kg \cdot m^{-3} \cdot day^{-1}$).

Thermophilic anaerobic digestion of vinasse allows higher loads of organic matter to be degraded, achieving similar treatment efficiencies and methane yields compared to mesophilic treatment (Wilkie et al. 2000). In addition, thermophilic temperatures improve process economics, since vinasse does not need to go through a cooling step after being produced. For ethanol production to be qualified as a sustainable process, due consideration for the treatment and use of by-products from the vinasse residue is essential.

When one intends to favor the production of hydrogen in anaerobic digestion processes, some operating conditions must be followed. The evaluation of physicochemical factors such as pH, temperature, concentration of organic matter, and inoculum selection are fundamental for the efficiency of hydrogen production. Table 9.6 presents different studies that evaluated the operating conditions in order to maximize the production of hydrogen in the fermentation of vinasse, molasses, and sugarcane juice.

Several techniques can be selected to interrupt the methanogenesis step, such as the use of chemical compounds (sodium bromoethanesulfonate, iodopropane, and chloroform) and the creation of adverse conditions for methanogenic archaea, which are more sensitive to changes in the environment when compared to hydrogen-producing fermentative bacteria (Wang et al. 2013). A decrease in pH (<5.0) or an increase in the temperature of the medium inhibits or inactivates the archaea in the process, selecting only endospore-forming hydrogen-producing bacteria, such as those of the genus Clostridium spp. (Olguín-Araneda et al. 2015).

Lazaro et al. (2014) thermally pretreated a mesophilic methanogenic microbial consortium in order to evaluate the hydrogen production under mesophilic (37 °C) and thermophilic (55 °C) conditions from sugarcane vinasse fermentation. The authors reported higher hydrogen yields (2.31 mmol $H_2 \cdot g^{-1}$ $COD_{applied}$) under thermophilic conditions, with a vinasse concentration of 2 g $COD \cdot L^{-1}$. The authors observed that under mesophilic conditions the microbial community present in the medium (mainly affiliated with the genus *Clostridium*) was more tolerant to inhibitory compounds of high concentrations of vinasse. Similarly, Albanez et al. (2016b) verified the need for thermal pretreatment, determined by Kim et al. (2006), performing a thermal shock on microorganisms. The authors analyzed two reactors with identical operating conditions, except for the inoculum of one of them that underwent pretreatment. Albanez et al. (2016a) reported favoring hydrogen production due to inoculum pretreatment. The daily molar productivity of hydrogen (1.9 mol $H_2 \cdot L^{-1}$ day^{-1}) in the reactor with inoculum pretreatment was 36.84% higher than that observed in the reactor without inoculum pretreatment.

Choosing the proper operating temperature is a very important factor in maximizing hydrogen production. Several studies indicate a range between 40 and 65 °C (thermophilic), as advantageous for the release of biogas from the liquid medium, facilitating the production of biogas and eliminating pathogenic microorganisms present in the microbial consortium. In addition, the fact that the vinasse leaves the distillation column at a temperature of approximately 90 °C makes the operation of reactors under thermophilic conditions suitable for faster adaptation of microorganisms and the start of fermentation. Ramos and Silva (2017) evaluated the effect of temperature at 55 °C and 75 °C on the fermentation of sugarcane vinasse for hydrogen production in anaerobic fluidized bed reactors. The authors reported that the highest hydrogen production occurred at a thermophilic temperature of 55 °C with a maximum hydrogen yield of 1.64 ± 0.22 mmol $H_2 \cdot g$ COD^{-1} (4 h TDH) and maximum hydrogen production rate of 0.71 ± 0.16 L $H_2 \cdot h^{-1} \cdot L^{-1}$ (0.5 h TDH). At a temperature of 75 °C there was a reduction in carbohydrate conversions due to the greater difficulty in adapting the thermophilic microbial groups to higher temperatures (75 °C).

The separation of the anaerobic digestion process into two phases aims to favor the different microbial groups of the consortium used for the degradation of organic

Table 9.6 Hydrogen production from sugarcane vinasse under different operating conditions

Anaerobic reactor	Parameters	Production	References
AFBR	Temperature: 55 °C; TDH—8–1 h; OLR—26.6–225.3 kg COD m^{-3}·day^{-1}; 5.000 mg COD·L^{-1}	18.72 L H$_2$ day^{-1} L^{-1}	Santos et al. (2014a)
2 AFBR	Temperature: 55 °C; AFBR 1: TDH—6–1 h; OLR—60–360 kg COD m^{-3}·day^{-1}; 10.000 mg COD·L^{-1}; AFBR 2: OLR—60–480 kg COD m^{-3}·day^{-1}; 30.000 mg COD·L^{-1}	AFBR 1: 47.04 L H$_2$ day^{-1} L^{-1} AFBR 2: 19.44 L H$_2$ day^{-1} L^{-1}	Santos et al. (2014b)
2 AFBR	Temperature: 55 °C; HRT—6–1 h; AFBR 1: OLR—40–240 kg COD m^{-3} day^{-1}; 10.000 mg COD·L^{-1}; AFBR 2: TDH—8–1 h; OLR—90–720 kg COD m^{-3} day^{-1}; 30.000 mg COD·L^{-1}	AFBR 1: 35.76 L H$_2$ day^{-1} L^{-1} AFBR 2: 28.80 L H$_2$ day^{-1} L^{-1}	Santos et al. (2014c)
Batch	Temperature—55 °C; 2 g CDO·L^{-1}	2.31 mmol H$_2$·g^{-1} COD applied	Lazaro et al. (2014)
AFBR	Temperature: 30 °C; OLR—20–120 kg COD m^{-3} day^{-1}	13.68 L H$_2$·day^{-1}·L^{-1}	dos Reis et al. (2015)
APBR	Temperature: 25 °C; HRT—24 h; OLR—36.2 kg COD m^{-3} day^{-1}	0.084 L H$_2$·day^{-1}·L^{-1}	Ferraz Júnior et al. (2015a)
APBR	Temperature: 55 °C; HRT—10.2 h; OLR—84.2 kg COD m^{-3} day^{-1}; 35.200 mg COD·L^{-1}	2.3 L H$_2$·day^{-1}·L^{-1}	Ferraz Júnior et al. (2015b)
APBR	Temperature: 55 °C; HRT—7.5 h; OLR—84.2 kg COD m^{-3} day^{-1}; 28.300 mg COD·L^{-1}	0.79 ± 0.59 L H$_2$ day^{-1} L^{-1}	Fuess et al. (2016)
AFBR	Temperature: 55–75 °C; HRT– 8–0.5 h; OLR—30–480 kg COD m^{-3} day^{-1}; 28.600 mg COD·L^{-1}	17.4 L H$_2$·day^{-1}·L^{-1}	Ramos and Silva (2017)
AFBR	Temperature: 55 °C; HRT—8–1 h; OLR—30–240 kg COD m^{-3} day^{-1}; 28.600 mg COD·L^{-1}	2.54 L H$_2$·day^{-1}·L^{-1}	Ramos and Silva (2018)
APBR	Temperature: 55 °C; HRT—7.5 h; 28.400 mg COD·L^{-1}	1.1 L H$_2$ day^{-1} L^{-1}	Fuess et al. (2018)
ASTBR	Temperature: 55 °C; HRT—24–4 h; TCO—40–120 kg COD m^{-3} day^{-1}; 40.000 mg COD·L^{-1}	2.41 L H$_2$ day^{-1} L^{-1}	Fuess et al. (2019)
AFBR mesophilic + AFBR thermophilic	Mesophilic: Temperature: 30 °C; thermophilic: Temperature: 55 °C; HRT—8–1 h; OLR—15–120 kg COD m^{-3} day^{-1}; 5.000 mg COD·L^{-1}	30 °C: 0.27 ± 0.07 L H$_2$·day^{-1}·L^{-1} 55 °C: 6.42 ± 1.46 L H$_2$·day^{-1}·L^{-1}	Rego et al. (2020)
AFBR in two stages	Temperature: 55 °C; 1° stage: HRT—4 h; 5.000–10.000 mg COD·L^{-1}; 2° stage: HRT-24–10 h; 5.000–10.000 mg COD·L^{-1}	1.30 ± 0.16 L H$_2$·day^{-1}·L^{-1}	Ramos and Silva (2020)

AFBR anaerobic fluidized bed reactor; *APBR* anaerobic packed-bed reactor; *ASTBR* anaerobic structured-bed reactor matter. These different microbial groups need different operating conditions to act in order to maximize the production of biogas, such as fermentative bacteria and methanogenic archaea (Ferraz Júnior et al. 2016; Fuess et al. 2017a, b; Ramos and Silva 2020). In this way, it becomes possible to increase the efficiency of hydrogen and methane production, in addition to increasing the removal of organic matter and stabilization of the systems. The division of the process occurs in the separation of phases in different anaerobic reactors. According to Ramos and Silva (2020), one of the main objectives of these systems is to offer optimal conditions for the production of hydrogen and organic acids without destabilizing the methanogenic step.

Ramos and Silva (2020) investigated the feasibility of generating hydrogen and methane from sugarcane vinasse, in a two-stage system at 55 °C, using anaerobic fluidized bed reactors. In the first-stage reactor, the authors varied vinasse concentrations between 5 and 10 g $COD{\cdot}L^{-1}$ with a HRT of 4 h. For the second-stage reactor, different HRTs were evaluated (24 to 10 h). Ramos and Silva (2020) reported better conditions for hydrogen production in the vinasse concentration of 10 g $COD{\cdot}L^{-1}$ ($23.9 \pm 5.6\% H_2$), production rate of 1.30 ± 0.16 L $H_2{\cdot}day^{-1}{\cdot}L^{-1}$, and yield of 0.34 ± 0.08 mmol $H_2{\cdot}g\ COD_{applied}{}^{-1}$. In order to compare the efficiencies of anaerobic digestion in two and one stage, different concentrations of vinasse (5 to 10 g $COD{\cdot}L^{-1}$) were also observed in the 24 h HRT. Ramos and Silva (2020) found that the two-stage system showed an energy yield 52.8% higher than the single-stage system, achieving similar organic matter treatment efficiencies (COD removal of up to $77.3 \pm 9.2\%$ in single stage and up to $69.4 \pm 6.9\%$ in two stages). Furthermore, the methane content of $74.5 \pm 6.0\%$ CH_4 in two stages was higher than that observed in the single-stage reactor ($68.4 \pm 7.2\%$ CH_4). The authors observed a production rate of 5.57 ± 0.38 L $CH_4{\cdot}g\ COD^{-1}$ at a vinasse concentration of 10 g $COD{\cdot}L^{-1}$ (10 h TDH) without signs of organic overload.

9.2.2.2 Anaerobic Digestion of Molasses and Juice

In addition to vinasse, among the various organic raw materials for the production of bioenergy in the form of hydrogen and methane, molasses and juice, used in the production of sugar or ethanol, are economically viable and available alternatives, due to their low production costs. Furthermore, these by-products have high concentrations of sugars such as sucrose, fructose, and glucose that facilitate the biodegradation and conversion of these substrates into bioenergy and value-added products, adding more value to sugarcane processing (Fuess et al. 2020). Some studies seek to examine the potential of anaerobic digestion of molasses and juice on the production of bioenergy.

Turkdogan-Aydınol and Yetilmezsoy (2010) reported an average daily production value of 166.55 L methane, when evaluating methane production from sugarcane molasses under anaerobic conditions at 35.2 ± 0.7 °C (UASB reactor). The authors also observed an average organic matter removal efficiency of 93% and an average volumetric organic matter removal rate of 6.87 ± 3.93 kg $COD_{removed}{\cdot}m^{-3}{\cdot}day^{-1}$, indicating a remarkable performance in the anaerobic digestion process. Based on the results, it is possible to assume that sugarcane processing molasses has a great bioenergetic potential in the form of methane and organic matter treatment at high levels of up to 98%.

Park et al. (2010) investigated the anaerobic digestion in a two-stage system from sugarcane molasses, in anaerobic fixed-bed reactors (35 °C), for the production of bioenergy in the form of hydrogen and methane. The authors observed from the HRT variation (24 to 5 h) that the maximum hydrogen production occurred in the 6 h HRT, with a hydrogen production rate and a hydrogen content of 2.8 ± 0.22 L $H_2 \cdot L_{reactor}{}^{-1} \cdot day^{-1}$ and 27 ± 0.7%H_2, respectively. Furthermore, a maximum removal of organic matter (75.1%) was observed in the second-stage reactor (methanogenic stage) with 6-day HRT, and a maximum methane production rate of 1.48 ± 0.09 L $CH_4 \cdot L_{reactor}{}^{-1} \cdot day^{-1}$. The overall removal of organic matter (first and second stage) was 79.8%. The authors affirmed, through an economic evaluation, the excellent potential of molasses for the sequential production of hydrogen and methane by a two-stage anaerobic digestion process.

In addition to hydrogen and methane, other biofuels can be generated from sugarcane molasses. Abd-Alla et al. (2014) aimed to maximize the production of low-cost biofuels through sequential batch fermentation (37 °C) in three stages. The first stage consisted of producing biodiesel using sugarcane molasses as a substrate. The second stage consisted of producing hydrogen and the third aimed at the production of methane by methanogenic microorganisms. The authors reported the maximum accumulated volumetric hydrogen production of 1.45 $mL \cdot L^{-1}$ after 48 h of fermentation. The highest accumulated production of methane was 1.69 $mL \cdot L^{-1}$, obtained after 48 h. According to the authors, the energy produced from biodiesel, hydrogen and methane generated in three successive stages of fermentation from 84 g of molasses was 3928 $kJ \cdot mol^{-1}$. The results presented suggest an increase in the economic viability of bioenergy production from molasses.

Sugarcane juice also has a high potential for energy production due to its rich composition made up of fermentable sugars, such as sucrose. Thus, Reungsang et al. (2016) observed the efficiency of methane production from acidified effluent from sugarcane juice fermentation at 30 ± 2 °C in a UASB reactor. The authors investigated different OLR (3.41 ± 0.35 to 7.05 ± 0.13 kg $COD \cdot m^{-3} \cdot day^{-1}$) with HRT ranging from 6 to 3 days. The OLR of 5.25 ± 0.05 kg $COD \cdot m^{-3} \cdot day^{-1}$ (4-day HRT) resulted in a maximum methane production rate of 1.27 ± 0.05 L $CH_4 \cdot L^{-1} \cdot day^{-1}$ and methane yield of 348 ± 13 mL $CH_4 \cdot g^{-1}$COD. The total energy generated was 219.23 $kJ \cdot L^{-1}{}_{substrate}$ and the efficiency of removal of organic matter was 75.60%.

Evaluating the sequential production of hydrogen from sugarcane juice with a concentration of 25 g $COD \cdot L^{-1}$, Nualsri et al. (2016a) verified the influence of HRT on CSTR and UASB at 37 °C. The authors investigated the production of hydrogen in CSTR, decreasing HRT from 12 to 2 h. Meanwhile, the removal of organic matter was observed in UASB, decreasing the HRT from 12 to 2 days. The decrease in HRT from 12 to 3 h increased volumetric production, hydrogen content and yield from 1.18 to 17.50 $L \cdot day^{-1} \cdot L^{-1}$, from 20.8 to 30.3%, and from 0.30 to 1.32 mol $H^2 \cdot mol^{-1}{}_{hexose}$, respectively. The sequential hydrogen and methane production system obtained a carbohydrate removal of 97.5% in the optimal HRT (3 h for H_2

Table 9.7 Energy yields from sequential production of hydrogen and methane from different substrates

Substrate	Reactor	Temp.	HRT	EPR (kJ·L^{-1}·day^{-1})	Total	References
	H_2	°C	h	H_2	EPR	
	CH_4		d	CH_4	(kJ·L^{-1}·day^{-1})	
Molasses	PBR	35	6	30.24	100.08	Park et al. (2010)
	PBR	35	6	69.84		
Food waste	CSTR	37	2	51.84	167.04	Elbeshbishy and Nakhla (2011)
	CSTR	37	7	115.20		
	CSTR	35	5	33.05		
Sugary wastewater	UASB	35	15	72.36	105.41	Wang et al. (2013)
	UASB	55	–	5.72		
Cassava wastewater	UASB	55	–	23.40	29.12	Intanoo et al. (2014)
	UASB	55	36	16.20		
Latex serum	UASB	55	9	25.56	41.76	Kongjan et al. (2014)
	ASBR	55	48	19.87[a]		
Palm oil wastewater	ASBR	55	48	19.87[a]	113.47	Mamimin et al. (2015)
	UASB	35	15	93.60[a]		
Palm oil wastewater	UASB	55	48	20.52[a]	135.72	Kumari and Das (2015)
	CSTR	37	5	115.20[a]		
Sugarcane juice	CSTR	37	3	189.00	270.00	Nualsri et al. (2016a)
	UASB	30	3	81.00		

ASBR sequential batches; *CSTR* continuous stirred tank reactor; *PBR* anaerobic packed-bed reactor; *UASB* upflow anaerobic sludge-bed reactor

[a] Calculated from the original data

and 3 days for CH_4). The authors observed satisfactory results in bioenergy production when compared to other studies. Table 9.7 shows the Energy Production Rate (EPR) obtained from the anaerobic digestion of different substrates.

Ferreira et al. (2019) evaluated the thermal pretreatment of microbial consortia, aiming to maximize the production of bioenergy in the form of hydrogen from sugarcane juice, under mesophilic (30 °C) and thermophilic (55 °C) temperatures. In addition, the authors used two distinct microbial consortia, considering the temperature conditions. A granular sludge from a mesophilic UASB was used under mesophilic conditions. While the inoculation of the thermophilic reactor used granular sludge from a thermophilic UASB that treated vinasse from the sugarcane processing itself. The authors reported higher rates of hydrogen production (501 mL H_2·h^{-1}·L^{-1} in the 1 h HRT) from the use of pretreated microbial consortium from sugarcane processing (55 °C). This result was associated with the adaptation of the thermophilic microbial consortium to sugarcane juice and the presence of specialized groups of hydrogen-producing bacteria at high temperatures with greater dominance in this inoculum.

Albanez et al. (2016b) reported an estimated energy generation of 26,328 MW per year from the co-digestion of molasses and vinasse in a system with 6 batch reactors configured in parallel, each with a volume of 27,297 m^3. These results demonstrate the high potential for energy generation from the anaerobic digestion of by-products generated from sugarcane processing. Fuess et al. (2020) reported that the anaerobic digestion of molasses processing increases the energy potential of biogas (methane and hydrogen) by more than 600% in sugarcane biorefineries, when compared to vinasse processing. The authors also observed that the separation of the process into two stages (fermentative and methanogenic) increases the energy potential by 13.1%, indicating the possibility of effectively reaching theoretical values of methane yield from fermented molasses.

Table 9.8 shows different works that aimed at the production of hydrogen, evaluating operational parameters such as HRT, OLR, and concentration of organic matter, in different configurations of biological reactors.

9.2.3 Value-Added Products

9.2.3.1 Production of Value-Added Products from Molasses and Juice

Table 9.9 shows the approximate market values of the main value-added products generated observed in the fermentation of sugarcane molasses, juice, and vinasse.

The production of organic acids (HAc, HBu, HPr, and HVa) was observed by Albanez et al. (2016b) in the anaerobic digestion of molasses for the production of hydrogen in an AnSBBR. This hydrogen production occurred through the metabolic pathways of formation of HAc, HBu, and HVa instead of just the acetic pathway. The authors reported that in the fermentation of vinasse and molasses, the substrate was first converted to HAc, HPr, HBu, HVa, and EtOH. Organic acids are then consumed in the formation of smaller chain acids and hydrogen. According to the analysis of the process, the authors affirm that the co-digestion of vinasse and molasses proved to be viable for the generation of bioenergy in the form of hydrogen, in addition to the generation of value-added products. Equations (9.1), (9.2), (9.3), (9.4), and (9.5) show the breakdown of carbohydrates into fermentable sugars (hydrolysis) and the conversion of the substrate (molasses and vinasse) into value-added products such as HAc, HPr, HBu, and HVa (acidogenesis). In Eqs. (9.6), (9.7), and (9.8), the conversions of these organic acids into acetate (acetogenesis) followed by the generation of hydrogen and ethanol are shown. Lastly, after substrate fermentation, the conversion of hydrogen and acetate to methane can occur, if in the microbial consortium there are acetoclastic and hydrogenotrophic methanogenic archaea (Eqs. 9.9 and 9.10).

- Conversion of sucrose and water to HAc, CO_2, and hydrogen:

$$C_{12}H_{22}O_{11} + 5\ H_2O \rightarrow 4\ CH_3COOH + 8\ H_2 + 4\ CO_2 \tag{9.1}$$

Table 9.8 Hydrogen production from molasses and juice from different raw materials

Reactor	Substrate	Parameters	Productivity	References
HBR pilot	Beet molasses	Temperature—35 °C; HRT—10.57–3.9 h; OLR—3.11–85.6 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$	5.57 $L\ H_2{\cdot}day^{-1}{\cdot}L^{-1}$	Ren et al. (2006)
ABR	Beet molasses	Temperature—35 °C; HRT—13.5 h; OLR—8.89 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$; 5000 mg $COD{\cdot}L^{-1}$	4.33 $L\ H_2{\cdot}day^{-1}{\cdot}L^{-1}$	Li et al. (2007)
Batch	Beet molasses	Temperature—39 °C; pH 6.5; 100000 mg $COD{\cdot}L^{-1}$	10.11 $L\ H_2{\cdot}day^{-1}{\cdot}L^{-1}$	Wang and Jin (2009)
CSTR	Beet molasses	Temperature—35 °C; HRT—6 h; OLR—8–40 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$; 2.000–10000 mg $COD{\cdot}L^{-1}$	9.72 $L\ H_2{\cdot}day^{-1}{\cdot}L^{-1}$	Ren et al. (2010)
CSTR	Sugarcane juice	Temperature—37 °C; HRT—36–4 h; 25000 mg $COD{\cdot}L^{-1}$	2.029 $L\ H_2{\cdot}day^{-1}{\cdot}L^{-1}$	Pattra et al. (2011)
Batch	Sugarcane juice	Temperature—37 °C; pH—4.5–7 h; 25000 mg $COD{\cdot}L^{-1}$	3.11 $L\ H_2{\cdot}day^{-1}{\cdot}L^{-1}$	Plangklang et al. (2012)
CSTR	Beet molasses	Temperature—35 °C; HRT—6 h; OLR—8–32 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$; 2.000–8000 mg $COD{\cdot}L^{-1}$	7.21 $L\ H_2{\cdot}day^{-1}{\cdot}L^{-1}$	Han et al. (2012b)
CSTR with baffles	Beet molasses	Temperature—35 °C; HRT—6 h; OLR—20–44 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$; 5.000–11000 mg $COD{\cdot}L^{-1}$	3.51 $L\ H_2{\cdot}day^{-1}{\cdot}L^{-1}$	Chang et al. (2011)
CSTR	Beet molasses	Temperature—37 °C; HRT—96–8 h; OLR—11.6–69.6 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$; 63.000–101000 mg $COD{\cdot}L^{-1}$	2.42 $L\ H_2{\cdot}day^{-1}{\cdot}L^{-1}$	Mariakakis et al. (2012)
CSTR	Sugarcane molasses	Temperature—35 °C; HRT—5 h; 8000 mg $COD{\cdot}L^{-1}$	12.27 mmol $H_2{\cdot}L^{-1}{\cdot}h^{-1}$	Wang et al. (2013)
AnSBBR	Sugarcane molasses and vinasse	Temperature—30 °C; 200 rpm; HRT—3 h; 6000 mg $COD{\cdot}L^{-1}$; 67% vinasse and 33% molasses; inoculum pretreatment	13.5 mol $H_2{\cdot}m^{-3}{\cdot}day^{-1}$	Albanez et al. (2016b)
CSTR	Sugarcane juice	Temperature—37 °C; HRT—12–2 h; 25000 mg $COD{\cdot}L^{-1}$	17.50 $L\ H_2{\cdot}day^{-1}{\cdot}L^{-1}$	Nualsri et al. (2016b)
Batch	Beet molasses and sucrose	Temperature—35 °C; pH—7.0; 10000 mg $COD{\cdot}L^{-1}$	0.1982 $L\ H_2{\cdot}day^{-1}{\cdot}L^{-1}$	Tunçay et al. (2017)
AnSBBR	Sugarcane molasses and vinasse	Temperature—30 °C; 200 rpm; 3.000 mg $COD{\cdot}L^{-1}$. 33% vinasse e 67% molasses; HRT—3 h.	3.8 mol $H_2{\cdot}m^{-3}{\cdot}day^{-1}$	Albanez et al. (2018)
EGSB	Sugarcane juice	Temperature—30 °C; HRT 24–1 h; 5.000–15.000 g $COD{\cdot}L^{-1}$	2.40 $L\ H_2{\cdot}day^{-1}{\cdot}L^{-1}$	de Menezes and Silva (2019)
EGSB	Sugarcane molasses	Temperature—35 °C; HRT—24–1 h; 5.000–15.000 mg COD L^{-1}	13.92 $L\ H_2{\cdot}day^{-1}{\cdot}L^{-1}$	Freitas et al. (2020)

(continued)

Table 9.8 (continued)

Reactor	Substrate	Parameters	Productivity	References
AnSTBR	Sugarcane molasses	Temperature—55 °C; HRT—4 h; OLR—60 kg COD·m^{-3}·day^{-1}; 5.000–10.000 mg COD L^{-1}	88.00 ± 47.15 mL H_2·L^{-1}·h^{-1}	Oliveira et al. (2020)

ABR compartmented anaerobic reactor; *AnSBBR* anaerobic sequencing bath biofilm reactor; *AnSTBR* anaerobic structured-bed reactor; *CSTR* continuous stirred tank reactor; *CMISR* CSTR with immobilized bed; *EGSB* expanded granular sludger-bed reactor; *HBR* flocculated activated sludge

Table 9.9 Prices of the main value-added products generated in the fermentation of sugarcane juice, molasses, and vinasse (Freitas et al. 2020)

Value-added products	Formula	Production (t/t_{sugar})	Price (US$/$t_{sugar}$)
HAc	$C_2H_4O_2$	1.000	600
HBu	$C_2H_6O_3$	0.587	411
HPr	$C_3H_5O_2$	0.704	845
HLa	$C_3H_6O_3$	1.000	1900
HCa	$C_6H_{10}O_2$	0.483	966
EtOH	C_2H_5OH	0.511	357

- Conversion of sucrose and hydrogen to HPr and water:

$$C_{12}H_{22}O_{11} + 4\ H_2 \rightarrow 4\ CH_3CH_2COOH + 3\ H_2O \tag{9.2}$$

- Conversion of sucrose and water to HBu, CO_2, and hydrogen:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2\ CH_3CH_2CH_2COOH + 4\ H_2 + 4\ CO_2 \tag{9.3}$$

- Conversion of sucrose to HVa, CO_2, and hydrogen:

$$8\ C_{12}H_{22}O_{11} \rightarrow 13\ CH_3CH_2CH_2CH_2COOH + 31\ CO_2 + 23\ H_2 \tag{9.4}$$

- Conversion of sucrose and water to EtOH and CO_2:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 4\ CH_3CH_2OH + 4\ CO_2 \tag{9.5}$$

- Conversion of HPr and water to HAc, CO_2, and hydrogen:

$$CH_3CH_2COOH + 2\ H_2O \rightarrow CH_3COOH + 3\ H_2 + CO_2 \tag{9.6}$$

- Conversion of HBu and water to HAc, CO_2, and hydrogen:

$$CH_3CH_2CH_2COOH + 2\ H_2O \rightarrow 2\ CH_3COOH + 2\ H_2 \tag{9.7}$$

- Conversion of HVa and water to HBu, CO_2, and hydrogen:

$$CH_3CH_2CH_2CH_2COOH + 2\ H_2O \rightarrow CH_3CH_2CH_2COOH + CO_2 + \mathbf{3\ H_2} \tag{9.8}$$

- Conversion of HAc to CH_4 and CO_2:

$$CH_3COOH \rightarrow \mathbf{CH_4} + CO_2 \tag{9.9}$$

- Conversion of hydrogen and CO_2 to CH_4 and water

$$4\ H_2 + CO_2 \rightarrow \mathbf{CH_4} + 2H_2O \tag{9.10}$$

de Menezes and Silva (2019) report the production of HAc, HBu, HPr, HLa, and EtOH from the fermentation of sugarcane juice in an expanded granular sludge bed (EGSB) under mesophilic conditions (30 ± 1 °C). The authors observed that at concentrations of 5 and 10 g L^{-1} of sugarcane juice, the main metabolites were HAc (35.0–59.0%), HBu (10.0–44.0%), and HPr (8.0)–23.0%). At the concentration of 15 g·L^{-1} of sugarcane juice, HLa and EtOH together comprised more than 53.0% of all value-added products. The authors indicate that the high concentrations of HAc detected (59.0%, 50.0%, and 25.0% for concentrations of 5, 10, and 15 g·L^{-1}, respectively) can be attributed to the process called homoacetogenesis. In this process, homoacetogenic bacteria use hydrogen and carbon dioxide to produce HAc, as in Eq. (9.11). Homoacetogenic bacteria are tolerant to extreme environmental conditions, unlike methanogenic archaea. Furthermore, according to the authors, the syntrophic and competitive relationships between HLa-producing microorganisms, HPr and homoacetogenic HAc-producing bacteria reduced the hydrogen yield, producing antimicrobials.

- *Conversion of CO_2 and hydrogen to HAc and water:*

$$2CO_2 + 4H_2 \rightarrow C_2H_4O_2 + 2H_2O \tag{9.11}$$

Among the main metabolites observed in the work of de Menezes and Silva (2019) (HAc, HBu, HPr) the production of HAc allows the production of 8 mol H_2·mol^{-1} of sucrose (Eq. 9.1). The HBu pathway allows the production of 4 mol H_2·mol^{-1} sucrose (Eq. 9.3). On the other hand, the production of propionate is undesirable because its production as a final metabolite consumes 4 mol H_2·mol^{-1} of sucrose (Eq. 9.2).

In order to add value to the sugarcane chain, Freitas et al. (2020) evaluated the fermentation of sugarcane molasses for the production of hydrogen and value-added products, in EGSB at 30 ± 1 ° C. According to the authors, at the concentration of

5 g·L^{-1} of molasses, no hydrogen production was detected. However, the majority production of HAc (30.0–50.0%), HBu (13.0–30.0%), and HPr (13.0–45.0%) was observed. Similar to the work by de Menezes and Silva (2019), the absence of hydrogen in the fermentation of 5 g·L^{-1} of molasses can be explained by the formation of acetic acid by the homoacetogenesis process (23–51%). Freitas et al. (2020) reported that the maximum rates of hydrogen production occurred in 1 h HRT at concentrations of 10 (4.56 L·day^{-1}·L^{-1}) and 15 g L^{-1} of molasses (13, 92 L·day^{-1}·L^{-1}). The main value-added products in these fermentations were HBu (8.0–51.0%), HLa (6.0–50.0%), and HPr (4.0–57.0%).

The increased production of HLa, at the molasses concentrations of 10 and 15 g·L^{-1}, combined with the presence of HAc and HBu and low concentrations of HPr was associated with the production of hydrogen. However, the hydrogen yield via the lactic acid formation pathway is lower than the hydrogen production via the HAc and HBu pathways. Equation (9.12) shows the production of HBu and hydrogen by the conversion of lactic and acetic acid.

- *Conversion of HLa and HAc to Hbu, CO_2, water, and hydrogen*:

$$\begin{aligned}&CH_3CH(OH)COOH + 0.4CH_3COOH\\&\quad \rightarrow 0.7\ CH_3(CH_2)2COOH + CO_2 + 0.4\ H_2O + 0.6H_2\end{aligned} \tag{9.12}$$

Similarly, Fuess et al. (2020) observed the production of lactic acid in the fermentation of sugarcane juice and molasses at 55 °C, using two anaerobic structured-bed reactors (ASTBR) operated continuously in parallel. The authors reported that there was an increase in lactic acid production independent of the HRT considered (24–6 h) and medium pH (4.0–5.5). According to the authors, the conditions established for the medium were favorable for capnophilic lactic fermentation. In this case, the formation of hydrogen from the acetic type is diverted to a lactic fermentation pathway. Despite the increase in HLa production, there was no decrease in hydrogen production, suggesting the establishment of parallel sources of hydrogenogenic activity such as the co-production of hydrogen and HBu. The production of HPr was also identified in the fermentation of sugarcane juice and molasses, which can be attributed to the increase in OLR and, consequently, organic overload. The authors state that HPr production is used to control the partial pressure of hydrogen in the system. Hydrogen consumption for the formation of HPr from the glucose molecule is presented in Eq. (9.13). Hydrogen consumption from sucrose conversion can be seen in Eq. (9.2).

- *Conversion of glucose and hydrogen to HPr and water:*

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O \tag{9.13}$$

Table 9.10 shows the main value-added products generated from the fermentation of molasses and juice from sugarcane under different operating conditions, as well as

Table 9.10 Production of value-added products from the fermentation of molasses and juice from different raw materials

Reactor	Substrate	Parameters	Main value-added products	References
HBR pilot	Beet molasses	Temperature—35 °C; HRT—10.57–3.9 h; OLR—3.11–85.6 kg COD·m^{-3}·day^{-1}	EtOH, HAc, HBu	Ren et al. (2006)
ABR	Beet molasses	Temperature—35 °C; HRT—13.5 h; OLR—8.89 kg COD·m^{-3}·day^{-1}; 5000 mg COD·L^{-1}	EtOH, HAc, HPr	Li et al. (2007)
Batch	Beet molasses	Temperature—39 °C; pH 6.5; 100.000 mg COD·L^{-1}	HBu, HLa, HAc	Wang and Jin (2009)
CSTR	Beet molasses	Temperature—35 °C; HRT—6 h; OLR—8–40 kg COD·m^{-3}·day^{-1}; 2000–10000 mg COD·L^{-1}	EtOH, HAc	Ren et al. (2010)
CSTR	Sugarcane juice	Temperature—37 °C; HRT—36–4 h; 25000 mg COD·L^{-1}	HAc, HBu, HPr, HLa	Pattra et al. (2011)
Batch	Sugarcane juice	Temperature—37 °C; pH—4.5–7 h; 25000 mg COD·L^{-1}	HAc, HBu, HPr, HLa	Plangklang et al. (2012)
CSTR	Beet molasses	Temperature—35 °C; HRT—6 h; OLR—8–32 kg COD·m^{-3}·day^{-1}; 2000–8000 mg COD·L^{-1}	HAc, HBu, HPr, EtOH, BuOH	Han et al. (2012a)
CSTR with baffles	Beet molasses	Temperature—35 °C; HRT—6 h; OLR—20–44 kg COD·m^{-3}·day^{-1}; 5000–11000 mg COD·L^{-1}	EtOH, HAc	Chang et al. (2011)
CSTR	Beet molasses	Temperature—37 °C; HRT—96–8 h; OLR—11.6–69.6 kg COD·m^{-3}·day^{-1}; 63000–101000 mg COD·L^{-1}	HBu, HAc	Mariakakis et al. (2012)
CSTR	Sugarcane molasses	Temperature—35 °C; HRT—5 h; 8000 mg COD·L^{-1};	HAc, HBu, EtOH	Wang et al. (2013)
CSTR	Wastewater from beet molasses	Temperature—35 °C; HRT—8 h; OLR—12–18 kg COD·m^{-3}·day^{-1}; 4000 mg COD·L^{-1}	EtOH, HAc	Zhu et al. (2013)
CSTR	Beet molasses	Temperature—35 °C; HRT—10–4 h; OLR—30–48 kg COD·m^{-3}·day^{-1}; 8.000 mg COD·L^{-1}	EtOH, HAc	Wang et al. (2013)
AnSBBR	Sugarcane molasses and vinasse	Temperature—30 °C; 200 rpm; THR—3 h; 6000 mg COD·L^{-1}; 67% vinasse e 33% molasse; inoculum pretreatment	HAc, HBu, HVa	Albanez et al. (2016b)
CSTR	Sugarcane juice	Temperature—37 °C; HRT—12–2 h; 25000 mg COD·L^{-1}	HAc, HBu, HPr, HLa, HFo, HSuc, HCi	Nualsri et al. (2016a)

(continued)

Table 9.10 (continued)

Reactor	Substrate	Parameters	Main value-added products	References
Batch	Beet molasses and sucrose	Temperature—35 °C; pH—7.0; 10000 mg COD·L^{-1}	HAc, HBu, HLa	Tunçay et al. (2017)
AnSBBR	Sugarcane molasses and vinasse	Temperature—30 °C; 200 rpm; 3.000 mg COD·L^{-1}. 33% vinasse e 67% molasses; HRT—3 h	HAc, HPr, HBu, EtOH	Albanez et al. (2018)
EGSB	Sugarcane juice	Temperature—30 °C; HRT 24–1 h; 5000–15000 g COD·L^{-1}	HAc, HBu, HLa, EtOH	de Menezes and Silva (2019)
EGSB	Sugarcane molasses	Temperature—35 °C; HRT—24–1 h; 5000–15000 mg COD L^{-1}	HAc, HPr, HBu, HLa	Freitas et al. (2020)
ASTBR	Sugarcane molasses and juice	Temperature—55 °C; HRT—24–6 h; OLR—20–100 kg COD·m^{-3}·day^{-1}; 5000–25000 mg COD L^{-1}	HAc, HPr, HBu, HLa	Fuess et al. (2020)
AnSTBR	Sugarcane molasses	Temperature—55 °C; HRT—4 h; OLR—60 kg COD·m^{-3}·day^{-1}; 5000–10000 mg COD L^{-1}	HAc, HLa	Oliveira et al. (2020)

ABR compartmented anaerobic reactor; *AFBR* anaerobic fluidized bed reactor; *AnSBBR* anaerobic sequencing bath biofilm reactor; *ASTBR* anaerobic structured-bed reactor; *CSTR* continuous stirred tank reactor; *CMISR* CSTR with immobilized bed; *EGSB* expanded granular sludger-bed reactor; *HBR* flocculated activated sludge

the generation of these products from beet molasses, in order to compare the different productions of organic acids and alcohols.

9.2.3.2 Production of Value-Added Products from Vinasse

Vinasse, molasses and sugarcane juice can be used to produce value-added compounds. In this way, the use of this residue within the biorefinery concept to generate a greater range of bioproducts maximizes the use of sugarcane plots, offering more environmental and economic gains to the sugar production process and ethanol from sugarcane (Table 9.11).

Ferraz Júnior et al. (2015b) used an APBR (55 °C), with an HRT of 10.2 h (OLR of 84.2 kg COD·m^{-3}·day^{-1}), using raw vinasse (36.2 g COD·L^{-1}) for the production of hydrogen and value-added products. The authors report that the maximum values for the percentage of hydrogen and production were, respectively, 38.7% and 0.76 L day^{-1} L^{-1}. The main value-added products observed by the authors were HBu (2.3 g·L^{-1} = 36.7%) and HAc (2.8 g·L^{-1} = 44%), followed by HPr (0.7 g·L^{-1} = 11.18%), HVa (0.21 g·L^{-1} = 3.35%), and HCa (0.17 g·L^{-1} = 2.71%).

Table 9.11 Production of value-added products from the fermentation of sugarcane vinasse

Reactor	Parameters	Main value-added products	References
ASBR	Temperature—37 °C; HRT—32–13 h; 20–60 g COD·L^{-1}	HBu, HVa, HAc, HPr	Searmsirimongkol et al. (2011)
APBR	Temperature—55 °C; HRT—24–8 h; OLR—36.6–108.6 kg COD·m^{-3}·day^{-1}	HBu, HVa, HAc, HPr, Hca, EtOH	Ferraz Júnior et al. (2014)
Batch	Temperature—37–55 °C; 2 g CDO·L^{-1}	HAc, HBu, HPr, EtOH	Lazaro et al. (2014)
AFBR	Temperature: 55 °C; TDH—8–1 h; OLR—26.6–225.3 kg COD m^{-3}·day^{-1}; 5000 mg COD·L^{-1}	Hsuc, HLa, HBu, HISoBu, HAc	Santos et al. (2014a)
2 AFBR	Temperature: 55 °C; AFBR 1: TDH—6–1 h; OLR—60–360 kg COD m^{-3}·day^{-1}; 10000 mg COD·L^{-1}; AFBR 2: OLR—60–480 kg COD m^{-3}·day^{-1}; 30000 mg COD·L^{-1}	Hsuc, HAc HBu, HPr	Santos et al. (2014b)
2 AFBR	Temperature: 55 °C; HRT—6–1 h; AFBR 1: OLR—40–240 kg COD m^{-3} day^{-1}; 10000 mg COD·L^{-1}; AFBR 2: TDH—8–1 h; OLR—90–720 kg COD m^{-3} day^{-1}; 30000 mg COD·L^{-1}	HBu, HISoBu, HLa, HPr	Santos et al. (2014c)
APBR	Temperature—55 °C; HRT—10.12 h; OLR—84.2 kg COD m^{-3} day^{-1}. 36000 mg COD·L^{-1}	HAc, HBu, HPr, HVa, Hca	Ferraz Júnior et al. (2015b)
APBR	Temperature—55 °C; HRT—7.5 h; OLR—84.2 kg COD m^{-3} day^{-1}; 28300 mg COD·L^{-1}	HAc, HBu, HPr	Fuess et al. (2016)
AFBR	Temperature—30–55 °C; HRT—8–1 h; OLR—8–32 kg COD·m^{-3}·day^{-1}; 2000–8000 mg COD·L^{-1}	HAc, HPr e HBu, HLa, EtOH	Rego et al. (2020)
AFBR in two stages	Temperature—55 °C; HRT—5 h; 10.000–11000 mg COD·L^{-1}	HAc, HBu, HISoBu, HPr, Hla, Hca	Ramos and Silva (2020)

AFBR anaerobic fluidized bed reactor; *APBR* anaerobic packed-bed reactor; *ASBR* sequential batches

The production of various value-added products was also observed by Rego et al. (2020). The authors investigated the production of hydrogen and value-added products under mesophilic (30 °C) and thermophilic (55 °C) conditions using AFBR. The authors reported that at both temperatures, the formation of HAc, HPr, and HBu (at 30 °C) and HAc, HPr, HBu, and EtOH (at 55 °C) was observed in the 2 h HRT. According to Rego et al. (2020), although fresh vinasse has a high concentration of HLa, this acid was not detected in fermentation. The authors indicate that HLa can be metabolized into HPr, HAc, HBu, and hydrogen, under conditions of low carbohydrate availability. At mesophilic temperature, the authors reported that the majority of HAc production formed from the conversion of HLa.

Furthermore, other metabolites were identified in vinasse fermentations under mesophilic (HMa, HIsoBu, HCa, HVa, and HSu) and thermophilic (HMa, HBu, Hci, HVa, HCa) conditions in different fractions.

Ramos and Silva (2020) also observed from the fermentation of sugarcane vinasse the production of soluble metabolites, at a temperature of 55 °C, in anaerobic fluidized bed reactors in two stages. The authors reported in a first-stage reactor (fermentation stage) (4 h HRT and 10 g vinasse concentration of 10 g COD·L^{-1}) the majority of HAc generation (18.8 ± 1.6%), followed by HBu production (31.4 ± 3.5%), HPr (13.2 ± 2.0%), HLa (10.2 ± 0.4%) HCa (10.2 ± 1.1%), and HIsBu (16.2 ± 1.3%). In the second-stage reactor (methanogenic stage), the authors observed the formation mainly of HPr (27.7%–62.5%) and HAc (34.2%–72.7%). HVa acid (7.9%) was also identified in 18 h HRT. Reducing HRT from 18 h to 10 h reduced HPr concentrations and increased HAc concentrations. According to Ramos and Silva (2020), in a one-stage reactor the main metabolites identified were also HPr (39.0%–62.5%) and HAc (37.5%–61%) and that the increase in the concentration of organic matter from 5 to 10 g COD·L^{-1} decreased HPr concentrations, and HAc concentrations remained stable.

In this context, it is possible to observe the variety of value-added products that can be generated in the fermentation of residues (vinasse, juice, and molasses) from the processing of sugarcane for the production of sugar and ethanol. This range of products and the generation of bioenergy (hydrogen and methane) add value to the sugarcane chain and increase the energy efficiency of the plant's processing and energy generation. In addition, anaerobic digestion, as a pretreatment of these residues, minimizes the polluting potential, making the disposal of vinasse, juice, and molasses environmentally appropriate. In this way, the choice of environmental conditions and physicochemical parameters can maximize the production of bioenergy and value-added products and increase the removal of organic matter. Therefore, it is advisable to explore the influence of all factors that affect process efficiencies, aiming at its economic and environmental viability, and increasing the energy potential.

9.3 Dairy Production Process and Its Wastewaters

The global agricultural commodities market has undergone an intense evolution of volume and price, starting in the second half of the 1990s. During this period, there was volatility and an increase in dairy prices due to higher demand. In 2017, global dairy market reached the volume of 812 billion liters of milk, with Brazil being the fourth largest producer with about 34.3 billion liters (de Pithan-Silva et al. 2017).

In Brazil, the dairy activity can be considered one of the most important in agriculture, as it is present in about 1.3 million properties in the country and it is estimated that its contribution is approximately 10% of the total revenue of the food industry. According to sector projections, production is expected to grow over the next 10 years at an annual rate between 2.1 and 3.0%, reaching values between 43.0 and 48.0 billion liters in the period 2026 and 2027 (de Pithan-Silva et al. 2017).

The dairy industry is responsible for the processing of milk, and a diverse range of products ranging from pasteurized milk, butter, and cheese to a line of more elaborate products such as creams, various types of cheese, ricotta, cream cheese, ice cream, yogurts, powdered milk, condensed milk, among others (Kawano 2012).

For the transformation of raw milk into its derivatives, several manufacturing processes and steps are required. Initially, there is an inspection stage where laboratory analyses are performed to monitor and control the quality of the milk. Then, the milk is directed to the sectors where it will be processed, the main sectors are: yogurts, liquids, cheeses, and desserts. Depending on the destination sector, a series of unit operations are carried out, such as homogenization, concentration, sterilization/pasteurization, drying, and fermentation, with the entry of other raw materials such as sugar, natural and biological yeasts, fruit pulp, and aroma. Then, the products are taken to the filling and packaging steps, being stored and later shipped.

A state organ in Brazil called IPARDES (Federal Government of Brazil 2017) conducted a survey with 301 dairies in the state of Paraná in order to obtain some information about their production, types of products, and annual gross sales, classifying the sizes of industries, as observed in Table 9.12. In this context, there are a large number of small dairy products, whose processing capacity ranged from

Table 9.12 Number of dairies in 2009 by company size in the state of Paraná, Brazil (Federal Government of Brazil 2017)

Size	Employed technology	Annual gross revenue (BRL)	Average capacity (L milk·month^{-1})	Number of dairies
Micro	Does not pasteurize milk or perform slow pasteurization	Up to 1.2 million	Up to 55,000	80
Small	Slow or fast pasteurization. Production of pasteurized milk, cheeses, butter, yogurt, dairy drinks, cream, fresh cream, fat, dairy dessert, curds, curd, and dulce de leche	Up to 2.4 million	2500–900,000	159
Medium	Fast pasteurization. Production of the same products as small dairy products	Between 2.4 and 10.5 million	75,000–2,700,000	33
Medium-large	Fast pasteurization. In addition to the products mentioned in small and medium dairy products, it can produce industrial concentrated milk, industrial concentrated milk cream, and concentrated whey	Above 10.5 million	1,200,00–5,000,000	15
Large	Fast pasteurization. In addition to the products mentioned in the medium-large dairy products, it can produce UHT milk, powdered milk, and powdered whey	Above 60 million	Above 3,000,000	14

2,500 to 900,000 L per month. However, a more common classification criteria to define the size of this type of industry is the average volume of milk received by the dairy: small size is up to 10,000 L·day^{-1}, medium size is between 10,000 and 100,000 L·day^{-1}, and large size is over 100,000 L·day^{-1} (de Lima et al. 2018).

In Brazil, most small industries dispose of whey, generated mainly in the cheese preparation process (Fig. 9.2), for disposal, for swine nutrition, or even for effluent treatment systems with low efficiency or high cost. This effluent has a high

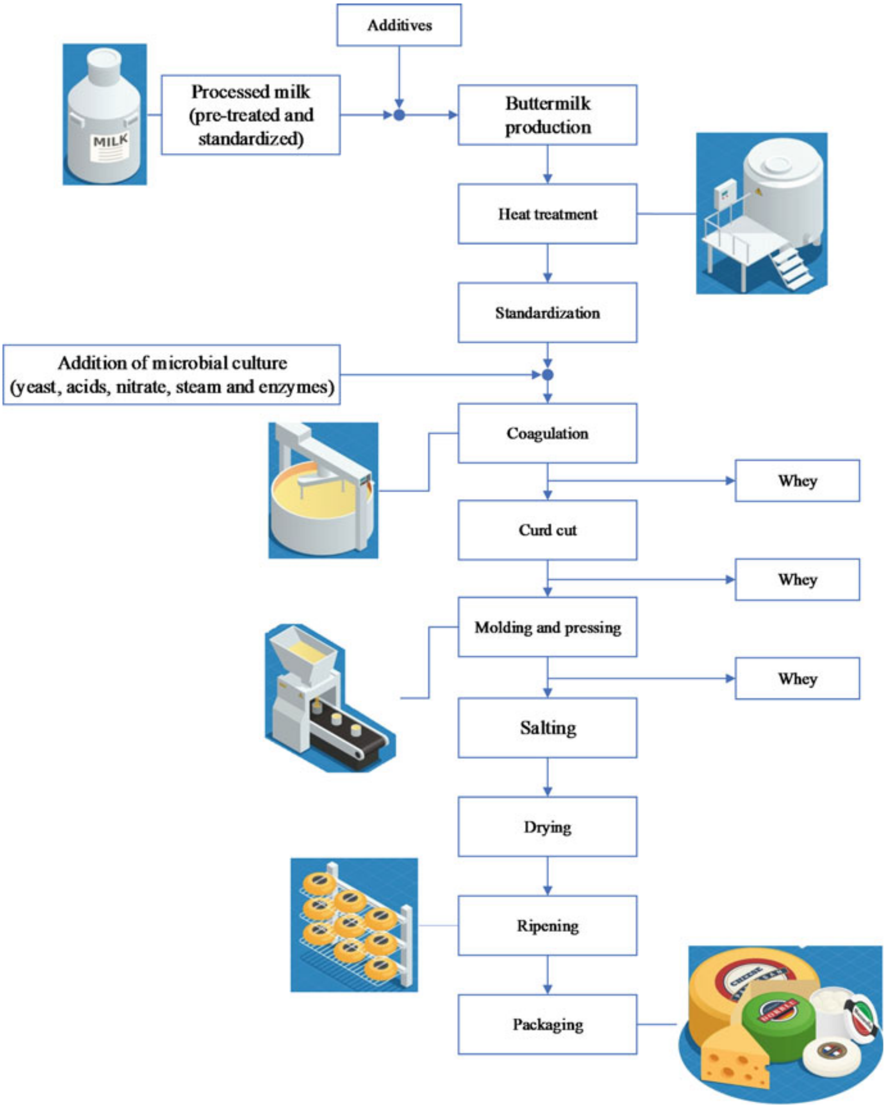


Fig. 9.2 Cheese production flowchart (Kawano 2012)

nutritional value, containing about 50% of the nutrients in milk (soluble proteins, lactose, vitamins, and minerals) and represents 80% to 90% of the total volume of milk entering the process. These characteristics allow to improve the sustainability of small industries in Brazil with the use of whey to obtain products with higher added value (Carvalho et al. 2013).

9.3.1 Cheese Whey

The cheese manufacturing industry is responsible for the three main types of effluents: cheese whey (CW—resulting from cheese production), second cheese whey (resulting from cottage cheese production), and the washing water of pipelines, storage, and tanks which generates a wastewater called cheese whey wastewater (Carvalho et al. 2013).

CW is a green-yellow liquid, with an estimated worldwide production of about 190 billion kg year^{-1}. On a global scale, only 50% of all of the cheese whey that is produced is used in industries. Due to its high organic and volumetric load, CW is considered the main polluting waste stream in dairy industries. The CW composition depends on the cheese production process, on the milk source (sheep, goat, cow, or buffalo), as well as on the quantity of water, detergents, and sanitizing agents used. In general, CW accounts for 85–95% of the milk volume, retains 55% of milk nutrients (vitamins and minerals) and 20% of milk proteins, and is characterized by COD and BOD concentrations of 50–102 and 27–60 g L^{-1}, respectively, more than 90% of which is made up of lactose. CW also contains sodium, potassium, and calcium salts (0.46–10%) and has a pH of 3.8–6.5 depending on the whey type (acidic or sweet), and a low alkalinity (Prazeres et al. 2012; Carvalho et al. 2013; Asunis et al. 2020).

Currently, a large share of dairy effluents, including about 50% of the CW produced worldwide, is discharged into the environment without any treatment. Among the available treatment options, the traditional activated sludge process is not economically sustainable due to the high organic load of dairy effluents, which would require large quantities of oxygen for process aeration. Furthermore, high quantities of sludge, which require further treatment, would be produced. Thermo-catalytic treatment has also been proposed for CW valorization, but the high temperature required (450–600 °C) and the production of solids make such a process expensive (Asunis et al. 2020).

Bioprocesses such as anaerobic digestion or fermentation have the advantage of coupling the treatment of dairy effluents with the production of bioenergy and/or biochemical commodities at mild temperature conditions. Though promising, none of the mentioned options alone represents the ultimate solution for CW treatment, since the energy/chemicals production rates are too small for an economically sustainable scale-up. The implementation of an integrated process, including a combination of physical, chemical, and biological processes, is therefore the key for a cost-effective and efficient valorization of dairy effluents (Asunis et al. 2020).

9.3.2 Environmental Compliance and Energy Production

The research on the biological digestion of cheese whey started in the 1970s, with the application of aerobic processes such as activated sludge, trickling filters, lagoon storage, etc. However, these old processes were usually limited by the variability in the inlet properties of effluents and the extremely high pollution load of CW, energy requirements for oxygen supplying, excessive sludge production, difficulties in solids settling and thickening, etc. In the mid-1980s, anaerobic digestion achieved a great development despite facing difficulties in small and medium factories when installing anaerobic digesters. Thus, in the aerobic process, each kg of degraded COD forms 0.6 kg of sludge while 0.1 kg remains in the final effluent. In contrast, the anaerobic process only generates 0.1 kg of sludge per kg of COD transformed. Additionally, the anaerobic process converts the pollutants into gaseous final products, mainly carbon dioxide and methane that can be used as an alternative energy source (Prazeres et al. 2012).

Within this framework, after several researchers have successfully produced methane while treating CW appropriately, the twenty-first century began with research on the co-processing of CW and other waste/wastewater as shown in Table 9.13.

Dereli et al. (2019) and Yan et al. (1988) carried out whey mono-digestion in an AnMBR and a UASB, respectively, both with low organic loading rate, achieving significant yield, productivity, and organic matter removal. Fernández et al. (2015) used a thermophilic sequencing batch reactor (SBR) for CW treatment, and the organic matter removal efficiency achieved in their work was between 3 and 12% lower than the obtained by Dereli et al. (2019) and Yan et al. (1988), respectively. Nevertheless, the SBR achieved a methane yield 5–30% higher than Dereli et al. (2019). Lovato et al. (2016) obtained a biogas with 73.0% of methane, the richest compared to the 58.2% and 46.1% from Fernández et al. (2015) and Yan et al. (1988), respectively.

Charalambous et al. (2020) analyzed a full-scale internal circulation bioreactor with 140 m^3 operating under mesophilic temperature (35 °C) which treated 550–650 m^3 cheese whey per day and could generate 275.7 kWh of electricity from biogas per day. The operation was carried out with a neutral pH and achieved a potential electricity generation 53% higher than the one carried out with acid pH (5–6). Increasing the pH to 7.0 required an amount of 0.32 kg NaOH per CW m^3.

Kavacik and Topaloglu (2010) investigated the co-digestion of whey with dairy manure, which would allow treating whey in existing facilities. The results showed more benefits in treating the two wastes together than individually. The authors recommended as a start-up strategy mixing both substrates right from the beginning of the operation in order to avoid acidification of the reaction medium.

Considering that CW has high carbohydrates contents, this effluent frequently is chosen to be the co-substrate in anaerobic digestion of wastes/wastewaters with low C: N ratio. Jung et al. (2016) treated *Ulva* biomass, a macroalga with high nitrogen and sulfur content, considered as a sea waste. Indeed, the co-digestion,

Table 9.13 Production of methane and organic matter removal by the anaerobic digestion of cheese whey and other agroindustry waste/wastewater

Reactor	Substrate	HRT (d)	OLR ($kg\cdot m^{-3}\cdot day^{-1}$)	Performance	COD removal efficiency	References
UASB	CW	5	5.96	9.6 $LCH_4\cdot L^{-1}$ day^{-1}	99%	Yan et al. (1988)
CSTR	CW + DM	5	5.8	0.9 $LCH_4\cdot L^{-1}$ day^{-1}	23% COD 20% VS	Kavacik and Topaloglu (2010)
SBR	CW	8.3	4.6	14.0 mol $CH_4\cdot kg$ COD 1.4 $LCH_4\cdot L^{-1}$ day^{-1}	87.4%	Fernández et al. (2015)
AnSBBR	CW	0.33	7.5	12.6 mol $CH_4\cdot kg$ COD 2.1 $LCH_4\cdot L^{-1}$ day^{-1}	90%	Lovato et al. (2016)
CSTR	CW + UB	20	0.25	0.08 $LCH_4\cdot L^{-1}$ day^{-1} 13.4 mol $CH_4\cdot kg$ COD^{-1}	68.5% COD 62.1% VS	Jung et al. (2016)
AnMBR	CW	5–13	5	9.6–13.3 mol $CH_4\cdot kg$ COD^{-1}	90–99%	Dereli et al. (2019)
AnSBBR	CW + G	0.2	11.8	4.2 $LCH_4\cdot L^{-1}$ day^{-1} 15.8 mol $CH_4\cdot kg$ COD^{-1}	96%	Lovato et al. (2020)
AnSBBR	CW + G	0.33	19.0	4.6 $LCH_4\cdot L^{-1}$ day^{-1} 15.7 mol $CH_4\cdot kg$ COD^{-1}	68%	de Albuquerque et al. (2020)
IC	CW	0.2	20	3 mol $CH_4\cdot kg$ COD^{-1}	80%	Charalambous et al. (2020)

AnMBR anaerobic dynamic membrane bioreactor; *AnSBBR* anaerobic sequencing batch biofilm reactor; *CSTR* continuous stirred tank reactor; *DM* dairy manure; *DW* dairy wastewater; *G* glycerin; *IC* internal recirculation bioreactor; *UB Ulva* biomass; *SBR* sequencing batch reactor; *UASB* upflow anaerobic sludge-bed reactor carried out with low OLR, achieved a methane production rate up to 36% and 20% higher than the mono-digestion of *Ulva* biomass and whey, respectively.

Lovato et al. (2020) proposed as co-substrate the major by-product of the biodiesel industry: glycerin. Readily biodegradable and with a suitable pH, anaerobic digestion is a promising treatment for glycerin. The co-digestion with 75% whey and 25% glycerin on COD basis would be able to generate 12.0 $MJ \cdot kg\ COD^{-1}$ considering a small dairy with capacity to process 687 m^3 of milk per month. If the fossil fuels used in boilers would be replace by the energy from AD, the monthly savings could reach up to US$ 13,920.

9.3.3 Value-Added Products

Dark fermentation is a promising option for CW valorization due to its high carbohydrate content, which can be converted to biohydrogen and VFAs. In the absence of CW pretreatments and external inoculum, dark fermentation of CW mainly involves three steps, including (i) lactose hydrolysis into glucose and galactose, (ii) conversion of monomeric sugars into lactate by homolactic microorganisms, and (iii) conversion of lactate into H_2 and VFAs by fermentative microorganisms (Asunis et al. 2020).

The molar production of hydrogen can reach a maximum yield of 8.0 mol $H_2 \cdot mol\ lactose^{-1}$ by the acetic route and 4.0 mol $H_2 \cdot mol\ lactose^{-1}$ by the butyric route, as shown in Eqs. (9.1) and (9.3). Table 9.14 presents the main comparative studies of hydrogen production using cheese whey as a substrate in different reactor configurations.

Collet et al. (2004) carried out the continuous cultivation of *C. thermolacticum* in an anaerobic thermophilic bioreactor (58 °C) with a concentration of 10 $g \cdot L^{-1}$ of lactose, testing different conditions of dilution rates (0.012 to 0.19 h^{-1}) and pH. The maximum value of volumetric hydrogen productivity was 2.58 $mmol \cdot L^{-1} \cdot h^{-1}$ at the dilution rate of 0.058 h^{-1}. On the other hand, the hydrogen yield was approximately constant in all experiments, with a maximum value of 3 mol $H_2 \cdot mol\ lactose^{-1}$. The main metabolites produced were acetate, ethanol, and lactate. The yield lower than the theoretical value was justified by the presence of large amounts of hydrogen in the gaseous phase, changing the metabolic route to ethanol production.

Ottaviano et al. (2017) obtained a hydrogen yield close to the theoretical value for the butyric route operating two thermophilic AFBR. For the first one, the influent concentration of 4.9 mg $lactose \cdot L^{-1}$ was fixed, and the HRT ranged between 0.5–8 h. In the second reactor the HRT was set to 6 h with a concentration ranging from 2.8 to 14.6 g $lactose \cdot L^{-1}$. The highest H_2 yield was observed in the first reactor operated at 30 $kg \cdot m^{-3} \cdot day^{-1}$. However, in this condition, H_2 productivity was only 0.4 $LH_2 \cdot L^{-1} \cdot h^{-1}$. The best productivity of 4.1 $LH_2 \cdot L^{-1}\ h^{-1}$ was achieved at OLR of 240 $kg \cdot m^{-3} \cdot day^{-1}$, but with a poor yield of 0.6 mol $H_2 \cdot mol\ lac^{-1}$. The bacterial community of the first reactor, analyzed by a 16SrRNA gene sequence analysis, was

Table 9.14 Production of hydrogen and value-added products from the fermentation of CW

Reactor	HRT (h)	OLR ($kg{\cdot}m^{-3}{\cdot}day^{-1}$)	Productivity	Yield	Metabolites	References
CSTR	35.7	6.7	1.4 $LH_2{\cdot}L^{-1}{\cdot}day^{-1}$	3 mol $H_2{\cdot}mol\ lac^{-1}$	HAc; EtOH; HLa	Collet et al. (2004)
CSTR	24	14	–	2.3 mol $H_2{\cdot}kg\ COD^{-1}$	HAc; HBu EtOH	Yang et al. (2007)
CSTR	6	184.4	1.14 $LH_2{\cdot}L^{-1}\ h^{-1}$	2.8 mol $H_2{\cdot}mol\ lac^{-1}$	HBu; HPr HAc	Davila-Vazquez et al. (2008)
CSTR	24	47.4	0.1 $LH_2{\cdot}L^{-1}\ h^{-1}$	1.8 mol $H_2{\cdot}kg$ COD	HAc; HLa; HBu	Antonopoulou et al. (2008)
UASB	12	20	122 mL $H_2{\cdot}L^{-1}{\cdot}day^{-1}$	–	HAc; HBu HPr	Castelló et al. (2009)
CSTR	24	30	2.9 $LH_2{\cdot}L^{-1}\ h^{-1}$	0.78 mol $H_2{\cdot}mol\ gli^{-1}$	HBu; HAc EtOH; HLa	Venetsaneas et al. (2009)
CSTR	6	182	1.0 $LH_2{\cdot}L^{-1}\ h^{-1}$	2.5 mol $H_2{\cdot}mol\ lac^{-1}$	HAc; HPr; HBu; EtOH	Cota-Navarro et al. (2011)
UASB	6	20	0.38 $LH_2{\cdot}L^{-1}{\cdot}day^{-1}$	–	HPr; HAc HBu	Carrillo-Reyes et al. (2012)
Fixed bed	24	37	1.0 $LH_2{\cdot}L^{-1}\ h^{-1}$	1.1 mol $H_2{\cdot}mol\ lac^{-1}$	HAc; HBu HPr; HLa	Perna et al. (2013)
AFBR	4	30	0.23 $LH_2{\cdot}L^{-1}\ h^{-1}$	1.3 mol $H_2{\cdot}mol\ lac^{-1}$	EtOH; MetOH HAc; HBu	Rosa et al. (2014)
SBR	3	12.7	0.15 $LH_2{\cdot}L^{-1}\ day^{-1}$	0.54 mol $H_2{\cdot}kg\ COD^{-1}$	HAc; HPr	Fernández et al. (2015)
AFBR	4	30	0.4 $LH_2{\cdot}L^{-1}\ h^{-1}$	3.7 mol $H_2{\cdot}mol\ lac^{-1}$	HAc; HBu HPr; HLa; EtOH	Ottaviano et al. (2017)

(continued)

Table 9.14 (continued)

Reactor	HRT (h)	OLR ($kg{\cdot}m^{-3}{\cdot}day^{-1}$)	Productivity	Yield	Metabolites	References
UASB	24	60	1.2 $LH_2{\cdot}L^{-1}\ h^{-1}$	0.8 mol $H_2{\cdot}$mol $gli_{eq}{}^{-1}$	HAc; HBu HPr; HLa; EtOH	Dessì et al. (2020)
AFBR	108	6.6	0.03 $LH_2{\cdot}L^{-1}\ h^{-1}$	8.0 mol $H_2{\cdot}$kg COD^{-1}	HAc; HBu HPr	Mikheeva et al. (2021)
AnSBBR	3	33	3.4 $LH_2{\cdot}L^{-1}{\cdot}day^{-1}$	3 mol $H_2{\cdot}$mol lac^{-1}	HAc; HBu HPr; HLa; EtOH	Lovato et al. 2021)

AFBR anaerobic fluidized bed reactor; *AnSBBR* anaerobic sequencing batch biofilm reactor; *UASB* upflow anaerobic sludge blanket; *SBR* sequencing batch reactor; *UASB* upflow anaerobic sludge-bed reactor constituted with 48.42% abundance by *Thermoanaerobacterium* and *Thermohydrogenium kirishiense*.

Lovato et al. (2021) also appointed *Thermoanaerobacterium* as the selected bacteria genus from the reactor start-up strategy realized in a thermophilic AnSBBR that consisted of increasing, gradually, reactor temperature (30–55 °C) and influent concentration (1 g $COD{\cdot}L^{-1}$) in the start-up period and in all transition between conditions (15, 24, and 33 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$). This strategy did not incur in additional costs for the process and was capable to suppress methanogenesis successfully. The selected *Thermoanaerobacterium* and *Clostridium* microorganisms which coexisted in synergy in the AnSBBR might have boosted hydrogen production.

Indeed, *Thermoanaerobacterium* is a bacteria genus capable of converting different substrates (including lactose, which is the main CW compound) into hydrogen with an optimal grown temperature around 55 °C—same temperature utilized by Lovato et al. (2021) and Ottaviano et al. (2017). This genus belongs to the family *Thermoanaerobacterales* (III) recognized for achieving high substrate conversion efficiency in comparison to the families *Clostridiaceae* and *Enterobacteriaceae*. (McClure 2006; Rittmann and Herwig 2012; Chou et al. 2020).

Mikheeva et al. (2021) also proposed a reactor start-up strategy for a mesophilic anaerobic filter (AF) and an anaerobic fluidized bed reactor (AFBR). Primally, two inoculums have been chosen: (i) a thermophilic anaerobic sludge from a CSTR treating food waste and sewage sludge and (ii) a mesophilic anaerobic sludge from an UASB treating brewery wastewater. Both inoculums were pre-treated, with acid or heat, to suppress the methanogenic activity. The start-up strategy consisted in increasing the OLR from 2 to 15 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$. Regarding inoculum pretreatment, the results show an improvement in hydrogen production when acid treatment was used for thermophilic inoculum and the heat treatment for mesophilic inoculum. Both AF and AFBR were inoculated with heat-treated mesophilic sludge, and the AFBR had the best performance at 6.6 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$. The genus *Lactobacillus* (40%) and *Bifidobacterium* (30%) were predominant, and a relatively low (0.1%) presence of methanogenic archaea, in the microbial community, was observed.

Rosa et al. (2014) operated two AFBR to produce hydrogen in mesophilic temperature from CW. One reactor was inoculated with sludge from a UASB reactor treating swine wastewater and the other with sludge from a UASB reactor treating poultry slaughterhouse wastewater. Both inoculums were pre-treated with heat. Nevertheless, when Rosa et al. (2014) operated the reactors with an HRT of 1 h, methane was produced concurrently with hydrogen (0.68 $LCH_4{\cdot}L^{-1}$ h^{-1} and 0.51 $LH_2{\cdot}L^{-1}$ h^{-1}). Cloning of the 16S rRNA gene sequences indicated *Methanobacterium sp*, a hydrogenotrophic methanogenic archaea, as affiliated genera by the microbial community. Bundhoo and Mohee (2016) mentioned in their review several inoculum pretreatments as a strategy to suppress hydrogen consumers, but they alerted that some studies reported that this suppression did not work out and put in doubt the effectiveness of pretreatments.

Considering that acetic and butyric acids production routes are the pathways for higher hydrogen yields in dark fermentation, Dessì et al. (2020) proposed a promising technology capable of facilitating downstream processing for the recovery of volatile fatty acids. The system has been composed by a UASB reactor and an *in-line* silicone membrane extraction module to separate butyric acid from another metabolites (acetic acid, propionic acid, lactic acid, and ethanol). The extraction module did not compromise hydrogen production and the system obtained a butyric acid outflow with 2.5 g L^{-1} and a purity higher than 90%.

Thermophilic reactors with immobilized biomass seem to be a promising technology to produce hydrogen and volatile fatty acids, contributing to treat and add value to CW. Within this framework, Girotto et al. (2017) cited volatile fatty acids as precursors for biopolymers and medium chain length fatty acids production. Among the possible biopolymers there are poly-lactic acid (PLA), polyvinyl acetate (PVA), and polyhydroxyalkanoates (PHA). The fatty acids could be used as antimicrobials, corrosion inhibitors, and other bio-based chemical production processes.

Many researchers are studying the use of volatile fatty acids, produced in dark fermentation, to produce methane. The main advantages of splitting the AD process into two stages are (acidogenesis and methanogenesis) are (i) increase the energetic production by generating H_2 and (ii) designing and operating each reactor in optimal conditions. Table 9.15 shows some studies about this technology, which is capable

Table 9.15 Production of hydrogen and methane from the anaerobic digestion of cheese whey in two stages

Reactor	HRT (d)	OLR ($kg \cdot m^{-3} \cdot day^{-1}$)	Productivity	Yield	References
(I) CSTR	1	47.4	2.5 $LH_2 \cdot L^{-1}$ day^{-1}	1.8 mol $H_2 \cdot kg$ COD	Antonopoulou et al. (2008)
(II) PABR	4.4	46.2	5.0 $LCH_4 \cdot L^{-1}$ day^{-1}	13.8 mol $CH_4 \cdot kg$ $COD^{-1,}$	
(I) CSTR	1	60.0	2.9 $LH_2 \cdot L^{-1}$ day^{-1}	2.5 mol $H_2 \cdot kg$ COD^{-1}	Venetsaneas et al. (2009)
(II) CSTR	20	49.1	0.33 $LCH_4 \cdot L^{-1}$ day^{-1}	6.0 mol $CH_4 \cdot kg$ COD^{-1}	
(I) CSTR	0.25	182	25 $LH_2 \cdot L^{-1}$ day^{-1}	2.5 mol $H_2 \cdot mol$ lac^{-1}	Cota-Navarro et al. (2011)
(II) UASB	0.25	20.0	5.0 $LCH_4 \cdot L^{-1}$ day^{-1}	8.6 mol $CH_4 \cdot kg$ COD^{-1}	
(I) SBR	3	12.7	0.15 $LH_2 \cdot L^{-1}$ day^{-1}	0.54 mol $H_2 \cdot kg$ COD^{-1}	Fernández et al. (2015)
(II) SBR	12.5	2.4	0.81 $LCH_4 \cdot L^{-1}$ day^{-1}	15 mol $CH_4 \cdot kg$ COD^{-1}	

(I): first stage—acidogenic reactor; (II): second stage—methanogenic reactor; *CSTR* continuous stirred tank reactor; *UASB* upflow anaerobic sludge blanket reactor; *PABR* periodic Anaerobic Baffled Reactor; *SBR* sequencing batch reactor to operate at high OLRs and achieve meaningful productivities and yields (Lovato et al. 2020).

9.4 Biodiesel Production Process and Its Wastewaters

The interest in biodiesel production has grown in the last decade as shown in Fig. 9.3. The production expectation for 2021 is around 43 million m^3 of biodiesel and the forecast to 2023 is an average of 46 million m^3 (increase of 6.98%) (IEA 2020a).

Biodiesel is the second most produced biofuel in Brazil, reaching a record production in 2019 of 5.9 million m^3 (Federal Government of Brazil 2021). In the European Union, it has been produced on a large scale since 1992, maintaining an exponential growth and achieving a record of 15.7 million m^3 in 2019, which corresponds to 32.7% of all biodiesel and HVO (Hydrotreated Vegetable Oil) production in the world. The Asia-Pacific region is a large producer of this biofuel, just Indonesia produced 7.2 million m^3 of biodiesel in 2019. The USA produced 8.4 million m^3 of biodiesel and HVO, a record production as well (Quispe et al. 2013; IEA 2020a).

Efforts to replace fossil diesel for biodiesel are aligned with the 17 Sustainable Development Goals of the United Nations. Furthermore, biodiesel is derived from renewable sources, it is biodegradable, it has a higher combustion efficiency, it is non-toxic, and it has a low emissions of pollutants, such as sulfates (Tabatabaei et al. 2019; Ramos et al. 2019).

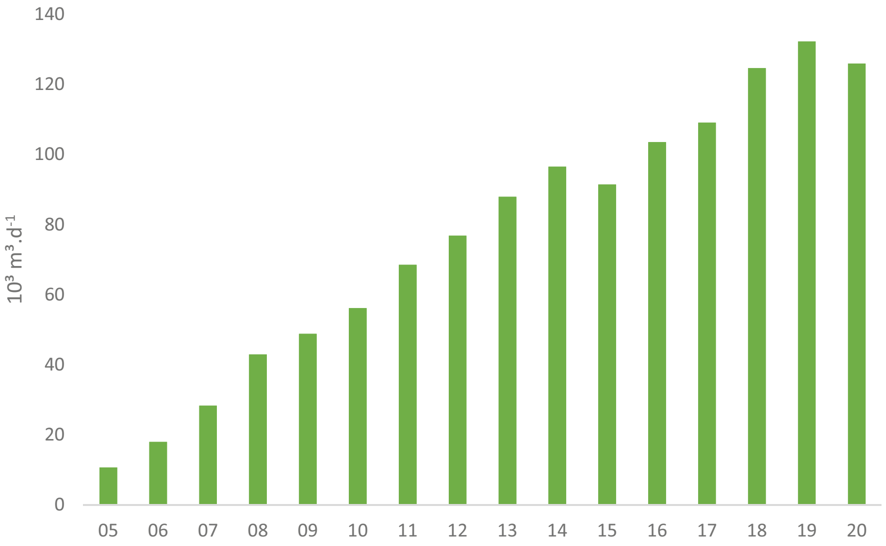


Fig. 9.3 Biodiesel and HVO production world in thousand m^3 per day (IEA 2020a)

Biodiesel is mostly produced from a transesterification reaction between a triglyceride (oils and fats) and short-chain alcohol, usually, methanol or ethanol, catalyzed by an acid or base. The most efficient catalysts are sodium hydroxide (NaOH) and potassium hydroxide (KOH). The transesterification reaction happens in three steps, as described in Eqs. (9.14)–(9.16). At the end of the reaction three biodiesel molecules are formed and one of glycerol. Glycerol and biodiesel are immiscible substances and compound a heterogeneous solution—the upper phase is biodiesel and crude glycerol is the lower phase (Leung et al. 2010).

$$\text{Triglyceride} + \text{Methanol} \leftrightarrow \text{Diglyceride} + \text{Biodiesel}) \tag{9.14}$$

$$\text{Diglyceride} + \text{Methanol} \leftrightarrow \text{Monoglyceride} + \text{Biodiesel} \tag{9.15}$$

$$\text{Monoglyceride} + \text{Methanol} \leftrightarrow \text{Glycerol} + \text{Biodiesel} \tag{9.16}$$

Biodiesel production involves raw material preparation, transesterification reaction, phases separation, alcohol recuperation and dehydration, biodiesel and glycerol purification as shown in Fig. 9.4. Raw material is submitted to previous treatment (filtration, neutralization, drying). Then, it is sent to a tank reactor with excess alcohol and catalyst for the reaction. Phase separation takes place by decantation or centrifugation. The separation effectiveness of biodiesel and crude glycerol may determine the quality of the biofuel. Each phase has unreacted alcohol which is recovered, usually by evaporation. The methyl or ethyl ester passes through purification steps of washing and drying until it becomes commercial biodiesel. In the

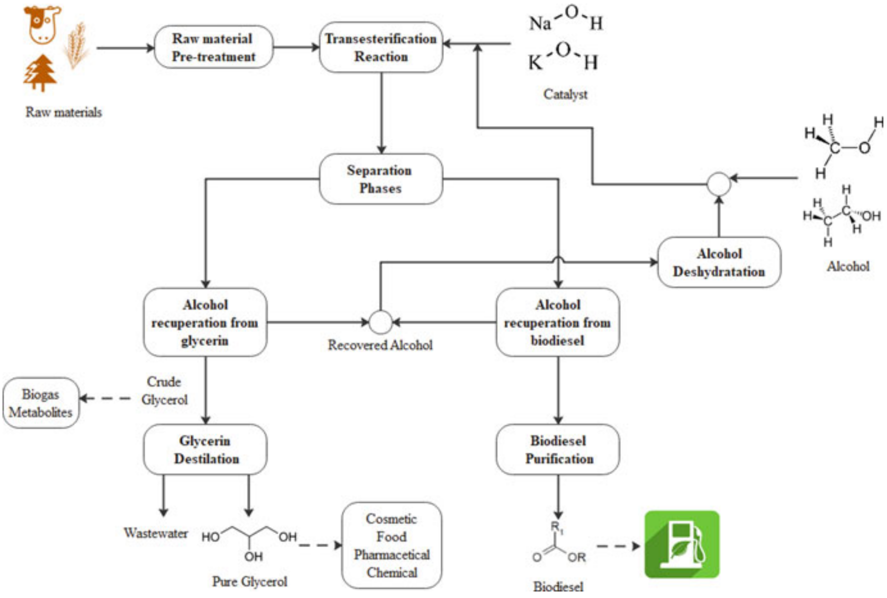


Fig. 9.4 Flow diagram of biodiesel production

same way, crude glycerol is distilled successively until it reaches high purity (>95%) to be commercialized (Tabatabaei et al. 2019; Rezania et al. 2019).

The source of oils and fats could be animal or vegetal. Palm oil in Indonesia, soybean oil in Brazil and USA, rapeseed oil in Europe are the main potential sources due to their availability. Beyond that, it is also possible to use waste cooking oils (Souza et al. 2018; Kaur et al. 2020).

9.4.1 Glycerin

Glycerin is the commercial term of glycerol or propane-1,2,3-triol (IUPAC name). This compound is from the alcohol family and its chemical formula is $C_3H_5(OH)_3$. Under normal conditions, glycerin is a viscous, colorless, odorless, and sweet-tasting liquid. The three hydroxyl radicals (–OH) give it hygroscopic properties, great water solubility, and molecular stability. However, its molecular stability impairs its oxidation easily and it demands a high oxygen concentration for biodegradation (Ayoub and Abdullah 2012; Quispe et al. 2013).

The worldwide production of glycerol will be around 41.9 million m^3 and 66% will come from the biodiesel output (Kaur et al. 2020). The others manufacturing processes that can originate this molecular compound are: soap production, ethanol production, biological fermentation, and chemical synthesis. Almost 10 wt.% of crude glycerol can be obtained as the main by-product of biodiesel production, which means 1 kg of crude glycerol for each 10 kg of biodiesel (Viana et al. 2012).

It is not possible to quantify some crude glycerol properties such as melting point, boiling point, flash point due to its impurities. A comparison of pure and crude glycerol properties is presented in Table 9.16.

Crude glycerol from biodiesel production is considered a wastewater because it has 50–20% of impurities which give it a dark brown color. Its main impurities are methanol, water, fatty free acids, salts, soap, metals—Table 9.17 shows the content impurities of crude glycerol. Thus, it needs a purification process to be

Table 9.16 Pure and crude glycerol properties (Kaur et al. 2020)

Property	Pure glycerol	Crude glycerol
Color	Colorless	Dark brown
Odor	Odorless	–
Solubility	Miscible in water	–
Viscosity (Pa·s)	0.93	1.21
Density ($g \cdot cm^{-3}$)	1.31	1.01 to 1.20
pH	6.4	2.0 to 10.8
Vapor pressure (mmHg)	0.13	–
Melting point (°C)	17.8	–
Boiling point (°C)	290	–
Flash point (°C)	>400	–

Table 9.17 Crude glycerol composition (Gupta and Kumar 2012; Quispe et al. 2013; Kaur et al. 2020)

Compound	Content (%)
Alcohol (methanol)	6.0–20.0
Ash	1.0–9.0
Free fatty acids	5.0–18.0
Glycerol	50.0–80.0
Salts and soup	0–16.0
Water	2.0–10.0

commercialized and used in pharmaceuticals, chemicals, cosmetics, textiles, food industries, and many more. Even though pure glycerol has a high market value, the interest in studies for an alternative application and valorization of crude glycerol is getting more relevant because of the exorbitant costs to purify the glycerol (Viana et al. 2012; Quispe et al. 2013; Kaur et al. 2020).

9.4.2 Environmental Compliance and Energy Production

The main concern about crude glycerol is its high polluting potential if disposed in the environment, considering a scenario of large generation (caused by the increased biodiesel production) and low market demand. Crude glycerol has around 925–1600 g $COD{\cdot}L^{-1}$ which requires a large amount of oxygen to be degraded. Additionally, the great supply of glycerol in the market has dropped its price. As an alternative for the environmental and economic issue, biological fermentation of crude glycerol has shown promising application with biogas and biohydrogen production, and other value-added compounds (1,3-propanediol, ethanol, propionic acid, butyric acid, acetic acid, succinic acid, among others). Biogas and biohydrogen could be converted into thermic or electric energy and biomethane and biohydrogen could be fuels for vehicles (Ayoub and Abdullah 2012; Kaur et al. 2020). 2.5 million hydrogen-powered cars are expected to circulate around the world up to 2030 (IEA 2020a).

The metabolic pathways of anaerobic digestion of glycerol are well-known and a considerable number of microorganisms can degrade it (Viana et al. 2012; Kaur et al. 2020). Glycerol anaerobic degradation may occur by reductive or oxidative pathway depending on environmental condition and enzymes present on each microorganism (Biebl et al. 1999). Figure 9.5 shows the compounds formed in each pathway.

9.4.2.1 Hydrogen Production

Hydrogen gas is an interesting biofuel for the production of clean energy. It has high calorific power (around 130.9 $MJ{\cdot}kg^{-1}$ at 25 °C) and a low environmental impact because its combustion produces just steam (Dawood et al. 2020). Considering this,

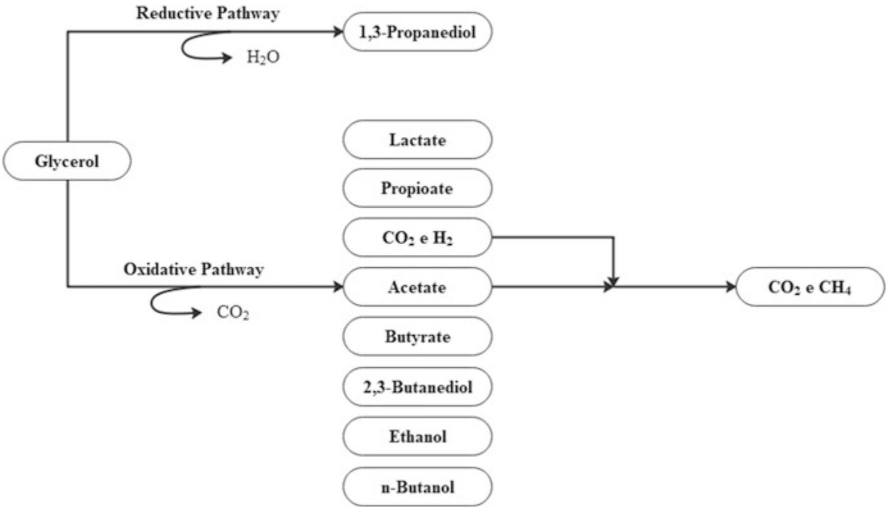


Fig. 9.5 Metabolic pathways of anaerobic digestion of glycerol and compounds formed

many studies have been publishing about biohydrogen production from glycerol (Table 9.18).

Ito et al. (2005) evaluated the crude and pure glycerol fermentation using *Enterobacter aerogenes* HU-101 to H_2 production. Initially, the biological process was carried out in batch in pH of 6.8 and temperature at 37 °C. When crude glycerol concentration was increased from 1.7 to 25.0 $g{\cdot}L^{-1}$ the H_2 yield decreased from 1.12 to 0.71 mol $H_2{\cdot}mol^{-1}$ glycerol. The same behavior happened with trials of pure glycerol. The H_2 yield decreased from 1.05 to 0.82 mol $H_2{\cdot}mol^{-1}$ glycerol, when increasing substrate concentration from 5.0 to 25.0 $g{\cdot}L^{-1}$. In experiments with continuous fixed-bed reactor, self-immobilized cells, fixed temperature at 37 °C, and glycerol concentration of 10.13 $g{\cdot}L^{-1}$, H_2 volumetric productivity for crude and pure glycerol was 30 $mmol{\cdot}L^{-1}{\cdot}h^{-1}$ and 80 $mmol{\cdot}L^{-1}{\cdot}h^{-1}$, respectively. Conversely, in continuous fixed-bed reactor experiments, with support material (Nagao Porcell), fixed temperature at 37 °C, and glycerol concentration of 10.0 $g{\cdot}L^{-1}$, the authors reached a maximum H_2 volumetric productivity of 63 $mmol{\cdot}L^{-1}{\cdot}h^{-1}$ for crude glycerol. During these studies, the authors identified ethanol, 1,3-propanediol, and other metabolites production as well.

Hydrogen production from pure and crude glycerol was also studied by Selembo et al. (2009), in conjunction with 1,3-propanediol production. The anaerobic digestion was carried out in batch at 3.0 $g{\cdot}L^{-1}$ substrate concentration, under mesophilic conditions (30 °C), using mixed culture from wheat soil. The inoculum was heat-treated to inhibit methane generation. The authors achieved hydrogen yields of 0.28 mol $H_2{\cdot}mol^{-1}$ $glycerol_{CONSUMED}$ for pure glycerol and 0.31 mol $H_2{\cdot}mol^{-1}$ $glycerol_{CONSUMED}$ for crude glycerol.

Table 9.18 Literature resume of the hydrogen yields using glycerol as the sole carbon source.

Reactors	Inoculum	Operational parameters	HY (mol H_2·mol^{-1} $glycerol_{CONSUMED}$)	References
Batch PBR	*E. aerogenes* HU-101	Temp. 37 °C; glycerol 1.7–25.0 g·L^{-1} Temp. 37 °C; HRT 0–1^a and 0–0.67^a h; OLR 0–243^b and 0–358^b kg·m^{-3}·day^{-1}	1.12 –	Ito et al. (2005)
Batch	Mixed culture	Temp. 30 °C; glycerol 3.0 g·L^{-1}	0.31	Selembo et al. (2009)
Batch	*T. neapolitana* DSM 4359	Temp. 75 °C; glycerol 5.0 g·L^{-1}	2.73	Ngo et al. (2011)
Batch	*T. marítima* DSM 3109 *T. neapolitana* DSM 4359	Temp. 80 °C; glycerol 2.5 g·L^{-1}	2.75	Maru et al. (2012)
Batch	Mixed culture	Temp. 37 °C; glycerol 0.5–5.0 g·L^{-1}	1.10	Mangayil et al. (2012)
Batch	Mixed culture	Temp. 55 °C; glycerol 20.33 g·L^{-1}	0.30	Sittijunda and Reungsang (2012)
CSTR	*C. pasteurianum*	Temp. 35 °C; HRT 12 h; OLR 20^b kg·m^{-3}·day^{-1}	0.77	Lo et al. (2013)
Batch	*T. marítima* DSM 4359	Temp. 80 °C; glycerol 2.5 g·L^{-1}	2.84	Maru et al. (2013)
UASB	*E. aerogenes* ATCC 13048	Temp. 37 °C; HRT 12 h; OLR 30^b kg·m^{-3}·day^{-1}	0.41	Reungsang et al. (2013)
UASB	Mixed culture	Temp. 40 °C; HRT 12–2 h; OLR 20–360^b kg·m^{-3}·day^{-1}	4.08^b	Chookaew et al. (2014)
UFCB	Mixed culture	Temp. 35 °C; HRT 24–48 h; OLR 8.7–29.7 kg·m^{-3}·day^{-1}	0.50^b	Dounavis et al. (2015)
Batch	Mixed culture	Temp. 37 °C; glycerol 10.0 g·L^{-1}	2.20	Rodrigues et al. (2016)
UASB	Mixed culture	Temp. 37 °C; HRT 9.6–24.0 h; OLR 62.5–25.0^b kg·m^{-3}·day^{-1}	0.58	Sittijunda and Reungsang (2017)
Batch	*Clostridiales* sp. (DF) *Clostridiales* sp and *Rhizobiales* sp. (PF)	Temp. 37 °C; glycerol 1.0–3.0 g·L^{-1}	28^c	Rodrigues et al. (2020)

(continued)

Table 9.18 (continued)

Reactors	Inoculum	Operational parameters	HY (mol H_2·mol^{-1} $glycerol_{CONSUMED}$)	References
UASB	Mixed culture	Temp. 55 °C; HRT 8–24.0[b] h; OLR 75.0–25.0 kg·m^{-3}·day^{-1}	2.9	Sittijunda and Reungsang (2020)

[a] Calculated as the inverse of the dilution rate

[b] Calculated based on information presented in the article or verified graphically

[c] mmol H_2·mol^{-1} $COD_{CONSUMED}$

CSTR continuous stirred tank reactor; *PBR* anaerobic packed-bed reactor; *UASB* upflow anaerobic sludge-bed reactor; *UFCB* upflow column bed reactor; *DF* dark fermentation; *PF* photo fermentation

The studies of Ito et al. (2005) and Selembo et al. (2009) were both conducted in batches under mesophilic conditions. However, the fact of Ito et al. (2005) used pure culture instead of mixed culture provided the highest hydrogen yield, even if in higher concentrations.

Ngo et al. (2011) analyzed the hydrogen production by *Thermotoga neapolitana* DSM 4359, a hyperthermophilic microorganism. Batch trials containing pure and crude glycerol at 5.0 g·L^{-1} concentration were performed at 75 °C and pH of 7. Crude glycerol was pre-treated to remove methanol and ethanol. The H_2 yield was 1.02 and 1.28 mol H_2·mol^{-1} $glycerol_{CONSUMED}$ for pure and crude glycerol, respectively, after 49 h. Up to 56 h of T. *neapolitana* cultivation, the H_2 production was 1.97 mol H_2·mol^{-1} $glycerol_{CONSUMED}$ for crude glycerol, being almost 1.55 times higher than the pure glycerol (1.27 mol H_2·mol^{-1} $glycerol_{CONSUMED}$). Thus, substrate pretreatment had a fundamental role in the hydrogen conversion of crude glycerol by T. *neapolitana*. The pH control and nitrogen introduction into the system were to optimize microbial growth rate and increase hydrogen production, which ranged from 1.24 to 1.98 mol H_2·mol^{-1} $glycerol_{CONSUMED}$. The application of 0.05 M HEPES (N-2-hydroxyethylpiperazine-N0-2 ethanesulphonic acid) optimized H_2 yield to 2.73 mol H_2·mol^{-1} $glycerol_{CONSUMED.}$

Considering crude glycerol impurities, Mangayil et al. (2012) evaluated its hydrogen production compared to pure glycerol performance. Batch experiments to analyze the effect of crude glycerol concentrations (0.5–5.0 g·L^{-1}) were carried out at pH 6.5 and temperature 40 °C. The crude glycerol had a purity of 45%. The inoculum used came from a wastewater treatment plant. It was observed the H_2 yield increased with the crude glycerol concentration up to 1.0 g·L^{-1}, reaching the optimal condition in this concentration. The maximum H_2 yield was 1.1 mol H_2·mol^{-1} $glycerol_{CONSUMED}$. The authors also found that hydrogen production was not affected by impurities. The accumulated volume of hydrogen produced for crude and pure glycerol was 20.9 and 14.8 mL, respectively. According to the authors, the cumulative hydrogen production for crude glycerol increased because of the free fatty acids and organic compounds in this substrate. Acetate, butyrate, and ethanol were the metabolites observed and the predominant microbial consortium was *Clostridium* sp.

Thermotoga maritima DSM 3109 and *Thermotoga neapolitana* DSM 4359 metabolize crude glycerol mainly to acetate and hydrogen, according to the studies of Maru et al. (2012). The authors carried out batch trials at a constant temperature of 80 °C with crude glycerol concentrations of 2.5 $g{\cdot}L^{-1}$. The hydrogen yield was 2.75 and 2.65 mol $H_2{\cdot}mol^{-1}$ $glycerol_{CONSUMED}$ by *T. maritima* and *T. neapolitana*, respectively. Furthermore, the effect of initial pH (5.0–8.5) and different concentrations of yeast extract (0.5–4.0 $g{\cdot}L^{-1}$) on glycerol fermentation by *T. neapolitana* were investigated. The initial pH of 7 was great for hydrogen production by *T. neapolitana*. The lower concentration of yeast extract resulted in lower H_2 production, however increasing the concentration from 2.0 to 4.0 $g{\cdot}L^{-1}$ did not affect H_2 production. Among the fermentation by-products, 90% corresponded to acetic acid, thus justifying the values of H_2 yields close to the theoretical (3.0 mol $H_2{\cdot}mol^{-1}$ $glycerol_{CONSUMED}$).

Sittijunda and Reungsang (2012) found a high efficiency of hydrogen production from crude glycerol using nutrients and thermophilic mixed culture (55 °C) in batch trials. The optimal composition was 20.33 $g{\cdot}L^{-1}$ of crude glycerol, 0.16 $g{\cdot}L^{-1}$ urea, 3.97 $g{\cdot}L^{-1}$ Na_2HPO_4, and 0.20 $mL{\cdot}L^{-1}$ of nutritional medium. Under these conditions, H_2 yield was 0.30 mol $H_2{\cdot}mol^{-1}$ $glycerol_{CONSUMED}$. The maximum H_2 volumetric production was 1502.84 mL $H_2{\cdot}L^{-1}$. At the end of the validation experiment, the authors noticed 1,3-propanediol and ethanol were the most relevant metabolites. Hydrogen-producing microorganisms belonged to *Thermoanaerobacterium* sp.

Maru et al. (2013) evaluated hydrogen production from crude glycerol by the hyperthermophilic microorganism *Thermotoga maritima* DSM 4359. The trials were in batch under hyperthermophilic conditions (80 °C). *T. maritima* converted glycerol mainly to acetate, CO_2, and H_2. The greatest H_2 yield was 2.84 mol $H_2{\cdot}mol^{-1}$ $glycerol_{CONSUMED}$. The optimum H_2 production was found in pH between 7–7.5 and 2.0 $g{\cdot}L^{-1}$ of yeast extract. Low metabolite diversity at the end of fermentation enhanced higher H_2 yields above than those usually achieved for mesophilic microorganisms.

Analyzing Ngo et al. (2011) and Maru et al. (2012, 2013) works, it is possible to notice the better performance of *Thermotoga maritima* DSM 4359 regarding hydrogen production than *Thermotoga neapolitana* DSM 4359. The highest yield was achieved by *Thermotoga maritima* DSM 4359 isolated under hyperthermophilic conditions.

Batch trials are sometimes unfeasible on an industrial scale. Taking this into account, Lo et al. (2013) evaluated the feasibility of crude and pure glycerol for hydrogen production in a continuous stirred tank reactor (CSTR). The anaerobic process was carried out by isolated strains of microorganisms (*Clostridium butyricum*, *Clostridium pasteurianum*, and *Klebsiella sp.*). Among the strains analyzed, C. *pasteurianum* exhibited the best performance regarding hydrogen production under mesophilic temperature (35 °C), initial pH 7, and glycerol concentration 10 $g{\cdot}L^{-1}$. When pure glycerol was used, the average H_2 volumetric productivity and yield were 103.1 $mL{\cdot}h^{-1}{\cdot}L^{-1}$ and 0.50 mol $H_2{\cdot}mol^{-1}$ glycerol, respectively. In contrast, when crude glycerol was used as a carbon source, the H_2 volumetric productivity and yield were 166.0 $mL{\cdot}h^{-1}{\cdot}L^{-1}$ and 0.77 mol $H_2{\cdot}mol^{-1}$ glycerol, respectively. Under such conditions, the H_2 percentage obtained was 75%.

Reungsang et al. (2013) researched hydrogen production from pure and crude glycerol (25.0 $g{\cdot}L^{-1}$) in UASB reactor. The inoculum used was methanogenic granular sludge from brewery wastewater UASB reactor, which passed through heat treatment for subsequent immobilization of *Enterobacter aerogenes* ATCC 13048. The operating temperature was 37 °C (mesophilic condition) and pH was 5.5. They evaluated the organic loading rate (OLR) in order to maximize the H_2 production. As reported by authors, the change in OLR led to a variation in hydrogen content and hydrogen volumetric productivity. It was observed increased H_2 production up to a OLR of 50 $g{\cdot}L^{-1}{\cdot}day^{-1}$. This OLR was the optimal operational point, obtaining the best hydrogen content and production rate for pure and crude glycerol of 37.1% and 9 mmol $H_2{\cdot}L{-}^{1}{\cdot}h^{-1}$ and 24.2% and 6.2 mmol $H_2{\cdot}h^{-1}{\cdot}L^{-1}$, respectively. In addition, the maximum H_2 yield was 410 mmol $H_2{\cdot}mol^{-1}$ glycerol (pure glycerol) and 324 mmol $H_2{\cdot}mol^{-1}$ glycerol (crude glycerol).

The work of Chookaew et al. (2014) analyzed hydrogen production by immobilization of *Klebsiella* sp. TR17 in UASB reactors. The reactors were operated under mesophilic conditions (40 °C) and pH 8, with HRT between 12 and 2 h. The substrate was crude glycerol with 50% purity, at different concentrations (10.0, 20.0, and 30.0 $g{\cdot}L^{-1}$). The inoculum was methanogenic granular sludge from a UASB reactor, which was subjected to heat treatment and then immobilization of *Klebsiella* sp. TR17. The optimal HRT was 4 h, which achieved the highest hydrogen volumetric productivity (242.15 mmol $H_2{\cdot}h^{-1}{\cdot}day^{-1}$) and hydrogen yield (44.27 mmol $H_2{\cdot}mol^{-1}$ $glycerol_{CONSUMED}$). It was noticed that for the same HRT of 4 h the increasing glycerol concentration (10.0–30.0 $g{\cdot}L^{-1}$) also increased hydrogen volumetric productivity (165.21–242.15 mmol $H_2{\cdot}h^{-1}{\cdot}day^{-1}$) and decreased hydrogen yield (44.27–29.00 mmol $H_2{\cdot}mol^{-1}$ $glycerol_{CONSUMED}$). However, there was no effect on the hydrogen content (42–43%). 1,3-propanediol was the most predominant metabolite in all conditions.

Dounavis et al. (2015) operated an upflow column bed reactor (UFCB) using cylindrical ceramic granules under mesophilic conditions (35 °C). The inoculum was sludge obtained from an anaerobic digester, which was subjected to heat treatment. In order to evaluate the effect of crude glycerol concentration, pH, and HRT on H_2 production, the concentration ranged from 10.0 to 25.0 $g{\cdot}L^{-1}$, the HRT was between 24 and 48, and the initial pH was between 6 and 7. The optimal glycerol consumption (96.1%) was at 10.0 $g{\cdot}L^{-1}$, HRT 36 h, pH 6, and OLR 8.7 g $COD{\cdot}day^{-1}{\cdot}L^{-1}$. The maximum volumetric production of 4.23 $L{\cdot}day^{-1}$ was observed with crude glycerol concentration of 25.0 $g{\cdot}L^{-1}$, HRT 24 h, pH 7, and OLR 29.77 g $COD{\cdot}day^{-1}{\cdot}L^{-1}$. Hydrogen proportion in the gas phase was slightly affected by operational changes (ranging from 40.2 to 45.2%). In contrast, hydrogen yield increased when the glycerol concentration increased from 10.0 to 20.0 $g{\cdot}L^{-1}$, and decreased when the HRT increased from 36 to 48 h.

Hydrogen production from crude glycerol (10.0 $g \cdot L^{-1}$) under mesophilic conditions (37 °C) and initial pH 7 was evaluated by Rodrigues et al. (2016). Crude glycerol was treated to adjust pH in order to remove impurities. The inoculum applied: (I) granular sludge from thermophilic vinasse treatment UASB reactor and (II) granular sludge from municipal effluent treatment UASB reactor. Both inoculums were submitted to a thermal pretreatment and used in batch trials. Crude glycerol was not consumed completely during the batch trials. It was observed just 26.9% and 31.7% conversion during 69.1 h and 68.7 h of operation using inoculum (I) and (II), respectively. According to the authors, probably there were impurities in the substrate which caused inhibition of microbial growth. This interfered in the metabolic pathways of both inoculums (I and II), triggering a low consumption of crude glycerol. Cumulative hydrogen concentration and H_2 yields were 28.49 mmol $H_2 \cdot L^{-1}$ and 2.2 mol $H_2 \cdot mol^{-1}$ glycerol, and 19.14 mmol $H_2 \cdot L^{-1}$ and 1.1 mol $H_2 \cdot mol^{-1}$ glycerol, for (I) and (II), respectively. The main metabolites produced were ethanol, acetic and butyric acid.

Sittijunda and Reungsang (2017) operated a UASB reactor under mesophilic conditions (37 °C) for hydrogen and metabolites production from pure and crude glycerol by mixed culture. The inoculum was activated sludge from brewery wastewater treatment. The substrate concentration was 25 g $COD \cdot L^{-1}$ and HRT was from 24 to 9.6 h. Thus, the organic loading rates ranged up 25.0 to 62.5 g $COD \cdot L^{-1} \cdot day^{-1}$. It was added NaOH (2 $mol \cdot L^{-1}$) to adjust the affluent pH to 5.5. Anaerobic digestion of pure and crude glycerol achieved optimal hydrogen production results at OLR 50 $g \cdot L^{-1} \cdot day^{-1}$. Pure glycerol, in this condition, reached a consumption of 97.5%, productivity of 6 mmol $H_2 \cdot L^{-1} \cdot h^{-1}$, and yield of 579.7 mmol $H_2 \cdot mol^{-1}$ glycerol. Crude glycerol achieved a consumption of 81.5%, productivity of 3.3 mmol $H_2 \cdot L^{-1} \cdot day^{-1}$, and yield of 368.1 mmol $H_2 \cdot mol^{-1}$ glycerol. There was a predominance of microorganisms *Enterobacter* sp., *Clostridium* sp., F. *bacterium,* and *Actinobacterium*. The main metabolites produced were 1,3-propanediol and ethanol.

Rodrigues et al. (2020) produced biohydrogen through dark fermentation, in a first stage, and photo-fermentation (second stage) of crude glycerol from biodiesel production by waste cooking oil. For dark fermentation, they used *Clostridiales* sp. and for photo fermentation, the microbial consortium was enriched with *Rhizobiales* sp. The tests were carried out in batch. Dark fermentation was performed with an initial concentration of 20.0 g $COD \cdot L^{-1}$, temperature at 37 °C, and pH 5.5. The effluent from the first stage was subjected to centrifugation and filtration process. Then, it was diluted into the enriched sludge with concentrations of 1.2 and 3.0 g $COD \cdot L^{-1}$. The photo-fermentation process took place at an initial pH of 7.0, temperature at 37 °C, and light intensity of 18.5 $W \cdot m^{-2}$. In the first stage, a glycerol consumption of 45.74% and a hydrogen yield of 1.75 mol $H_2 \cdot mol^{-1}$ glycerol were achieved. In the second stage, the maximum hydrogen production rate (3.0 mmol $H_2 \cdot L^{-1}$) was observed in the lowest COD concentration (1.0 $g \cdot L^{-1}$). Higher COD concentrations decreased H_2 production due to impurities from the raw glycerol which leaded to microbial growth inhibition. It was also observed great COD removal (76.10%) and consumption of metabolites (ethanol—76.86%, acetic acid—95.73%, butyric acid—94.76%, and methanol—99.18%) for 1.0 g COD·L^{-1}. The methanol presence in crude glycerol could be toxic and hinder for metabolic process. The integration of dark and photo-fermentation processes led to a maximum hydrogen yield of 28 mmol H_2·mol^{-1} COD$_{CONSUMED}$.

Hydrogen, 1,3-propanediol, and ethanol production from pure and crude glycerol under thermophilic conditions (55 °C) were evaluated by Sittijunda and Reungsang (2020). The study was conducted in UASB reactors similarly to Sittijunda and Reungsang (2017). Substrate concentration was 25 g·L^{-1}. Organic loading rates were changed from 25 to 75 g·L^{-1}·day^{-1}. The inoculum was thermophilic mixed culture: anaerobic granules from brewery wastewater treatment. The anaerobic granules were subjected to pretreatment at 100 °C. In order to adjust the pH around 5.5, it was added 1N NaOH. Optimum operational point was reached at OLR of 62.5 g·L^{-1}·day^{-1} for pure and crude glycerol. Hydrogen yields, hydrogen concentration and H_2 content were 2.90 and 2.05 mol H_2·mol^{-1} glycerol$_{CONSUMED}$, 750.00 and 457.52 mmol H_2·L^{-1}, and 40.42 and 24.07%, respectively. Above OLR of 62.5 g·L^{-1}·day^{-1}, hydrogen, 1,3-propanediol, and ethanol production dropped. This phenomenon is linked with microbial growth inhibition. In the first moment, pure glycerol was favorable to the oxidative pathway while crude glycerol promoted the reductive pathway, according to the authors. Microbial communities belong to *Enterobacter sp*., *Klebsiella* sp., and *K. pneumoniae*.

Comparing Sittijunda and Reungsang (2017, 2020) studies under mesophilic and thermophilic conditions, the increasing temperature clearly optimized hydrogen yield. This behavior is already expected. Higher temperature provides more interactions between microorganisms and it stimulates chemical and biological reactions.

Table 9.18 resumes all main operational parameters and results of the aforementioned studies. Most researches were conducted in batch and used mixed culture as inoculum. The batch process demands fewer technology resources than continuous one. Besides, mixed culture presents a range of microbial consortiums which can degrade different compounds in crude glycerol, reaching high hydrogen productivity (Cabrol et al. 2017). In addition, there is greater metabolic adaptation and lower operating costs, since it is not necessary to undergo selection treatment (de Menezes and Silva 2019).

9.4.2.2 Methane Production

Methane is widely used as a fuel gas to generate heat and energy; it is also a raw material in the steam reforming process for hydrogen production (Pareek et al. 2020). The IEA—International Energy Agency (2020b) estimates the consumption of nearly 200 million tons of biomethane in 2040. The use of biomethane would avoid the emission of about 1 billion tons of greenhouse gases into the environment. Considering the interest in biomethane and concern about the huge production of waste glycerol, a great deal of studies has focused on the production of this biogas pro the biodiesel waste.

Yang et al. (2008) evaluated the biodegradation efficiency of synthetic wastes containing glycerol. They operated in semi-continuous mode two fixed-bed bioreactors with polyurethane foam as a support material, under mesophilic (35 °C) and thermophilic (55 °C) conditions. The HRT was established in 14 days. The inoculums were mesophilic and thermophilic sludge from a wastewater treatment plant. Under thermophilic conditions, they obtained an average efficiency of 87% of COD removal, while in mesophilic conditions the efficiency was 50%. The thermophilic reactor achieved the maximum methane production (0.45 $LCH_4{\cdot}g^{-1}$ $COD_{APPLIED}$ at a ORL 0.70 $g{\cdot}L^{-1}{\cdot}day^{-1}$). Molecular cloning of gene sequences indicated mainly *Methanobacterium* sp. and *Methanosarcina* sp in the thermophilic reactor.

The effect of increase in OLR and feed time in an ASBR (30 °C) operated in batch and fed-batch mode was studied by Selma et al. (2010). The crude glycerol concentration ranged between 0.5 and 3.0 g $COD{\cdot}L^{-1}$—leading to OLR from 0.6 to 3.82 g $COD{\cdot}L^{-1}{\cdot}day^{-1}$. The inoculum came from an UASB reactor which treated poultry slaughterhouse wastewater. The COD removal of ASBR in batch was 93, 81, and 66% for 0.5, 1.0, and 2.0 g $COD{\cdot}L^{-1}$ (0.6, 1.29 and 2.44 g $COD{\cdot}L^{-1}{\cdot}day^{-1}$), respectively. The operational stability was not achieved for 3.0 g $COD{\cdot}L^{-1}$ (3.82 g $COD{\cdot}L^{-1}{\cdot}day^{-1}$). The COD removal efficiency was 85% at 1.0 g $COD{\cdot}L^{-1}$ and feeding times of 2 and 4 h when the reactor was operated in fed-batch mode. It was observed that the use of fed-batch mode may improve and smooth the COD and volatile organic acids profiles throughout the cycle time. The maximum methane yield was 96 NmL $CH_4{\cdot}g^{-1}$ COD.

Phukingngam et al. (2011) evaluated anaerobic bed reactors (ABRs) performance for wastewater from the biodiesel production process treatment, under mesophilic condition (27 °C). The wastewater, containing glycerol, was diluted in 5.0 to 30.0 g $COD{\cdot}L^{-1}$ and the HRT was maintained constant in 10 days (corresponding to OLR between 0.5 and 3.0 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$). The reactors were inoculated with sludge from an UASB reactor which treated soft drink industry wastewater. The operation at OLR from 0.5 to 1.5 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$ was more efficient. In these conditions, the COD, methanol, and glycerol removal were between 98 and 100%. However, increasing OLR to 2.1 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$ decreased COD removal efficiencies and glycerol conversion. Applying OLR from 0.5 to 2.1 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$, volatile organic acids concentration ranged from 12 to 64 $mgHAc{\cdot}L^{-1}$ and pH between 7.07 and 7.51. The OLR of 3.0 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$ caused a significant increase in volatile organic acid concentration to 410 mg $HAc{\cdot}L^{-1}$. The volatile organic acids accumulation led to a drop in pH to 6.07, which is not favorable for methanogenesis. The biogas production rate increased from 2.1 to 12.4 $L{\cdot}day^{-1}$ when OLR was increased from 0.5 to 1.5 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$. The OLR 1.5 kg $COD{\cdot}m^{-3}{\cdot}day^{-1}$ presented the optimum biogas and methane production. The biogas had 64–74% methane content. A microbiological analysis of the sludge granules indicated *Methanosarcina* and *Methanosaeta* populations predominance.

In order to analyze the OLR effect on the efficiency, stability, and methane production of crude glycerol treatment in an AnSBBR, Bezerra et al. (2011) increased glycerol concentration from 1.0 to 4.0 g $COD{\cdot}L^{-1}$ (corresponding to OLR from 1.5 to 6.0 g $COD{\cdot}L^{-1}{\cdot}day^{-1}$). The inoculum came from an UASB reactor which treated poultry slaughterhouse wastewater and polyurethane foam cubes were used as support material. The increase in OLR resulted in a decrease in COD removal efficiency and an increase in the volatile organic acid concentration in the effluent. The OLR of 1.5, 3.0, 4.5, and 6.0 g COD·L^{-1}·day^{-1} resulted in removal efficiencies of 92, 81, 67, and 50%, respectively, while total volatile organic acids in the effluent were 42, 145, 386, and 729 mgHAc·L^{-1}, respectively. Furthermore, by increasing the OLR from 1.5 to 4.5 g COD·L^{-1}·day^{-1}, the methane yield increased from 29.5 to 55.5 NmL CH_4·g^{-1} COD. However, this yield dropped to 36.0 NmL CH_4·g^{-1} COD when the OLR was increased to 6.0 g COD·L^{-1}·day^{-1}, probably due to the higher concentration of volatile organic acids in the reactor.

Lovato et al. (2012) investigated the effect of different feeding times (2–6 h), to glycerol concentrations between 3.0 and 5.0 g COD·L^{-1}, in an anaerobic sequential batch reactor (AnSBBR) performance. The aim was organic matter removal and methane production at 4.5 to 7.5 g COD·L^{-1}·day^{-1}. The inoculum came from an UASB reactor which treated poultry slaughterhouse wastewater and polyurethane foam cubes were used as support material. The reactor was operated at 30 °C and pH close to 7. The maximum organic matter removal efficiency at 4.5 g COD·L^{-1}·day^{-1} was 87% with a feeding time of 4 h, and 84% with 2 and 6 h. At OLR of 6.0 g COD·L^{-1}·day^{-1}, COD removal efficiency was 84% with the feeding times of 4 and 6 h, and 71% in 2 h. Considering the OLR of 7.5 g COD·L^{-1}·day^{-1}, the organic material removal efficiency with 4 h of feeding was 77%. Thus, longer feeding times help to minimize volatile organic acids concentration during the cycle, ensuring the stability and safety of the process. The optimal methane yield was 5.28 mmol CH_4·g^{-1} $COD_{CONSUMED}$, with methane content in biogas of 75%, with a 2 h feed time, and OLR of 4.5 g COD·L^{-1}·day^{-1}.

It is possible to notice that Bezerra et al. (2011) and Lovato et al. (2012) conducted similar studies in AnSBBR at 30 °C. However, Lovato et al. (2012) achieved 87% of COD removal in a feeding time of 4 h, while Bezerra et al. (2011) achieved 67% of COD removal for the same OLR of 4.5 g COD·L^{-1}·day^{-1} using batch mode. Besides, Lovato et al. (2012) applied higher OLR and reached greater COD removal results. The use of fed-batch mode was effective in withstanding higher OLR and removing organic matter.

The work carried out by Vlassis et al. (2013a) aimed at methane and hydrogen production by pure glycerol. They operated a CSTR under mesophilic conditions (35 °C). The substrate contained 5.0 to 10.0 g COD·L^{-1} of glycerol, leading to OLR from 0.25 to 0.5 g COD·L^{-1}·day^{-1}, respectively. HRT was maintained in 20 days. Mesophilic methanogenic sludge from wastewater treatment plants was used as inoculum. Reactor operation did not support OLR above 0.25 g COD·L^{-1}·day^{-1}, due to the accumulation of volatile organic acids and pH reduction. At this OLR, the methane yield was 0.30 m^3 CH_4·kg^{-1} $COD_{APPLIED}$. Hydrogen production was evaluated in batch reactors under mesophilic conditions (35 °C), using heat-pretreated anaerobic microbial culture as inoculum. In the first assays, glycerol concentration effect (8.3–25 g COD·L^{-1}) was investigated. Lastly, pH influence on hydrogen production was studied, keeping the initial glycerol concentration fixed at 8.3 g COD·L^{-1} and varying pH from 4.5 to 8.0. The maximum hydrogen yield was 22.14 mL H_2·g^{-1} $COD_{APPLIED}$ at a pH of 6.5 and glycerol concentration of 8.3 g COD·L^{-1}. The main metabolic was 1,3-propanediol, while ethanol, butyric and acetic acids were detected in low concentrations.

Anaerobic digestion performance of pure glycerol in mesophilic (35 °C) continuous stirred tank reactor (CSTR) and periodic anaerobic baffled reactor (PABR) was studied by Vlassis et al. (2013b). The optimum OLR achieved by the CSTR was 0.25 g COD·L^{-1}·day^{-1}, with a methane productivity of 74 mL CH_4·L^{-1}·day^{-1}. The maximum OLR achieved by PABR was 3.0 g COD·L^{-1}·day^{-1}, resulting in methane productivity of 993 mL CH_4·L^{-1}·day^{-1}. Therefore, the PABR was more efficient, since it was submitted to an organic load 10 times higher than CSTR. Furthermore, its performance was better in terms of COD removal.

Dinh et al. (2014) observed microbial community changes during the adaptation phase for glycerol fermentation and methane production. The batch experiments were performed at mesophilic temperature (39 °C) and OLR at 2.5 kg COD·m^{-1}·day^{-1}. The inoculum was granular sludge from an UASB reactor treating brewery wastewater. The methane content was around 59–64% for an average biogas production rate of 910 L·m^{-3}·day^{-1}, resulting in a methane productivity of approximately 580 L·m^{-3}·day^{-1}. The VFA concentration remained stable until the end of the operation with less than 200 g·L^{-1}. Microbiological analyses concluded that microorganisms from the *Trichococcus* genus and the *Syntrophomonadaceae* family became dominant after adaptation phase. Archaea from the *Methanobacterium* and *Methanospirillum* genus gradually increased throughout operation.

Boonsawang et al. (2015) studied a two-phase anaerobic process for biodiesel wastewater treatment. The effect of pH, HRT, and OLR on reactor performance was evaluated using response surface methodology. All experiments were carried out at 30 °C and concentration of 10.0 g COD·L^{-1}. Regarding the acidogenic reactor, the optimal operation condition was pH 6.48, HRT of 16 h, and OLR of 26.0 g COD·L^{-1}·day^{-1}. In the methanogenic reactor, the optimum values for pH, HRT, and OLR were 6.95, 30 h, and 6.0 g COD·L^{-1}·day^{-1}, respectively. Applying these conditions experimentally, a high VFA production of 9.35 g·L^{-1}, low methane production and COD removal of 41.5% were obtained at the acidogenic reactor. However, in the methanogenic reactor a biogas production of 19.1 L·day^{-1}, 93.5% COD removal, and 0.14 m^3 CH_4·kg^{-1}.$COD_{removed}$ were achieved. The VFA were completely consumed.

The methane production from crude glycerol was studied in an anaerobic fluidized bed reactor (AFBR) under mesophilic and thermophilic conditions (30–55 °C) by da Costa et al. (2021). Different substrate concentrations (1–7 g COD·L^{-1}) with a fixed HRT of 24 h, leading to an OLR from 1.2 to 7.6 kg COD·m^{-3}·day^{-1} were assessed. pH was controlled at 7.9 and 8.1, adding $NaHCO_3$. The inoculum came from an UASB reactor which treated poultry slaughterhouse wastewater and grounded tire was used as support material. In mesophilic condition, COD removal ranged from 48.6 to 93.0%, reaching optimal removal in the lowest OLR (1.2 kg COD·m^{-3}·day^{-1}). The maximum methane yield was 266.6 mL CH_4·g^{-1} $COD_{REMOVED}$ for OLR 7.6 kg COD·m^{-3}·day^{-1}. An optimal thermophilic condition

Table 9.19 Literature resume of the methane yields using glycerol as the sole carbon source

Reactors	Operational parameters	COD removal (%)	MY (m^3 $CH_4 \cdot kg^{-1}$ $COD_{APPLIED}$)	References
PBR	Pure glycerol; 35 and 55 °C; HRT 336 h; OLR 0.25–0.70 and 0.25–1.0 $kg \cdot m^{-3} \cdot day^{-1}$	50 87	0.37 0.45	Yang et al. (2008)
ASBR	Crude glycerol; 30 °C; HRT 8 h^a and 2–4 h^a; OLR 0.60–3.82 kg $COD \cdot m^{-3} \cdot day^{-1}$ and 1.27–2.44 kg $COD \cdot m^{-3} \cdot day^{-1}$	66–93 77–85	0.10^b	Selma et al. (2010)
ABR	Crude glycerol; 27 °C; HRT 240 h; OLR 0.5–3.0 kg $COD \cdot m^{-3} \cdot day^{-1}$	98–100	0.28	Phukingngam et al. (2011)
AnSBBR	Crude glycerol, 30 °C; HRT 8 h^a; OLR 1.5–6.0 kg $COD \cdot m^{-3} \cdot day^{-1}$	50–92	0.06^b	Bezerra et al. (2011)
AnSBBR	Crude glycerol, 30 °C; HRT 2–6 h^a; OLR 4.5–7.5 kg $COD \cdot m^{-3} \cdot day^{-1}$	71–87	5.28^c	Lovato et al. (2012)
CSTR	Pure glycerol, 35 °C; HRT 480 h; OLR 0.25–0.50 kg $COD \cdot m^{-3} \cdot day^{-1}$	–	0.30	Vlassis et al. (2013a)
PABR	Pure glycerol, 35 °C; HRT 240 h; OLR 1.0–3.75 kg $COD \cdot m^{-3} \cdot day^{-1}$	–	0.33	Vlassis et al. (2013b)
Batch	Pure glycerol; 39 °C; OLR 2.5 kg $COD \cdot m^{-3} \cdot day^{-1}$	–	–	Dinh et al. (2014)
1S-R 2S-R	Crude glycerol, 30 °C; HRT 18–30 h; OLR 1.0–2.0 and 8.8 $kg \cdot m^{-3} \cdot day^{-1}$	41.5–93.5	0.14^b	Boonsawang et al. (2015)
CSTR	Pure and crude glycerol, 35 °C; HRT 480 h; OLR 0.77–3.71 $kg \cdot m^{-3} \cdot day^{-1}$	69.4–86.1	0.31^b	Dounavis et al. (2016)
AFBR	Crude glycerol, 30 and 55 °C, HRT 24 h; OLR 1.2–7.6 kg $COD \cdot m^{-3} \cdot day^{-1}$	48.6–93.0 67.7–94.2	0.27^b 0.33^b	da Costa et al. (2021)

[a] Feed time (h)
[b] $m^3 \cdot kg^{-1}$ $COD_{REMOVED}$
[c] mmol $CH_4 \cdot g^{-1}$ $COD_{REMOVED}$

ABR anaerobic bed reactor; *AnSBBR* anaerobic sequencing batch biofilm reactor; *ASBR* anaerobic sequencing batch reactor; *AFBR* anaerobic fluidized bed reactor; *CSTR* continuous stirred tank reactor; *PBR* anaerobic packed-bed reactor; *1S-R* one-stage reactor; *2S-R* two-stage reactor; *UASB* upflow anaerobic sludge-bed reactor

for COD removal (94.2%) and methane yield (330.8 mL $CH_4 \cdot g^{-1}$ $COD_{REMOVED}$) was OLR 3.5 kg $COD \cdot m^{-3} \cdot day^{-1}$.

Table 9.19 shows a resume of the main operational conditions, COD removal, and methane yield from works which aimed at methane production from glycerol treatment.

9.4.3 Value-Added Products

Besides the biogas and biohydrogen from anaerobic digestion, there are many other valuable products that could be obtained by crude glycerol processing such as 1,3-propanediol (1,3-PD), propionic acid (HPr), butyric acid (HBu), succinic acid, ethanol (EtOH), n-butanol, lactic acid (HLa), acetic acid (HAc), as mentioned in Fig. 9.5.

The most relevant metabolite produced from crude glycerol is the 1,3-propanediol. 1,3-PD is applied in solvents and adhesives manufacture, it also can be used for polymers and heterocyclic compounds synthesis (Sun et al. 2018; Kaur et al. 2020). Glycerol is the only compound which can be transformed into 1,3-PD through anaerobic digestion (reductive route), as reported by Homann et al. (1990). The reductive equation is shown below.

$$C_3H_8O_3 + H_2 \rightarrow HO(CH_2)_3OH + H_2O \tag{9.17}$$

Propionic acid is the main product from the oxidative route. As HPr has three carbons and the same oxidation number as of glycerol, the propionate pathway can maintain the redox balance and will not require another route to keep the ionic balance. Thus, propionic acid bioconversion (Eq. 9.18) is favored. Industrially, it is the raw material for animal feed, herbicides, cosmetics, thermoplastics, and perfumes production, it is also used as a food preservative (Nazareth et al. 2018; de Paranhos and Silva 2020).

$$C_3H_8O_3 \rightarrow CH_3CH_2COOH + H_2O \tag{9.18}$$

In Zeng (1995) and Ahrens et al. (1998) studies about glycerol, metabolic reactions are described for *Klebsiella pneumoniae* and *Clostridium butyricum*. These reactions can produce or consume hydrogen simultaneously, as shown by Eqs. (9.19)–(9.27). Also, Biebl (2001) and Sarma et al. (2012) presented the conversion of glycerol into butanol (Eq. 9.24).

- Glycerol → Acetic acid + Formic acid

$$C_3H_8O_3 + H_2O \rightarrow CH_3COOH + CO_2 + 3\ H_2 \tag{9.19}$$

$$C_3H_8O_3 + H_2O \rightarrow CH_3COOH + HCOOH + 2\ H_2 \tag{9.20}$$

- Glycerol → Butyric acid

$$2\ C_3H_8O_3 \rightarrow CH_3CH_2CH_2COO + CO_2 + 4\ H_2 \tag{9.21}$$

- Glycerol → Latic acid

$$C_3H_8O_3 \rightarrow CH_3CH(OH)COOH + H_2 \tag{9.22}$$

- Glycerol → Succinic acid

$$C_3H_8O_3 \rightarrow HOOC(CH_2)_2COOH + H_2O \tag{9.23}$$

- Glycerol → Ethanol + Formic acid

$$C_3H_8O_3 \rightarrow CH_3CH_2OH + CO_2 + H_2 \tag{9.24}$$

$$C_3H_8O_3 \rightarrow CH_3CH_2OH + HCOOH \tag{9.25}$$

- Glycerol → 2,3-Butanediol

$$2\ C_3H_8O_3 \rightarrow (CH_3)_2(CHOH)_2 + 2\ CO_2 + 3\ H_2 \tag{9.26}$$

- Glycerol → Butanol

$$2\ C_3H_8O_3 \rightarrow CH_3(CH_2)_3OH + 2\ CO_2 + 2\ H_2 \qquad + H_2O \tag{9.27}$$

Theoretically, the maximum hydrogen yield of 3:1 mol H_2 per mol glycerol consumed can be achieved when acetate is the final fermentation product. However, all reactions are competing with each other. Thus, lower values are produced and the theoretical yield never is reached (Biebl et al. 1998; Ito et al. 2005).

The hydrogen production is totally associated with metabolites productions. All of them are produced in the primary fermentation step. Considering this, metabolites identified in some studies mentioned in Sect. 9.4.2.1 are described in Table 9.20. Beyond metabolites observed in hydrogen studies, other researches have reported crude glycerol valorization into value-add products.

Gallardo et al. (2014) verified the production of 1,3-propanediol (1,3-PD) using glycerol as carbon source on three EGSB reactors. Reactors 1, 2, and 3 were treated with granular sludge, granular sludge thermally treated, and fragmented granular sludge, respectively. The glycerol concentration was established at 25 $g{\cdot}L^{-1}$, temperature of 37 °C, and pH of 5.0 to 6.0 (HRT of 24 h to 12 h) and 4.0 to 5.0 (HRT of 6 h to 3 h). The glycerol conversion into 1,3-PD was not influenced by the inoculum pretreatment. The highest 1,3-PD yield (0.52 mol1,3-PD$\cdot mol^{-1}$ glycerol) and productivity (57 $g{\cdot}L^{-1}{\cdot}day^{-1}$) were achieved on R1 (HRT of 12 h and 3 h, respectively).

Zhang et al. (2015) investigated the feasibility of acetate and methane production from glycerol under hyperthermophilic conditions (70 °C). The anaerobic sludge was obtained from a treating brewery wastewater mesophilic UASB reactor. The operation was performed in a CSTR with HRT of 5.5 days and glycerol concentrations of 5.0–13.0 $g{\cdot}L^{-1}$. The maximum methane yield was obtained at a concentration of 5.0 $g{\cdot}L^{-1}$ (0.96 to 1.09 mol $CH_4{\cdot}mol^{-1}$ glycerol). The maximum acetate

Table 9.20 Literature resume of the main metabolites produced using glycerol as the only carbon source

Reactors	Inoculum	Operational parameters	Main metabolites	References
PBR	*E. aerogenes* HU-101	Temp. 37 °C; HRT 0–1[a] and 0–0.67[a] h; OLR 0–243[b] and 0–358[b] kg·m^{-3}·day^{-1}	EtOH; 1,3-PD	Ito et al. (2005)
Batch	Mixed culture	Temp. 30 °C; glycerol 3.0 g·L^{-1}	1,3-PD	Selembo et al. (2009)
Batch	Mixed culture	Temp. 55 °C; glycerol 20.33 g·L^{-1}	HBu; HPr; HAc; HFo; HLa; EtOH; 1,3-PD	Sittijunda and Reungsang (2012)
Batch	*T. marítima* DSM 4359	Temp. 80 °C; glycerol 2.5 g·L^{-1}	HAc	Maru et al. (2013)
UASB	Mixed culture	Temp. 40 °C; HRT 12–2 h; OLR 20–360[b] kg·m^{-3}·day^{-1}	1,3-PD; EtOH; HAc; 2,3-BtOH	Chookaew et al. (2014)
EGSB	Mixed culture	Temp. 37 °C; HRT 24–3 h; OLR 25–200[b] kg·m^{-3}·day^{-1}	1,3-PD	Gallardo et al. (2014)
CSTR	Mixed culture	Temp. 70 °C; HRT 132 h; OLR 5–13 kg·m^{-3}·day^{-1}	HAc	Zhang et al. (2015)
UASB	Mixed culture	Temp. 37 °C; HRT 9.6–24.0 h; OLR 62.5–25.0[b] kg·m^{-3}·day^{-1}	1,3-PD; EtOH	Sittijunda and Reungsang (2017)
AFBR	Mixed culture	Temp. 30 °C; HRT 8.0–0.5 h; OLR 15–240[b] kg·m^{-3}·day^{-1}	HPr; 1,3-PD; EtOH; HAc; HBu	Nazareth et al. (2018)
AFBR	Mixed culture	Temp. 30 °C; HRT 0.76–9.24 h; OLR 7.5–540[b] kg·m^{-3}·day^{-1}	1,3-PD, HPr	de Paranhos and Silva (2020)
UASB	Mixed culture	Temp. 55 °C; HRT 8–24.0[b] h; OLR 75.0–25.0 kg·m^{-3}·day^{-1}	1,3-PD; EtOH	Sittijunda and Reungsang (2020)

[a] Calculated as the inverse of the dilution rate

[b] Calculated based on information presented in the chapter

AFBR anaerobic fluidized bed reactor; *CSTR* continuous stirred tank reactor; *EGSB* expanded granular sludger-bed reactor; *UASB* upflow anaerobic sludge-bed reactor

yield was obtained at the glycerol concentration of 13.0 g·L^{-1} (0.74 to 0.80 mol HAc·mol^{-1} glycerol), representing more than 90% wt. of the metabolites produced. It might conclude the predominance of acetogenic organisms to obtain acetate.

Interested in propionic acid industrial value, Nazareth et al. (2018) evaluated HPr production in a mesophilic anaerobic fluidized bed reactor (AFBR), using crushed tire as support material. Crude glycerol concentration was 5.0 g·L^{-1}. The HRT ranged from 0.5 to 8.0 h. Sludge from an UASB reactor which treated poultry slaughterhouse wastewater was used as inoculum and subjected to heat treatment. The temperature was maintained at 30 °C and the pH around 4.5. The main metabolite produced was HPr, with maximum yields and productivity of 0.48 $gHPr \cdot g^{-1}$ $COD_{APPLIED}$ in the HRT of 6 h and 4.09 $g \cdot L^{-1} \cdot h^{-1}$ in the HRT of 0.5 h, respectively, It was also identified 1,3-PD, ethanol, acetic and butyric acid presence, but in low concentrations.

According to de Paranhos and Silva (2020), the anaerobic digestion of crude glycerol in AFBR under mesophilic condition (30 °C) and mixed culture can be favorable to produce hydrogen, 1,3-PD, and propionic acid. The authors applied a range of glycerol concentrations (2.9 to 17.1 $g \cdot L^{-1}$) and HRT (0.76 to 9.24 h). 1,3-PD and propionic acid were the most relevant products in all conditions. The maximum production rate of 1,3-PD and propionic acid was 1.04 and 0.14 $g \cdot h^{-1} \cdot L^{-1}$, respectively, for glycerol concentration of 15 $g \cdot L^{-1}$ and HRT of 2 h. Also, the optimum propionic acid yield (0.71 mol $HPr \cdot mol^{-1}$ $glycerol_{consumed}$) was obtained in this condition. However, the highest 1,3-PD yield (1.05 mol1,3-$PD \cdot mol^{-1}$ $glycerol_{consumed}$) was found at 10 $g \cdot L^{-1}$ and HRT of 9.24 h.

Table 9.20 presents a short resume of the valuable products that could be obtained in the anaerobic digestion of glycerol. The 1,3-propanediol presence is observed in almost all studies, followed by ethanol. Since bioethanol has other more effective sources of production, the main interest is in the 1,3-PD production, as mentioned before. de Paranhos and Silva (2020) achieved the highest 1,3-PD yield in comparison to the others works.

9.5 Cassava Processing and Its Wastewaters

Brazil is the fifth-largest producer of cassava in the world ranking, producing the equivalent of 17.64 million tons in the year of 2018. Cassava is a plant with high adaptability, cultivated in Brazil under various climatic conditions, being one of the main sources of carbohydrates for lower income consumers in tropical countries of Latin America. It is mainly produced by small producers, in complex production system, with a little or no use of modern technology (Food and Agriculture Organization of the United Nations 2021).

The industrial processing of cassava generates a large amount of wastewater, composed by root cleaning water, cassava milling wastewater, and cassava starch wastewater, which corresponds to the liquids contained in the roots diluted in water for extraction. This wastewater presents a high pollutant yield due to the carbohydrates, organic matter, and cyanogenic glucosides, especially linamarin, which can decompose to hydrogen cyanide (Barana and Cereda 2000). The composition of cassava wastewater can be influenced by factors (e.g., plant variety, soil type, climatic conditions, harvest time).

The production process (Fig. 9.6) begins in the mechanized or manually harvest of cassava roots. It cannot lay in the field for more than 24 h, in order to prevent the rotting of the roots and physiological and/or bacteriological intoxications. The

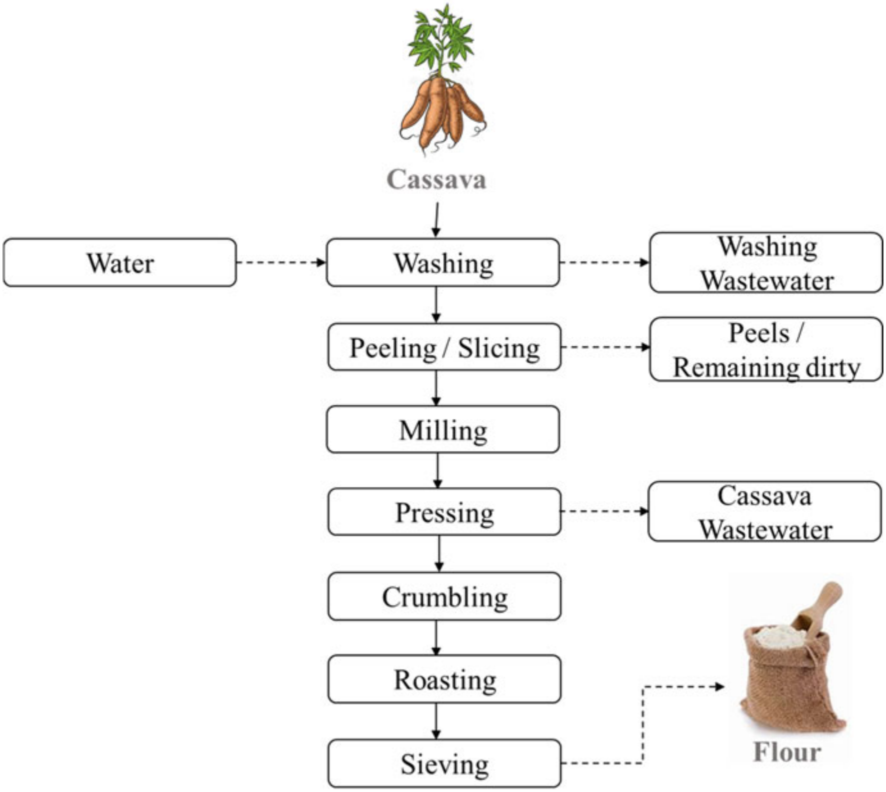


Fig. 9.6 Flow diagram of cassava processing

transport vehicles must be in good hygienic conditions to avoid the presence of contaminant products that may change the quality of the raw material. The roots shall be weighed and kept at room temperature. The washing is determined according to their peeling. In the manual peeling, the roots are washed in tanks with drinking water, peeled and sliced with stainless steel knives and again washed.

In mechanical peeling the roots are washed at the same time as they are peeled and sliced, and suitable machinery is used that only remove the peel. After washing and peeling the roots, they are placed in a sanitized container. In the process of milling, the roots, already peeled/sliced and washed, are transformed into mass in an electric grater, which is a stainless metal cylinder, with serrated steel blades. The next step in the cassava productive process is the pressing, which can be performed by manual or hydraulic presses. In both processes the dough is packed inside baskets and compressed. The excess water is removed to facilitate the roasting process and to reduce oxidation.

In the crumbling step, the compressed block, formed after the pressing process, is broken with a common grater. Then, the mass is roasted in an oven made by stainless material. In the sieving step, the mass is placed in a sieve (with thin, medium, and large mash) with vibrating movements. It removes the remaining slices of peel and roots, making the crumbly dough even. In the scalding, the crumbly mass undergoes the heat treatment, being heated to a temperature lower than that used in the roasting process, approximately 90 °C. This is performed in order to give greater granulometry to the flour, besides giving the characteristic flavor of the product and removing much of the cyanide acid, toxic to humans, which can still be present in the dough. This process aims to obtain two products: starch and flour (Sánchez et al. 2017).

9.5.1 Cassava Wastewater

The cassava variety used as a raw material in Brazilian cassava starch industries has a high concentration of carbohydrates, and the starch production can generate wastewater with high chemical oxygen demand and organic loads (Jiang et al. 2018; Amorim et al. 2018; dos Moura et al. 2018). The cassava wastewater (CS) is a milky yellowish liquid and may have different physical-chemical characteristics due to the harvest seasonality.

Intanoo et al. (2014) observed a chemical oxygen demand of 14.5 g L^{-1}, and a ratio of COD:nitrogen:phosphorus of 100:2.98:2.03. The CS used as a substrate by Sreethawong et al. (2010) presented COD of 20 g L^{-1} and a ratio of COD: nitrogen:phosphorus of 100:0.7–1.9:2.3–3.9. Andreani et al. (2019) and Mari et al. (2020) reported the following pH, COD, and carbohydrates: 4.9, 11.82 g L^{-1}, and 6.42 g L^{-1}, respectively. Table 9.21 shows the comparison of characterization between authors.

CS also has a large content of nutrients, such as nitrogen (212 mg L^{-1}), calcium (33 mg L^{-1}), phosphorus (31 mg L^{-1}), and iron (11 mg L^{-1}), main nutrients required in the anaerobic process for hydrogen, methane, and metabolites production (Torres et al. 2017; Amorim et al. 2018). Cappelletti et al. (2011) estimates that the CS production is around 6 L Kg^{-1} processed cassava. The wastewater is usually

Table 9.21 Physical-chemical parameters of the cassava wastewater (Rosa et al. 2016; de Barros et al. 2016; Andreani et al. 2019; Ribeiro et al. 2019)

Parameters	Average	Parameters	Average
COD ($g{\cdot}L^{-1}$)	61.27	Ca ($mg{\cdot}L^{-1}$)	241.62
Total carbohydrate ($g{\cdot}L^{-1}$)	58.11	P ($mg{\cdot}L^{-1}$)	220.35
Reducing sugars ($g{\cdot}L^{-1}$)	40.60	K ($mg{\cdot}L^{-1}$)	1247.92
pH	5.98	HAc ($mg{\cdot}L^{-1}$)	229
TSS ($mg{\cdot}L^{-1}$)	8841	HLa ($mg{\cdot}L^{-1}$)	1682
VSS ($mg{\cdot}L^{-1}$)	7621		

COD chemical oxygen demand; *TSS* total suspended solids; *VSS* volatile suspended solids; *Ca* calcium; *P* phosphorus; *K* potassium treated by anaerobic ponds, where greenhouse gas emissions occur, especially CH_4, which, in the stabilization ponds, is indiscriminately released on the atmosphere, impacting the environment.

9.5.2 Environmental Compliance and Energy Production

The high concentration of organic compounds in CS can decrease the dissolved oxygen on the water bodies, impacting the aquatic ecosystem. In addition, the linamarin in the CS can be decomposed into hydrogen cyanide, an extremely toxic compound to enzymes and intestinal flora of fish and other animals. Thus, the use of anaerobic reactors to treat this wastewater remains the most sustainable strategy, by reducing the organic load and, at the same time, producing biogas with potential for energy use (Sánchez et al. 2017).

Rosa et al. (2016) used two anaerobic fluidized bed reactors in thermophilic conditions (55 °C) to treat cassava wastewater. The experiment was divided in 5 conditions per reactor: R1 at 4 to 12 $kg{\cdot}m^3{\cdot}day^{-1}$, COD of 2 to 5 g $COD{\cdot}L^{-1}$, and HRT of 10 and 12 h, and R2 at 14 to 30 $kg{\cdot}m^3{\cdot}day^{-1}$, COD of 7 to 15 g $COD{\cdot}L^{-1}$, and HRT of 10 and 12 h. The authors achieved COD removal of 20 to 45% in the reactor R1 and 12 to 49% in the R2.

According to Hansupalak et al. (2016), the implantation of anaerobic reactors reduced the environmental degradation caused by the inadequate disposal of CS in Thailand. This treatment provided the biogas energetic utilization, replacing 43% of the electrical power consumed by the cassava processing industry. Also, there was a 40% reduction on greenhouse gas emissions by exchanging the treatment ponds for anaerobic reactors.

The CS treatment and biogas production were described in studies that used several anaerobic reactors, e.g., anaerobic reactor with ascending flow and PVC bracket (Barana and Cereda 2000), anaerobic baffled reactor (Ferraz et al. 2009), anaerobic sequencing batch reactor (Sreethawong et al. 2010), anaerobic reactor with ascending flow (Sun et al. 2012), compartmentalized anaerobic reactor (Thanwised et al. 2012), anaerobic fluidized bed reactor (Amorim et al. 2014), upflow anaerobic sludge blanket (Intanoo et al. 2014), horizontal flow reactors (Palma et al. 2018), upflow anaerobic fixed-bed reactor (Corbari et al. 2019), anaerobic sequential bath biofilm reactor (Andreani et al. 2019; Mari et al. 2020).

One ton of processed cassava can produce 5 $nm^3\ h^{-1}$ of CH_4 or 134 to 316 L CH_4 $kg^{-1}\ day^{-1}$ (kg of volatile suspended solids) (Sun et al. 2012). However, biogas production depends on the pH, organic loads, temperature, etc. Several studies investigated the use of CS as mono-substrate in the anaerobic digestion, aiming to verify the production of H_2, CH_4, and other value-added products. Biogas production and CS treatment were described in studies that used different configurations of anaerobic reactors.

Watthier et al. (2019) evaluated the treatment of CS in a horizontal anaerobic fixed-bed reactor (HAFBR) in the organic matter removal and biogas generation.

Two fixed-bed reactors filled with different types of support materials were used: bamboo rings (R1) and flexible PVC rings (R2). The reactors were constructed in polyvinyl chloride (PVC) with 90 cm length and 15 cm diameter. For this, 13 assays were carried out, with OLR increase (1.7 to 15.0 $g{\cdot}L^{-1}{\cdot}day^{-1}$) and HRT decrease (4.0 to 0.8 days). The highest biogas productions of 1.4 $L{\cdot}L^{-1}{\cdot}day^{-1}$ (R1) and 1.0 $L{\cdot}L^{-1}{\cdot}day^{-1}$ (R2) were verified in the assay A6 (influent concentration—15.1 $g{\cdot}L^{-1}$, OLR—5.6 $g{\cdot}L^{-1}{\cdot}day^{-1}$, HRT—2.7 day). COD removal reached values up to 99% and R1 and R2 achieved total solids removal efficiencies of 86.2 and 85.5%, respectively.

Sreethawong et al. (2010) aimed to determine the optimum OLR:N relation in an anaerobic sequencing batch reactor (ASBR). The nitrogen supplementation was tested on the COD:N relation of 100:2.2, 100:3.3, and 100:4.4, at an OLR of 30 kg COD m^{-3} and 6 cycles per day. The authors obtained maximum hydrogen production rates (HPR; 524 mL H_2 g^{-1} SSV) and hydrogen yields (HY; 438 mL H_2 g^{-1} COD) in OLR:N relation of 100:2.2.

Thanwised et al. (2012) evaluated the HRT (24, 18, 12, 6, and 3 h) on H_2 production and COD removal. The compartmentalized anaerobic reactor (CAR) operated at 32.3±1.5 °C with mixed culture and pH of 9. The CAR was submitted to OLR of 12.8 to 48 kg m^{-3} day^{-1}. In the HRT decrease of 24 to 6 h, there was an increase in hydrogen production rate (HPR: 164.45 to 883.19 mL H_2 L^{-1} day^{-1}) and COD removal (14.02% to 29.30%). The optimum HRT to the CAR operation was 6 h.

Intanoo et al. (2014) verified the H_2 and CH_4 production in a two-phase upflow anaerobic sludge blanket (UASB), subjected to thermophilic conditions (55±1 °C). A fraction of the effluent from the methanogenic reactor was recirculated to the acidogenic reactor. The acidogenic reactor was submitted to OLR of 20 to 150 kg COD m^{-3} day^{-1} and pH of 5.5. The methanogenic reactor was submitted to OLR of 5 to 25 kg COD m^{-3} day^{-1}. The highest HY (54.22 ml H_2 g^{-1} COD) and hydrogen content (40%) was at OLR of 90 kg m^{-3} day^{-1}. The highest MY (164.87 mL CH4 g^{-1} COD), methane content (68%), and COD removal (72%) was on OLR of 15 kg m^{-3} day^{-1}. The recirculation of methanogenic effluent on the acidogenic reactor reduced the alkaline supplementation.

Amorim et al. (2014) operated an anaerobic fluidized bed reactor (AFBR) to investigate the influence of HRT and OLR on the H_2 biological production. The inoculum was obtained in a swine wastewater treatment pond. The pH, temperature, and COD were maintained on 5, 28 ± 2 °C and COD of 4 g L^{-1}. The AFBR was submitted to HRT of 8 to 1 h and OLR increased from 28 to 161 kg COD m^{-3} day^{-1}. There was an enhancement of molar yield (0.13–1.91 mol H_2 mol^{-1} Carb) and carbohydrates consumption (65%) with the HRT decrease of 8 to 2 h (OLR of 126 kg COD m^{-3} day^{-1}). The highest HPR was 2.04 L h^{-1} L^{-1} with HRT 1 h and OLR of 161 kg COD m^{-3} day^{-1}.

Intanoo et al. (2016) operated an UASB in a two-phase system to produce H_2 and CH_4. The acidogenic reactor was operated at 37 °C. The pH was maintained at 5.5 and a fraction of the effluent was recirculated at a rate of 1:1. The OLR were 10, 20, 25, and 30 kg m^{-3} day^{-1}. The methanogenic reactor was fed with the acidogenic effluent, without pH correction, at OLR 2, 4, 6, 8, and 10 kg m^{-3} day^{-1}. The highest hydrogen production rate (0.39 L H_2 L^{-1} day^{-1}) and yield (39.83 L H_2 kg^{-1} COD) were achieved at OLR of 25 kg m^{-3} day^{-1}, and the highest methane production rate (0.91 L CH_4 L^{-1} day^{-1}) and molar yield (115.23 L CH_4 kg^{-1} COD) were observed at OLR of 8 kg m^{-3} day^{-1}.

Palma et al. (2018) operated two methanogenic horizontal flow reactors (HFR) to verify the efficiency of dolomitic limestone as a support material and alkalinity supplier, as well as the CH_4 production from the process. The reactors were submitted to OLR of 2.3 to 8.5 kg COD m^{-3} day^{-1}, temperature of 28.5 °C, and HRT of 1.1 to 4 days. The support material was able to maintain alkalinity in the system, releasing calcium and magnesium ions in both reactors, with no need to supply with alkaline solution. The largest removal of COD (95%) and molar yield (0.28 L CH_4 g^{-1} COD) were verified at OLR 3.01 kg COD m^{-3} day^{-1} and HRT of 3.1 days (72 h).

Andreani et al. (2019) evaluated the H_2 production in an anaerobic sequential bath biofilm reactor (AnSBBR). The reactor was submitted to HRT of 2, 3, and 4 h, OLR of 12, 14, and 18 kg COD m^{-3} day^{-1}. Conditions I, II, and III (OLR of 12, 18, and 18 kg COD m^{-3} day^{-1} and HRT of 4, 3, and 3 h, respectively) used the inoculum obtained through the natural fermentation of CS, while the conditions IV, V, IV, and VII (OLR of 12, 14, 18, and 18 kg COD m^{-3} day^{-1} and HRT of 4, 4, 2, and 2 h, in this order) were inoculated with thermally treated anaerobic sludge. The highest hydrogen productivity (0.72 L H_2 L^{-1} day^{-1}) was verified at 14 kg COD m^{-3} day^{-1}, HRT of 4 h, and thermally treated inoculum. The hydrogen yield (1.5 mmol H_2 g^{-1} Carb) was higher at 12 kg COD m^{-3} day^{-1}, HRT of 4 h, and inoculum obtained through the natural fermentation of CS.

Corbari et al. (2019) evaluated the biological production of H_2 in an upflow anaerobic fixed-bed reactor (UAFBR). The A1, A2, and A3 assays evaluated the effects of OLR (10; 20 and 20 kg COD m^{-3} day^{-1}, respectively) and inoculation strategies (thermally treated anaerobic sludge at 95 °C, previously used in a pilot scale reactor for the CS treatment and natural fermentation of the same effluent) in the reactor performance. The pH was adjusted to 6 and the A1, A2, and A3 assays were submitted to 4, 2, and 2 h of HRT, respectively. Assay A3 (OLR of 20 kg COD m^{-3} day^{-1}, HRT 2 h) presented the highest hydrogen productivity (550 mL H_2 L^{-1} day^{-1}) and yield (0.2 to 0.3 mol H_2 mol^{-1} Carb). Both inocula showed potential to be used in the acidogenic phase. The natural fermentation is more viable, as it is a simpler and more economical alternative for inoculation of continuous acidogenic reactors.

Table 9.22 resumes optimal H_2 yields using cassava wastewater as carbon source.

Mari et al. (2020) submitted an anaerobic sequential bath biofilm reactor (AnSBBR—in methanogenic phase), fed with previously acidified CS, to OLR of 3.7; 5.5 and 7.3 g L^{-1} day^{-1} (COD concentrations of 2.8 g L^{-1}), 5.4; 8.1 and 10.7 g L^{-1} day^{-1} (COD concentrations of 4.1 g L^{-1} day^{-1}) and 6; 9 and 12.0 g L^{-1} day^{-1} (COD concentrations of 6.0 g L^{-1}). The AnSBBR operated under mesophilic conditions (30±1 °C), with liquid phase recirculation, using anaerobic sludge from CS treatment. The OLR of 12.0 g L^{-1} day^{-1} reached the highest CH_4 content (78%),

Table 9.22 Comparison of the hydrogen production by cassava wastewater under different operating conditions

Anaerobic reactor	Parameters	Productivity	Yield	References
Mesophilic reactors				
ASBR	Temperature: 37 °C; HRT—4 h; OLR—30 kg COD $m^{-3}\cdot day^{-1}$; pH 5.5	5.68 L H_2 day^{-1} L^{-1}	438 mL H_2 g^{-1} Carb	Sreethawong et al. (2010)
ABR	Temperature: 32 °C; HRT—4 h; OLR—66 kg COD $m^{-3}\cdot day^{-1}$; pH 9	0.9 L H_2 day^{-1} L^{-1}	13.4 mL H_2 g^{-1} Carb	Thanwised et al. (2012)
AFBR	Temperature: 28 °C; HRT—2 h; OLR—126 kg COD $m^{-3}\cdot day^{-1}$; pH 5	–	1.91 mol H_2 g^{-1} Carb	Amorim et al. (2014)
UAFBR	Temperature: 36 °C; HRT—3 h; OLR—35 kg COD $m^{-3}\cdot day^{-1}$; pH 6	1.1 L H_2 day^{-1} L^{-1}	840 mL H_2 g^{-1} Carb	Andreani et al. (2015)
UASB	Temperature: 37 °C; OLR—25 kg COD $m^{-3}\cdot day^{-1}$; pH 5.5	0.39 L H_2 day^{-1} L^{-1}	39.8 mL H_2 g^{-1} COD	Intanoo et al. (2016)
AFBR	Temperature: 30 °C; HRT—12 h; OLR—10 kg COD $m^{-3}\cdot day^{-1}$; pH 5	1.66 L H_2 day^{-1} L^{-1}	2.0 mmol H_2 g^{-1} COD	Rosa et al. (2016)
UAFBR	Temperature: 36 °C; HRT –4 h; OLR—9,5 kg COD $m^{-3}\cdot day^{-1}$; pH 4.5	0.25 L H_2 day^{-1} L^{-1}	0.86 mol H_2 g^{-1} Carb	Torres et al. (2017)
AnSBBR	Temperature: 30 °C; HRT –4 h; OLR—13.5 kg COD $m^{-3}\cdot day^{-1}$; pH 6	–	3,67 mol H_2 g^{-1} Carb	Tonello et al. (2018)
UAFBR	Temperature: 30 °C; HRT—4 h; OLR—20 kg COD $m^{-3}\cdot day^{-1}$; pH 6	0.55 L H_2 day^{-1} L^{-1}	0.3 mol H_2 g^{-1} Carb	Corbari et al. (2019)
AnSBBR	OLR—12 kg COD $m^{-3}\cdot day^{-1}$; Temperature: 30 °C; HRT—4 h; pH 6 OLR—12 kg COD $m^{-3}\cdot day^{-1}$; Temperature: 30 °C; HRT—4 h; pH 6	0.72 L H_2 day^{-1} L^{-1} 0.45 L H_2 day^{-1} L^{-1}	0.73 mmol H_2 g^{-1} Carb 1.5 mmol H_2 g^{-1} Carb	Andreani et al. (2019)
Thermophilic reactors				
UASB	Temperature: 55 °C; OLR—90 kg COD $m^{-3}\cdot day^{-1}$; pH 5.5		54.22 mL H_2 g^{-1} COD	Intanoo et al. (2014)

ABR anaerobic baffled reactor; *AnSBBR* anaerobic sequencing batch biofilm reactor; *ASBR* anaerobic sequencing batch reactor; *AFBR* anaerobic fluidized bed reactor; *CMTR* continuous multiple tube reactor; *UAFBR* upflow anaerobic fixed-bed reactor; *UASB* upflow anaerobic sludge blanket

productivity (2.71 LCH_4 L^{-1} day^{-1}), and yield (0.262 L CH_4 g^{-1} COD). On the other hand, this condition achieved the lowest COD removal (60%). Table 9.23 resumes conditions with optimal CH_4 yields, using cassava wastewater as carbon source.

Table 9.23 Comparison of the methane production by cassava wastewater under different operating conditions

Anaerobic reactor	Parameters	Production	Yield	References
Mesophilic reactors				
UASB	Temperature: 37 °C; HRT—C; pH 5.5; OLR—8 kg COD m^{-3}·day^{-1}	0.91 L CH_4 day^{-1} L^{-1}	115.23 LCH_4 kg^{-1} COD	Intanoo et al. (2016)
HFR	Temperature: 30 °C; HRT—74 h; OLR—3.01 kg COD m^3·day^{-1}		0.28 LCH_4 g^{-1} COD Carb	Palma et al. (2018)
AnSBBR	Temperature: 30 °C; HRT—4 h; pH 6; OLR—13.5 kg COD m^3·day^{-1}	2.71 L CH_4 day^{-1}	0.262 LCH_4 g^{-1} COD	Mari et al. (2020)
Thermophilic reactors				
UASB	Temperature: 55 °C; OLR—15 kg COD m^3·day^{-1}	0.65 L CH_4 day^{-1}	164.87 mL CH_4 g^{-1} COD	Intanoo et al. (2014)

AnSBBR anaerobic sequencing batch biofilm reactor; *HFR* horizontal flow reactor; *UASB* upflow anaerobic sludge blanket

9.5.3 Value-Added Products

In addition to the studies related to CS treatment and biogas production (H_2 and CH_4), there are some studies related to energy generation from this effluent. The cassava processing industries are implementing technics that can both treat the effluent and achieve power generation to supply the installations demands. Intanoo et al. (2014) operating a thermophilic UASB in continuous mode, at OLR of 90 g L^{-1} day^{-1}, fed with CS, obtained an estimation of an energy productivity of 23.40 kJ·L^{-1} day^{-1}. Similarly, Mari et al. (2020) obtained an estimation of energy production of 97.6 kJ·L^{-1} day^{-1}.

Besides that, the anaerobic digestion can provide some other products with value added. Table 9.24 presents the results obtained in studies related to value-added products obtained by anaerobic digestion of cassava wastewater, in different conditions and reactor configurations.

9.6 Circular Economy Based on Wastewaters

The current production context is based on the exploitation of natural resources and the products waste disposal after use or consumption. The view of waste as materials without any added value is intrinsic to a large portion of society and industry. This

Table 9.24 Production of value-added products from the fermentation of cassava wastewater

Reactor	Parameters	Main value-added products	References
AFBR	Temperature—55 °C; HRT—8–1 h; OLR—28–161 kg COD·m^{-3}·day^{-1}; COD—4 g COD·L^{-1}	EtOH, HAc, HPr, HBu	Amorim et al. (2014)
AFBR	Temperature—55 °C; HRT—10–12 h; OLR—4–30 kg COD·m^{-3}·day^{-1}; COD—2–15 g COD·L^{-1}	EtOH, MetOH, HAc, HAl, HPr, HBu, HVa	Rosa et al. (2016)
Batch	Temperature—30 °C; COD—10–40 g O_2·L^{-1}	EtOH, HAc, HBu, HCa, HPr	Amorim et al. (2018)
AnSBBR	Temperature—35 °C; HRT—2–4 h; OLR—12–18 kg COD·m^{-3}·day^{-1}; Carb—3200–5000 mg·L^{-1}	HAc, HBu, HPr, HLa	Andreani et al. (2019)
	Temperature—36 °C; HRT—2–4 h; OLR—10–20 g; Carb—1.4–2 g·L^{-1}; carb·L^{-1}·day^{-1};	BuOH, EtOH, HAc, HBu, HLa, HPr	Corbari et al. (2019)
Batch	C:N ratio—9.8–44.1; COD—10–30 g COD·L^{-1}; $(NH_4)_2SO_4$—5 g·L^{-1}	HOl, HLi	Ribeiro et al. (2019)

AFBR anaerobic fluidized bed reactor; *AnSBBR* anaerobic sequencial batch biofilm reactor; *UAFBR* anaerobic fixed-bed reactor; *HRT* hydraulic retention time; *OLR* organic loading rate; *COD* chemical oxygen demand; *Carb* carbohydrates; *HBu* butiric acid; *HAc* acetic acid; *HFo* formic acid; *HLa* latic acid; *HLi* linoleic acid; *Hol* oleic acid; *HPr* propionic acid; *HVa* valeric acid; *EtOH* etanol; *MetOH* methanol

Fig. 9.7 Flowchart of a classic linear economy process

processing pattern is called Linear Economy, whose slogan is “Take, make, and dispose,” and a typical flowchart is presented in Fig. 9.7 (Ghisellini et al. 2016; Coste-Maniere et al. 2019).

This model presents problems such as emissions to the environment (air, soil, and water), solid waste and wastewater generation and biodiversity loss, which compromise the balance of the planet’s ecosystem. Furthermore, the exploitation of natural resources faster than their regeneration, which causes a shortage of raw materials for the industry. Such negative environmental impacts caused this model to be questioned. Since the 70s, schools of thought have introduced debates on macroeconomic models seeking the development of sustainable alternatives from an environmental, social, and economic point of view, bringing the first closed-loop concepts, and after those other concepts as cradle-to-cradle, laws of ecology, regenerative design, industrial ecology, biomimicry, blue economy, natural capitalism, the concept of zero emissions. These studies culminated in the development of a model known as the circular economy (Lieder and Rashid 2016; Geissdoerfer et al. 2017; Korhonen et al. 2018; Rathinamoorthy 2019).

The circular economy is a proposal for a macroeconomic model in which production processes are reassessed and redesigned, seeking technologies for constructing a regenerative growth model and preserving the integrity of natural ecosystems, thereby balancing economic growth with the environment and society aspects. The basic premises and principles of this model are as follows: (i) dissociating economic growth from the exploitation of natural resources, rationally using materials and renewable energy sources to preserve them and allow their regeneration; (ii) design closed production cycles to get the most out of the raw material, containing emissions and add value to outputs throughout the entire chain; and (iii) design or adapt high-efficiency systems, identifying their negative impacts on the environment and society, ensuring that there is, in fact, a contribution to the sustainable development of the society/biosphere system in the long term. (Ghisellini et al. 2016; Korhonen et al. 2018; Rathinamoorthy 2019; Wiesmeth 2021)

To reach these goals, two cycles have been proposed: the technical cycle (TC) and the biological cycle (BC) (Fig. 9.8). The technical cycles allow the product reinsertion for consumers, and the product's components and materials return for the production cycle. The TC guarantees that the raw material is used by the entire chain, since its components, as a rule, cannot be used and degraded by nature. The closing

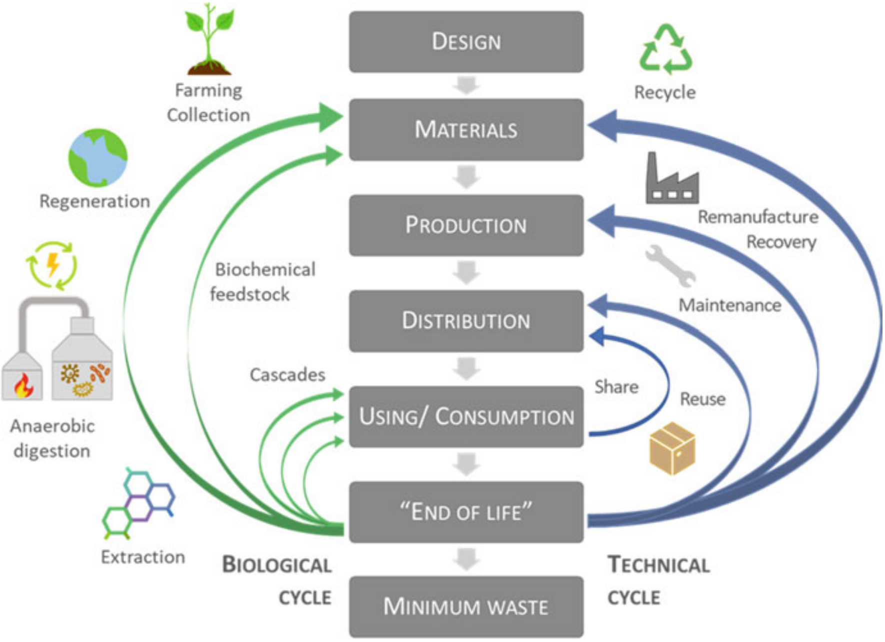


Fig. 9.8 Theoretical flowchart of a circular economy process incorporating technical and biological cycles (Ellen MacArthur Foundation 2017; Rathinamoorthy 2019)

of the technical cycle should preferably take place through the reuse, remanufacturing, and renovation process. A recycling process may occur if all previous options run out. Other materials or components which cannot be re-introduced into the TC must be biodegradable as they may be directed toward the biological cycle. Thus, these materials may be directed to a process of anaerobic digestion that allows energy recovery, and their nutrients will be used to regenerate the Earth's ecosystem and contribute to new production cycles or return in a cascade of subsequent uses (biorefinery concept) (Ghisellini et al. 2016; Ellen MacArthur Foundation 2017; Korhonen et al. 2018; Wiesmeth 2021).

The circular economy, therefore, seeks to preserve natural capital through its integration into the technical and biological cycles aimed at reducing or eliminating environmental impacts, considering waste as a source of raw material for new processes. In this quest, a prominent figure is a wastewater. Wastewater contains an estimated 50 and 100% of all not used waste resources. The constituents present in the wastewater depend on their source, but in general, carbon, nitrogen, phosphorus, biosolids, metals, and bioactive compounds should be present (Puyol et al. 2017; Karimi Estahbanati et al. 2021; Barragán-Ocaña et al. 2021).

It should be noted that just as the circular economy transcends the mere proposition of overcoming the adversities of the Linear Economy and redefines values, the wastewater resource recovery strategy not only mitigates the environmental impacts of conventional wastewater treatments and reduces costs, as well as provides the foundation for a circular economy capable of closing the production process looping supplying fundamental resources such as water, biofuels, biopolymer, biofertilizers, biosurfactants, organic acids, enzymes, pigments, metals, and cellulose (Puyol et al. 2017; Pott et al. 2018; Karimi Estahbanati et al. 2021; Nagarajan et al. 2021).

These products could be classified, according to Pott et al. (2018), into three distinct categories as identified in Fig. 9.9.

Among the recoverable resources, water and energy are noteworthy. Water is an essential resource for life and vital for industries and agriculture. Coste-Maniere et al. (2019) warn of possible future water scarcity crises in the absence of responsible and sustainable management. Responsible management practices include the

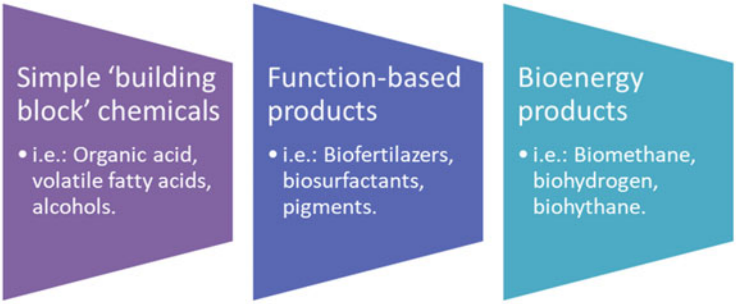


Fig. 9.9 Potential bioproducts of wastewater resource recovery (Pott et al. 2018)

reuse of adequate-treated industrial wastewater which may be used in the industry itself in cooling towers, boiler feed, fire protection, or directed to certain agricultural uses, depending on specific legislation (Karimi Estahbanati et al. 2021). The energy obstacle is discussed by Korhonen et al. (2018) who warns that, as with other processes, the Circular Economy process also requires energy. If the energy source has not come from renewable resources, this scenario could lead the system to unsustainable levels of resource depletion and waste/wastewater generation.

The energy issue is becoming a major challenge once approximately 75% of the world's current production coming from non-renewable sources (Korhonen et al. 2018). This demand for energy from renewable sources is forcing a large number of researchers to recover energy from industrial wastewater. Puyol et al. (2017) discussed biological technologies such as biodiesel production with oil extracted from oleaginous microorganisms (some species of bacteria, fungi, yeasts, and microalgae) and anaerobic digestion processes to produce biogas (methane) and biohydrogen, which using industrial wastewater as substrate.

Within this framework, hydrogen and methane production by anaerobic digestion (AD) has been increasingly investigated under multiple perspectives such as operation in two stages (acidogenic reactor preceded by methanogenic reactor), the influence of microorganism's selection in metabolic route, hythane production (H_2 and CH_4), mesophilic and thermophilic temperature operation (Ramos et al. 2020, 2021; Lovato et al. 2020; Fonseca et al. 2020). All the researches aim to obtain higher biofuels productivity and yields as well as treating industrial wastewater. These biofuels reduce the flux of virgin raw material for energy production and minimize greenhouse gas emissions (GGE) generated by untreated biodegradable industrial wastewater disposal (Moraes et al. 2017).

Despite several researches which developed or improved resource recovery technologies, Barragán-Ocaña et al. (2021) highlighted there are limitations that would be addressed technically and economically viable solutions for overcoming them.

Other concept related to wastewater using in a circular economy context is the circular bioeconomy. The concept of circular bioeconomy integrates principles of sustainability, circular economy, and bioeconomy, focusing on utilizing biomass in production processes involving multiple integrated outputs in where the value of feedstock is maximized by applying low-value by-products and waste/wastewater as raw materials in other processes (Nagarajan et al. 2021).

The circular economy regarding the macroeconomic model brings the concepts and requirements necessary for the construction of an economy that aims to balance its own growth and social/environmental aspects. EC construction is guided by knowledge of the environmental impacts due to anthropogenic actions and analyzes their potential consequences for the planet and future generations. But as with any major change, the construction of the circular economy must be firmly grounded, and a key foundation is how wastewater is perceived and treated by industries, government, and society.

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Chapter 10
Fats, Oils, and Grease (FOG): Opportunities, Challenges, and Economic Approaches

Jessica A. Deaver and Sudeep C. Popat

Abstract Fats, oils, and grease (FOG) represent a waste source with potential for producing bioenergy either as biodiesel or as biogas. FOG causes problems when allowed to enter wastewater collection systems due to the build-up of grease deposits in sewer pipes, and therefore grease traps are frequently deployed to collect FOG from high output sources. Consequently, an opportunity exists to direct FOG for renewable energy production instead of treating it at a wastewater treatment plant or landfilling it. Common methods for generating energy from FOG waste include anaerobic co-digestion with municipal, agricultural, or industrial wastewater sludges to improve biomethane production or conversion to biodiesel via a transesterification process. Other less explored uses include land application or composting. Challenges to reliable bioenergy production from FOG include its variable chemical composition, quality, and physical properties. Variability in composition leads to inconsistent biogas and biodiesel production, and current research seeks to address the underlying effect of composition on performance. Additional challenges include management of microbial resources in biological processes that recover energy from FOG, particularly in anaerobic co-digestion. Advances in culture-independent meta-omics techniques are enabling a deeper understanding of the role different groups of microorganisms play in FOG conversion and will continue to help enhance FOG conversion for bioenergy production. Furthermore, life cycle assessments offer important insights into the economic feasibility of incorporating FOG reuse into a circular economy. Overcoming these barriers will be essential for widespread, consistent implementation of FOG conversion to bioenergy products, facilitating a further loop closure in effort to obtain a full circular economy.

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Abbreviations

BMP	Biochemical methane potential
FAME	Fatty acid methyl esters
FOG	Fats, oils, and grease
GHG	Greenhouse gases
GTW	Grease trap waste
IUASB	Inverted upflow anaerobic sludge blanket
LCA	Life cycle assessment
LCFA	Long chain fatty acids
UASB	Upflow anaerobic sludge blanket
UCO	Used cooking oil

10.1 Fats, Oils, and Grease

10.1.1 Opportunities

The term fats, oils, and grease (FOG) covers a wide variety of waste products generated as by-products from food handling and preparation. There are three main categories of FOG waste: brown grease, yellow grease, and animal fats. Brown grease includes rendered trap or interceptor grease waste, yellow grease include used cooking oils (UCO), and animal fats includes tallow, white grease, and poultry fats (Badgett and Milbrandt 2020).

The lipids comprising FOG are primarily triglycerides, which are esters composed from a glycerol and three fatty acids, and free long chain fatty acids. The most common unsaturated fatty acids found in FOG wastes are oleic acid and linoleic acid, and the most common saturated fatty acids are palmitic acid and stearic acid (Elsamadony et al. 2021). Typically, grease waste and waste vegetable oils contain elevated levels of unsaturated fatty acids, while animal fats are rich in saturated fatty acids. Overall, FOG composition with regard to the percentage of each long chain fatty acid (LCFA) in the FOG waste is highly variable, especially over time and as per the source.

Despite the variations in physico-chemical characteristics of FOG waste, some consistencies exist. FOG is acidic with a typical pH between 4 and 5 due to the higher concentrations of free fatty acids formed by lipid hydrolysis or oxidation reactions that especially occur when deep frying food in the case of waste cooking oil and grease (Husain et al. 2014; Salama et al. 2019). The volatile solids content in FOG is also high, often representing more than 90% of the total solids. FOG also has a high C/N ratio due to its high lipid content. Additionally, the lipids comprising FOG have a higher theoretical biomethane yield than that of carbohydrates or proteins, 1 m^3 CH_4 kg^{-1} versus 0.42 m^3 CH_4 kg^{-1} or 0.63 m^3 CH_4 kg^{-1}, respectively (Jeganathan et al. 2006; Xu et al. 2018). FOG waste also typically has a high viscosity though the LCFA content affects the viscosity overall, with unsaturated fatty acid content inversely proportional to viscosity (Husain et al. 2014).

10.1.2 Sources

FOG waste is generated from the residential to industrial level. Residentially, waste oils and grease are generated from everyday cooking activities. Commercially, restaurants and other food handling businesses generate FOG that is typically collected in grease traps or interceptors. A typical grease trap holds approximately 50 gallons (190 L) of waste and is installed directly below the sink of the food preparation facility (Long et al. 2012). Grease interceptors are larger, typically 1000–2000 gallons (3785–7570 L) and are installed below ground outside of the building generating the waste. While grease traps and interceptors are designed to capture most of the FOG waste generated, some FOG may escape through, and their efficiency can be largely dependent on their maintenance (Wong et al. 2007). At the industrial level, FOG waste is generated at industrial food and animal processing plants. Milbrandt et al. (2018) estimated that 5 Tg FOG waste was generated in the USA in 2012. More than 50% of that FOG waste was animal fats, about 28% was from brown grease, and about 19% was from yellow grease.

10.1.3 Challenges

FOG waste creates problems at municipal and commercial levels when discharged into sewer systems. The direct release of waste oils and grease down drains can lead to the accumulation of FOG in sewer systems and downstream at wastewater treatment plants. In Scotland, an estimated 55% of sewer blockages are caused by residential disposal of FOG down drains (Arthur and Blanc 2013). In the Capital Regional District of British Columbia, Canada, residential sources account for 60% of the FOG entering sewer systems yearly. An estimated 2.2 billion liters of recoverable FOG waste is collected from grease traps/interceptors alone each year in the USA (Long et al. 2012). FOG sticks to the inside surfaces of pipes and drains, leading to build-up of fat deposits that reduce the flow of wastewater and can lead to sanitary sewer overflows (Husain et al. 2014). These overflows both pollute the environment and public built spaces. FOG waste can also form deposits onsite at treatment facilities, thus affecting unit operations for wastewater treatment. Because of the negative effects of FOG accumulation in sewer systems, handling and disposal of FOG wastes is typically regulated. The separation of FOG waste from other types of waste provides opportunity to direct FOG for potential uses.

Even when collected separately from other wastewaters, FOG waste is difficult to treat on its own. The high C/N ratio is not ideal for biological activity required to degrade FOG. Therefore, to treat FOG biologically, it must be mixed with other waste sources that provide an appropriate concentration of missing nutrients to support microbiological activity. Co-digesting FOG with municipal wastewater sludge can improve digester performance because sludge has a low C/N ratio, therefore FOG is a complementary waste. FOG additions have been shown to help maintain an ideal C/N ratio of ~25 (Li et al. 2011). Maintaining a proper FOG loading balance is also crucial because too much FOG can lead to a nitrogen deficiency, resulting in the build-up of volatile fatty acids and subsequent process failure (Salama et al. 2019).

10.1.4 Handling and Disposal

FOG wastes are transported (or remain on-site at) to rendering operations, publicly owned treatment works (POTW), municipal solid waste landfills, or other waste handling facilities for either disposal, re-purposing, or treatment (Badgett and Milbrandt 2020). Rendering plants often convert raw FOG types into valuable products, such as forms of yellow grease, brown grease, and animal fats useful for the industrial production of products, such as animal feed, oleochemicals, and biofuels. In industry terms, UCO is often distinguished from yellow grease and is considered rendered or filtered UCO. Consequently, restaurants often collect UCO separately from other grease trap wastes. Haulers collect UCO and either transport it to rendering facilities, landfills, or POTW or process it on-site, if possible. Filtered UCO has a market value for reuse, for example to produce biofuels or for use by oleochemical companies, therefore it is often regarded more like a product than a waste.

Animal fats are produced by meat processing facilities and the rendering processes for them are often split into two categories: edible and inedible (Badgett and Milbrandt 2020). Edible processing yields lard and edible tallow while inedible processing produces inedible tallow and grease frequently used as livestock feeds, oleochemicals, and other domestic products. These are also considered end-products rather than wastes because they have a market value.

Brown grease is distinguished from grease trap wastes under industry terms and is considered the rendered or processed form of grease trap wastes (Badgett and Milbrandt 2020). There is more variability in the end-of-use pathways for brown grease; depending on the location, brown grease may end up being processed by a rendering facility, disposed of in a landfill or POTW, recycled by private grease recycling facilities, or used for biofuels. As of May 2017, grease trap wastes are no longer allowed to be used in animal feed (AAFCO 2017). This new regulation limits a potential industrial application for brown greases, and is expected to lower the demand for brown greases thus increasing the amount sent to landfills and POTW (Badgett and Milbrandt 2020). There are several regulations directing the proper handling and disposal of FOG in the USA. Regulatory bodies in the USA include the EPA, DOT, FDA, and other state or local regulatory bodies. Regulations and governing bodies are described in depth by Badgett and Milbrandt (2020).

10.2 Reuse Options

10.2.1 Anaerobic Co-digestion

10.2.1.1 Opportunities

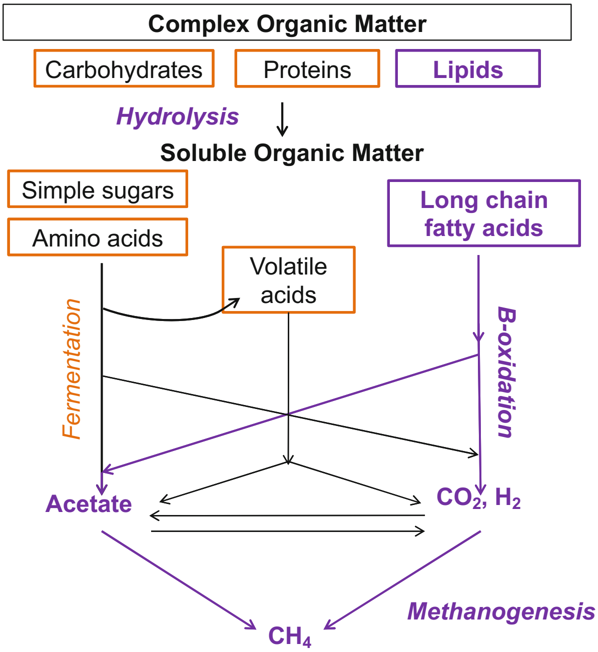
Anaerobic co-digestion with FOG contributes to a closed waste-to-energy loop by diverting FOG from less desirable disposal pathways, i.e., landfilling, while producing a value-added product, biogas, with the potential to generate revenue in the form of tipping fees and saving money by providing on-site combined heat and power (CHP) production. Municipal wastewater sludge is often treated via anaerobic digestion, a process that utilizes an anaerobic consortium of microorganism to degrade the organics in sludge and produce biogas that is composed of methane (50–75%), CO_2 (25–50%), N_2 (2–8%), and trace levels of other gases including H_2S, H_2, NH_3, and volatile compounds (Li et al. 2019). Estimates suggest 43% of US wastewater treatment facilities with anaerobic digestion do not have CHP; combined these facilities handle 60% of US wastewater flows (USEPA 2011). While a standard digester gas recovery system can recover 20–40% of the energy necessary to power wastewater treatment plant operations, addition of FOG waste can increase biogas production by 30% or more and allow over 50% of the WWTP's electricity to be generated on-site (Davidsson et al. 2008; Kabouris et al. 2008, 2009a, b; Crawford and Sandino 2010; Long et al. 2012; Grosser and Neczaj 2016). Using FOG for co-digestion offers potential economic benefits as well. Though the financial benefits ultimately depend on the location, demand, cost of digestion, and cost of disposal, the FOG tipping fee is negative, indicating that there is a greater economic benefit to receive FOG than the cost (Salama et al. 2019). Co-digestion is also the most economical when applied to existing digesters and at facilities with high electricity costs and low residual disposal costs (Parry and Fillmore 2016).

FOG co-digestion may also increase biogas quality. While proteins and carbohydrates can be converted into a biogas containing 50–58% methane, fats can be converted into a biogas containing 66–73% methane (Gujer and Zehnder 1983). This discrepancy in methane content is attributable to the lower mean oxidation state of carbon atoms in lipids compared to that of carbon atoms in protein or carbohydrates. Consequently, the higher the FOG loading, the greater the potential methane yield. Increasing the methane content of the biogas can help reduce costs associated with biogas upgrading necessary for downstream energy production purposes.

10.2.1.2 FOG Degradation

Lipids are the primary macromolecule comprising FOG in addition to simpler substrates, primarily long chain fatty acids (LCFA). The anaerobic food web with specific lipid degradation pathways highlighted is shown in Fig. 10.1. Hydrolytic bacteria excrete lipase, an enzyme that degrades lipids, convert them to their

Fig. 10.1 Anaerobic food web. Fats, oils, and grease are primarily composed of lipids. The lipid degradation pathway is highlighted in purple



elemental parts, LCFA and glycerol. LCFA are carboxylic acids with aliphatic chains that are either unsaturated, containing one or more double bonds, or saturated, containing only single bonds. As the main constituent and degradation product of FOG, LCFA conversion is integral to successful anaerobic FOG co-digestion. LCFA are degraded via β-oxidation, a cyclical series of catabolic reactions that produce acetate and hydrogen each cycle (Elsamadony et al. 2021). β-oxidation begins with activation of the LCFA by the enzyme fatty acyl-CoA synthetase (FACS) to form a fatty acyl CoA. The fatty acyl CoA then enters the β-oxidation cycle. The first reaction in the cycle is oxidation of the fatty acyl CoA by acyl-CoA dehydrogenase, which transfers two protons to the electron carrier $FADH_2$ and forms Trans-delta^2-Enoyl-CoA. The second reaction hydrates oxidized fatty acyl CoA to yield 3-L-Hydroxyacyl CoA. The third reaction uses 3L-hydroxyacyl-CoA dehydrogenase to oxidize 3-L-Hydroxyacyl CoA, transferring two more protons to the election carrier NADH and forming β-Ketoacyl CoA. H_2 gas is formed from the NADH molecule donating electrons to protons (Lin et al. 2016). The final reaction is thiolysis catalyzed by β-ketothiolase, which removes the terminal acetyl-CoA and yields an $_{n\text{-}2}$LCFA, which returns to the first oxidation step. The acetyl-CoA is hydrolyzed to acetate (Sousa et al. 2009). This summary of β-oxidation assumes an even number of carbon atoms and complete saturation. LCFA with odd numbers of carbon atoms generate propionate as well (Sousa et al. 2007). Additionally, the initial mechanism of unsaturated LCFA degradation is unknown. Two pathways have been suggested (Elsamadony et al. 2021). One, unsaturated LCFA are first fully saturated by hydrogenation, and then enter the previously described β-oxidation cycle. Two, direct unsaturated LCFA are decomposed by β-oxidation. It remains unclear which initial unsaturated LCFA degradation pathway is followed.

β-oxidation is a nonspontaneous, endogenous reaction. Thus, to make the overall energetics favorable and maintain a negative overall Gibbs free energy, LCFA-oxidizers depend on syntrophic partners to metabolize acetate and hydrogen to methane. Hydrogenotrophic methanogens use H_2 as an electron donor and CO_2 as a carbon source to produce methane. These archaea help maintain a low H_2 partial pressure necessary for efficient LCFA degradation. H_2 and CO_2 may also be used by homoacetogens in some cases to produce acetate. Additionally, acetoclastic methanogens and syntrophic acetate oxidizers use acetate to produce methane or H_2/CO_2, respectively. Ultimately, maintaining syntrophic interactions is essential for anaerobic co-digestion of FOG.

10.2.1.3 Challenges

Although FOG co-digestion has been shown to improve biogas production, operators are often still hesitant to implement FOG co-digestion because FOG co-digestion can also result in stalled digestion. Problems with FOG include sludge flotation and washout, digester foaming, and inhibition of methane production due to high concentrations of LCFA. Sludge floatation and washout appears to be an issue with high-rate systems, such as upflow anaerobic sludge blankets (UASB) (Jeganathan et al. 2006). UASB rely on maintaining a sludge bed at the bottom of the reactor enabling a longer solids retention time than hydraulic retention time. If that sludge bed floats due to a high lipid content, then there is a risk of losing the anaerobic microorganisms required for anaerobic degradation of organics to washout. One novel solution is to use an inverted UASB (IUASB) designed by Alves et al. (2009). In an IUASB, the sludge bed is maintained at the top of the reactor rather than the bottom, taking advantage of floatation of high lipid wastes.

Digester foaming occurs due to the surfactant properties of lipids. Surfactants have both hydrophilic and hydrophobic ends. The hydrophobic end moves toward the headspace of a reactor, disrupting the surface tension and enabling foaming. Digester foam may clog gas collection pipes and block gas mixing devices, leading to operational problems. Digester foaming has been reported in some cases, but not others. More research is needed to understand the operational parameters that increase the risks of digester foaming when co-digesting FOG.

LCFA are also potentially inhibitory to the anaerobic digestion process. β-oxidation of LCFA appears to be slower than hydrolysis of lipids, thus risking accumulation of LCFA (Cirne et al. 2007). Originally, LCFA were suggested to exert a bactericidal effect via cell membrane lysis, and recovery of methane production after an overloading event was attributed to the survival of a few methanogens (Koster and Cramer 1987; Angelidaki and Ahring 1992; Rinzema et al. 1994). However, other studies have demonstrated that LCFA can limit methanogenesis above specific thresholds, but not irreversibly (Shin et al. 2003; Kim et al. 2004; Deaver et al. 2020). This phenomenon has been attributed to the reduction in mass transport of substrates and products due to LCFA adsorbing to bacterial cell membranes (Pereira et al. 2003; Pereira et al. 2004).

10.2.1.4 Solutions

Several mechanisms for alleviating the potential negative effects of FOG have been studied including pretreatment of FOG, use of additives, and microbial acclimatation. FOG pretreatment methods attempted include mechanical, chemical, and biological treatment methods (Salama et al. 2019). Mechanical methods include high pressure homogenization, which utilizes an externally applied pressure to homogenize fat globules that form in high lipid wastes, such as FOG. Originally developed to stabilize food and dairy emulsions, high pressure homogenization has been shown to decrease fat globule size in dairy milk (Thiebaud et al. 2003) and is a suggested option for FOG pretreatment (Salama et al. 2019).

Microwave radiation is another potential mechanical treatment option. Irradiation with microwaves rapidly and efficiently heats substrates, which allows decreased reaction times. More research is necessary to elucidate the effectiveness of microwave pretreatment on FOG, but other high lipid wastes have been effectively pretreated with microwave irradiation. One study applied this technique to palm oil mill effluent. An irradiation frequency of 2450 MHz for 3 min increased the soluble COD from 11% to 21% and improved biomethane production by 57% during treatment by anaerobic digestion (Saifuddin and Fazlili 2009).

Ultrasonication is another mechanical treatment option. This method produces ultrasound waves that promote microbubble formation that grow and implode (cavitate) when they reach an unstable diameter. Each cavitation event increases the local pressure and temperature at the liquid–gas barrier, which results in intensive mixing of insoluble liquids, such as oil and water, thus forming stable emulsions (Salama et al. 2019). However, Li et al. (2013) demonstrated that ultrasonication of FOG prior to anaerobic digestion did not improve methane yield, and even increased the lag phase from FOG addition to methane production.

Thermal pretreatment is a method that has been applied on an industrial scale for biomass hydrolysis, including sludge, manure, lignocellulosic wastes, and algal biomass. Studies have shown thermal pretreatment has the potential to increase methane production potential from FOG by more than 30% and decrease the lag phase to methane production by 82% (Wilson et al. 2012; Li et al. 2017b). Thermal pretreatment increased FOG degradation to volatile fatty acids, such as acetate and propionate, which are more readily used for methane production reactions. Because LCFA may be more inhibitory than lipids, pretreatment that helps reduce LCFA intermediates in the lipid to methane pathways may be the best pretreatment tool. Furthermore, thermo-chemical treatment methods that integrate an elevated pH via the addition of basic compounds, such as NaOH or KOH, have also been shown to be effective pretreatment for lipid-rich wastes including FOG. The combination of temperature and alkali addition promotes saponification to convert insoluble triglycerides to their component parts, LCFA and glycerol in the form of suspended

LCFA-salt micelles, which are more accessible to microorganisms (Elsamadony et al. 2021).

Studies have also demonstrated successful pretreatment of FOG with lipase, an enzyme that hydrolyzes lipids. FOG wastes pretreated with lipase include meat processing waste, oil processing waste, dairy wastewater, fish processing wastewater, and FOG-rich food waste. Meng et al. (2015) demonstrated that addition of lipase to the substrate, FOG-rich food waste, improved methane production, but addition directly to an anaerobic digester did not. A follow-up study demonstrated that compared to untreated wastes, lipase treated animal fat, vegetable oil, and floatable grease increased methane production by 81–154%, 27–54%, and 37–41%, respectively, when treated for 24 h at 40-50 °C and overall digestion time also declined. Highlighting lipase addition as a pretreatment, not directly to the anaerobic digestion reaction is an important caveat. In addition to Meng et al. demonstrating lipase as a more effective pretreatment strategy, Cirne et al. (2007) demonstrated a lengthened lag phase when treating triolein, a triglyceride comprised of a glycerol head and three oleate units. Enhanced lipid hydrolysis during anaerobic digestion may initially inhibit methane production due to the accumulation of LCFA that exert an inhibitory effect on methanogenesis.

Additives have been explored to mitigate LCFA-induced inhibition in anaerobic digestion as well. Addition of metal cations, including Na^+, K^+, Ca^{2+}, Mg^{2+}, and Fe^{2+}, has been shown to reduce LCFA-induced inhibition (Elsamadony et al. 2021). Studies on addition of Ca^{2+} ions suggest that Ca^{2+} helps to stimulate lipase activity (Mostafa et al. 2017; Hendriks et al. 2018). Torcello-Gómez et al. (2018) demonstrated that electrostatic interactions between negative charge on lipase and the Ca^{2+} reduce intermolecular repulsion forces between lipase and triglyceride, thus enhancing lipase activity. Additionally, Salama et al. (2020) demonstrated that a 1 g/L Ca^{2+} concentration doubled the relative abundance of *Syntrophomonas*, a common LCFA-degrading bacterial genus, during anaerobic co-digestion of FOG. Other additives include natural adsorbents, such as bentonite or zeolite, which provide a scaffolding for microorganisms that enables biomass protection from washout and increased substrate uptake. The adsorbents have acidic sites that attract the negatively charged lipid cell membranes as well as LCFA as described by Elsamadony et al. (2021). Studies examining the effect of natural adsorbent additions have described increases in maximum methane production rate from 12% to 310% (Palatsi et al. 2009, 2012; Elsamadony et al. 2021). Temperature or chemical pretreatment of natural adsorbents may also increase their performance (Delkash et al. 2015; Li et al. 2017a; Ma et al. 2018).

Microbial acclimatation may also improve the chances of successful FOG co-digestion. Several studies have demonstrated that increasing the FOG organic loading rate stepwise alters microbial communities and allows them to adapt to high FOG conditions without resulting in an inhibition phase (Silvestre et al. 2011; Ziels et al. 2016; Amha et al. 2017; Saha et al. 2019). The microbial community changes during acclimatation will be discussed further in Sect. 10.3. Overall, the strategies discussed here from FOG pretreatment to microbial acclimation are all potential strategies for continuing to improve methane production from FOG wastes for use in renewable energy applications.

10.2.2 Biodiesel Production

10.2.2.1 Opportunities

Biodiesel is an alternative to petroleum-based diesel products typically produced from vegetable oils or animal fats (Rodionova et al. 2017). Biodiesel is produced by transesterification, a process that involves chemically reacting oils or fats with an alcohol, typically methanol or ethanol, in the presence of a homogenous or heterogenous catalyst to produce fatty acid methyl esters (FAME) (Naik et al. 2010). The final product yields a mixture of glycerol and FAME. In biodiesel, glycerol comprises 10% (w/w) of the final product (Yang et al. 2012). Glycerol is a high value co-product primarily used as a feedstock for value-added chemicals and in animal feeds. Waste grease are potential fat and oil sources for biodiesel product. Re-purposing waste FOG for biodiesel production is advantageous over biodiesel produced from vegetable oils because vegetable oils have dual purpose as a feed crop. Thus, an opportunity exists to offset agricultural demand while reducing dependence on traditional fossil fuels by re-purposing waste FOG from a variety of sources, such as chicken fat (Alptekin and Canakci 2011), UCO (Foteinis et al. 2020), and grease trap waste (Hums et al. 2018).

10.2.2.2 Transesterification Mechanism

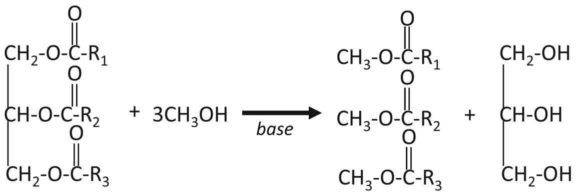
The vegetable oils that biodiesel is traditionally derived from are comprised primarily of triglycerides. These triglycerides are composed of a mix of linear fatty acids with an average of 18 carbons and zero to three double bonds and a glycerol head (Santacesaria et al. 2012). To produce biodiesel, these triglycerides undergo transesterification to produce esters. Commercial-scale biodiesel production most commonly employs base-catalyzed transesterification using an alcohol. Typically, methanol is used because of its low cost and advantageous chemical properties (Ma and Hanna 1999). Methanol is the shortest chain alcohol and polar allowing it to react quickly and to readily dissolve bases like NaOH.

Transesterification proceeds in a series of steps (Ma and Hanna 1999). First, the alkaline catalyst, usually NaOH or KOH, first reacts with methanol to form an alkoxide, which is a stronger nucleophile. Then, the carbonyl carbon undergoes a nucleophilic attack by the alkoxide to form a tetrahedral intermediate. The intermediate can either revert to its original form or proceed to form a methyl ester. This step repeats three times, first converting the triglyceride to a diglyceride and a FAME, then converting the diglyceride to a monoglyceride and another FAME, and finally converting the monoglyceride to glycerol and a third and final FAME. The final product contains FAME and crude glycerol. The reversible nature of the transesterification process also means that the various reaction forms will exist in equilibrium, requiring an excess of methanol to be supplied to drive reaction equilibrium to the products. Stoichiometrically, a 3:1 ratio of alcohol to triglyceride is required for complete transesterification, therefore exceeding this ratio drives the reaction to maximum FAME yield (Ma and Hanna 1999). Additionally, the reaction must remain dry because moisture hinders the reaction by encouraging fatty acid formation via hydrolysis. Acid catalyzed transesterification is also possible, but not often used commercially because the process proceeds more slowly.

10.2.2.3 Challenges

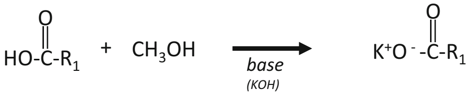
The variable composition and high concentrations of free fatty acids (FFA) in FOG lead to challenges for conversion to biofuels. While traditional vegetable oils are mainly comprised of triglycerides with few FFA (<0.5% w/w), FOG wastes contain a higher percentage of FFA. The percentage FFA in FOG can vary drastically, although on average FOG collected from restaurants contains approximately 15% FFA (Abomohra et al. 2020). During base-catalyzed transesterification, free fatty acids react with the base catalyst to form soap (Fig. 10.2). Saponification is undesirable because it leads to catalyst and ester loss which degrades the quality of the product (Lotero et al. 2005). Thus, other methods for converting waste FOG to biodiesel product are necessary. Consequently, current research focuses on developing methods for efficient and cost-effective conversion of both triglycerides and

Fig. 10.2 Base and acid catalyzed FAME production pathways from TG or FFA. (**a**) TG base catalyzed transesterifiation. (**b**) FFA base catalyzed transesterifiation. (**c**) FFA acid catalyzed transesterifiation



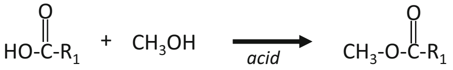
$$\begin{array}{l} CH_2\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_1 \\ | \\ CH\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_2 \\ | \\ CH_2\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_3 \end{array} + 3CH_3OH \xrightarrow[\text{base}]{} \begin{array}{l} CH_3\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_1 \\ CH_3\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_2 \\ CH_3\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_3 \end{array} + \begin{array}{l} CH_2\text{-OH} \\ | \\ CH\text{-OH} \\ | \\ CH_2\text{-OH} \end{array}$$

(a) TG base catalyzed transesterification



$$HO\text{-}\overset{\overset{O}{\|}}{C}\text{-}R_1 + CH_3OH \xrightarrow[\substack{\text{base} \\ (KOH)}]{} K^+O^-\text{-}\overset{\overset{O}{\|}}{C}\text{-}R_1$$

(b) FFA base catalyzed transesterification



$$HO\text{-}\overset{\overset{O}{\|}}{C}\text{-}R_1 + CH_3OH \xrightarrow[\text{acid}]{} CH_3\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_1$$

(c) FFA acid catalyzed esterification

free fatty acids in FOG wastes to biodiesel. Potential methods for accomplishing this feat are described in the following section. The biodiesel produced must ultimately meet quality standards defined by EN14214 and ASTM D6751.

10.2.2.4 Solutions

A wide variety of catalytic methods have been explored to efficiently and cost-effectively to convert waste FOG into high-quality biodiesel. Compared to homogenous base catalysts, homogenous acid catalysts are a better option for high FFA wastes because they are insensitive to FFA presence (Kulkarni and Dalai 2006). Acids, like sulfuric acid or hydrochloric acid, catalyze both esterification of FFA and transesterification of triglycerides simultaneously (Jacobson et al. 2008). Homogenous acid catalyst conversions greater than 90% have been reported using molar ratio of methanol to waste cooking oil of 20:1 or greater (Freedman et al. 1984; Wang et al. 2006). However, acid catalysis is not ideal because the reactions proceed more slowly, require a higher reaction temperature, require a high ratio of alcohol to oil, and may result in corrosion problems (Wang et al. 2006; Jacobson et al. 2008). Additionally, homogenous catalysts, either acids or bases, are liquids mixed into the reaction making their removal difficult (Lam et al. 2010). Consequently, homogenous acid catalysts have not been widely adopted at a commercial scale.

Another method is two-step homogenous acid and base transesterification. In this process, an acid catalyst is added first to esterify FFA with methanol, converting the FFA to FAME. Once the FFA content drops below 1%, then a base catalyst is added to transesterify triglycerides with methanol, converting the triglycerides to FAME (Lam et al. 2010). Conceptually a two-step process aims to overcome the limitations of homogenous acid or base-catalyzed transesterification alone. High FAME yields have been obtained using this method, however, it requires large amounts of catalyst additions. The first acid catalyzed step still proceeds slowly unless accelerated by addition of more acid catalyst. The acid catalyst must then be removed or neutralized by adding more base catalyst than the base-catalyzed reaction alone would require. Extra base additions raise the cost of the process, adding to the cost of biodiesel production (Kulkarni and Dalai 2006).

The drawbacks of homogenous acid or base-catalyzed transesterification led to the development of more easily removable heterogenous catalysts. Heterogenous acid catalysts include tungstate zirconia, zirconium oxide, sulfonic ion-exchange resins, and more as summarized by Lam et al. (2010). Benefits not only include those of homogenous acid catalysts, an insensitivity to FFA and simultaneously esterification and transesterification, but also easy removal from the reaction medium, elimination of the biodiesel washing step, catalyst reuse and recycling, and reduced incidence of corrosion. Ideally a heterogenous acid catalyst would have large pores with many strong acidic sites and a hydrophobic surface. The major drawback is that reaction rates are still limiting. The research focus for these catalysts includes exploring different types of solid acid catalysts and understanding the extract reaction mechanisms for triglycerides reacting with the acidic sites of the solid acid catalysts.

Enzyme catalysts are another option for the transesterification of FOG wastes to biodiesel. The advantages to enzyme catalysis include a high FAME recovery rate, ability to reuse the enzyme catalyst, no production of undesirable chemical by-products, and insensitivity to FFA (Kulkarni and Dalai 2006). At a commercial scale, however, enzymes are expensive to produce, reaction rates are slow, and there is risk of enzyme deactivation (Bajaj et al. 2010). Even so, research focused on producing various novel enzymes is demonstrating potential utility for this method to produce biodiesel from waste lipids. Yan et al. (2012) demonstrated that tandem lipases co-expressed by *E. coli* can be used to efficiently convert waste grease to biodiesel. The lipases esterified FFA and transesterified triglycerides simultaneously and could then be recovered and reused several times as well to enhance the economy of the method. However, the study was performed at a lab-scale, and scale-up remains a challenge for alternative methods to traditional homogenous base-catalyzed transesterification.

In addition to catalyst addition, other reaction parameters must also be optimized to maximize conversion of FFA. Temperature and reaction time are two significant parameters. Tran et al. (2018) demonstrated that shorter reaction time, 3 h versus 24 h, in combination with a higher temperature, 75 °C versus 55 °C, increased FFA conversion with a lower catalyst load, 3% w/w versus 10% w/w. The time and temperature will depend on the type of catalyst used as well, so studying these parameters using the various catalysts suggested will be necessary to determine the best conditions for optimizing biodiesel production. Mixing speeds are also an important consideration because methanol and lipids are immiscible. Therefore, some degree of mixing will typically be necessary to achieve adequate conversion.

Other solutions suggested have included numerous ways of pretreating waste FOG to reduce the FFA content. Besides acid esterification, other methods explored include steam stripping, nano-catalytic technology, biological conversion, glycerolysis, and supercritical esterification (Abomohra et al. 2020). Despite the wide range of in situ conversion methods and pretreatment techniques researched, there is no universal solution for scaling up biodiesel production from waste FOG because of the large variety of FOG sources and composition. The best biodiesel production method should be cost-effective, require low energy inputs, minimize chemical inputs, reduce toxic by-products, and scale up relatively easily.

10.2.3 Other Applications

10.2.3.1 Composting

Another alternative to landfill disposal of FOG wastes is composting. Composting involves the aerobic treatment of organics and is most used with food waste. One advantage of composting FOG is the production of a soil amendment that may be sold and reduce potential methane emissions from FOG in landfills (Long et al. 2012). The disadvantages of composting FOG are the energy expenditure possible during the composting process and potential inhibition of the composting biological processes, especially when composting wastes with large lipid fractions (Brown et al. 2008). As composting also depends on biological processes, nutrient levels, moisture, pH, temperature, and oxygen content are vital for process success. These properties are affected by the chemical composition of lipids, therefore affecting important parameters of the composting process such as pH, acidity, and time to reach the initial thermophilic stage (Chang and Hsu 2008). Studies examining composting of high fat wastes have studied the impact of fat percentage, physicochemical properties, such as pH control, and microbiology during the various composting phases. One study demonstrated the utility of a thermophilic oxic process for composting highly concentrated lipid wastes, but supplementation of a nutrient blend was necessary for achieving a high degree of lipid conversion (>60%) in 120 h (Nakano and Matsumura 2001). Sasaki et al. (2003) demonstrated maintaining a pH around 7 enables approximately 80% lipid degradation of a composted oil waste. The authors found that maintaining a C/N ratio between 10 and 40 also helped lipid conversion through nitrogen amendments. One disadvantage of composting FOG is its inherently high C/N ratio. Another method for maintaining an adequate C/N ratio is co-composting. Co-composting, similar in concept to co-digestion, is an altered composting strategy that involves simultaneously composting FOG wastes with other wastes, such as sewage sludge or municipal solid wastes, that have a low C/N ratio. Gea et al. (2007) demonstrated that a 30% fat content in co-composting with sewage sludge is ideal for achieving 80%–90% fat reduction, and that a maximum of 50% fat content can be achieved. However, higher percentages lengthen time to compost due to a longer initial thermophilic phase. Maximum lipase activity was also observed at thermophilic temperatures. Composting high fat wastes may enable FOG reuse, but the composting process must be carefully managed to ensure proper nutrient balances and to prevent biological inhibition from high lipid concentrations.

10.2.3.2 Land Application

Direct land application is another strategy explored for re-purposing FOG waste, particularly grease trap wastes. Land application of grease trap waste acts as a soil conditioner that can increase organic content, increase moisture, decrease nitrogen leaching, and improve soil structure (Rohm 2005). Increasing the organic content of the soil enables better moisture retention, and a slower release of nitrogen from organic materials results in decreased nitrogen leaching. The improved soil structure is attributed to an increase in microbial decay lending cellular materials that help bind silt and fine particles together. Land application of grease trap wastes is most successful when the land is well managed to maintain favorable soil conditions enabling soil microorganisms to readily degrade the grease trap waste. These conditions include warmth, high moisture, oxygenation, and nutrient, especially nitrogen, availability. Careful management record of application rates, crop management, and soil nutrient records are necessary to support purported benefits. Regulation of grease trap waste land application is covered in the USA at a national level by 40 CFR Part 257 to ensure proper handling and application of grease trap wastes to agricultural lands. Other high FOG wastes, such as food waste high in FOG, have also been studied for land application. Rashid and Voroney (2004) concluded that FOG application rates should not exceed 10 Mg/ha/year for the corn fields used in their study. Additional nitrogen supplements were required, but the additions significantly increase the organic carbon content of the soils. Overall, land application may be a viable and beneficial end-of-use pathway for some FOG waste.

10.3 Microbial Conversion of FOG Waste

The development of next generation sequencing techniques has made understanding anaerobic microbial processes in systems utilizing co-digestion a major research focus. Anaerobic microbial communities are composed of microorganisms that complete four main steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Hydrolytic microorganisms that excrete extracellular hydrolases break down particulate matter into soluble components. Acidogenic bacteria metabolize the products of hydrolysis to produce volatile fatty acids (VFA), CO_2, and H_2. Acetogenic bacteria further metabolize VFA to acetate, CO_2, and H_2. Methanogenic archaea use acetate, CO_2/H_2, or other small alcohols as their substrates to produce methane. Accumulation of acetate, CO_2, H_2, and VFA can lead to product-level inhibition of upstream processes, thus maintaining syntrophic interactions that consume products formed is vital for successful anaerobic co-digestion.

FOG wastes are high in lipids, requiring microorganisms capable of breaking down lipid waste via the pathways described in Sect. 10.2.1.2. Lipid hydrolyzing bacteria are found within the phyla *Firmicutes*, *Bacteroidetes*, *Fibrobacter*, *Spirochaetes*, and *Thermotogae* (Azman et al. 2015). The most abundant phyla are typically dictated by start-up and operation parameters, but *Firmicutes* and *Bacteroidetes* are often the most abundant. Bacteria in families *Syntrophomonadaceae* and *Syntrophaceae* degrade LCFA via β-oxidation. LCFA-grading genera include *Syntrophomonas, Syntrophothermus, Syntrophus,* and *Thermosyntropha* (Sousa et al. 2007). Microorganisms belonging to family *Syntrophomonadaceae* are metabolic specialists; they only metabolize fatty acids in syntrophy with hydrogen/formate utilizing microorganisms (McInerney et al. 2008). The specificity of LCFA-oxidizers to unsaturated versus saturated LCFA is also not well understood. Sousa et al. (2007) demonstrated that palmitate enriched cultures were able to degrade fatty acids with four to 18 carbons but could not degrade oleate (C18:2). Oleate enriched cultures were able to degrade a wider variety of fatty acids, including palmitate. With the initial step in the degradation of unsaturated fatty acids still unclear, it is also not conclusively known whether one or two microorganisms perform that initial step and β-oxidation (Sousa et al. 2009). However, it has been suggested that facultative anaerobes, *Pseudomonas* and *Rheinheimera*, can convert oleate to palmitate through mechanisms de-coupled with methanogenesis (Cavaleiro et al. 2016). Studies assessing co-digestion of municipal wastewater sludge with FOG using biochemical methane potential (BMP) assays and lab-scale semi-continuous digesters demonstrated that palmitic acid accumulates to much higher concentrations than other LCFA even when the initial FOG is primarily composed of equal proportions of oleic, linoleic, and palmitic acids (Deaver et al. 2020, 2021). Palmitic acid was also the primary LCFA to accumulate in BMP assays treating rendering wastewater (Xie et al. 2021). These studies suggest palmitic acid conversion may be key for enabling FOG conversion during anaerobic co-digestion.

LCFA-oxidizers act in syntrophy with acetoclastic and hydrogenotrophic methanogens to maintain low concentrations of hydrogen and acetate (Schink 1997; Sousa et al. 2009). Early reports suggested that LCFA irreversibly inhibited methanogens above threshold concentrations via cell membrane lysis, and any methane recovery was attributed to growth of ~0.2% cells that survived the toxic load (Kabara et al. 1977; Koster and Cramer 1987; Angelidaki and Ahring 1992; Rinzema et al. 1994). However, later studies demonstrated only a partial, reversible inhibition by LCFA at varying concentrations dispelling the idea that LCFA always cause major cell lysis (Shin et al. 2003; Kim et al. 2004; Pereira et al. 2004). Alternative potential inhibition mechanisms include mass transportation limitations due to LCFA adsorption onto biomass, digester foaming, and substrate-level inhibition (Pereira et al. 2003, 2005; Shin et al. 2003; Kim et al. 2004).

Syntrophic partnerships between methanogens and LCFA-oxidizers have been studied in both co-culture and native community bioreactor experiments. Common hydrogenotrophic methanogen partners used in co-culture with *Syntrophomonas* species are *Methanospirillum* and *Methanobacterium* (Sousa et al. 2009). Acetoclastic methanogens *Methanosaeta* and *Methanosarcina* also act syntrophy with LCFA-oxidizers. There are conflicting reports on whether *Methanosarcina* or *Methanosaeta* is more likely to be the dominant acetoclastic methanogen in bioreactors treating high lipid wastes. Anaerobic digesters with high concentrations of palmitic acid were reported to have higher concentrations of *Methanosaeta*, and *Methanosaeta* were shown to be more sensitive to palmitate in pure cultures (Silva et al. 2016). However, other studies have noted a predominance of *Methanosarcina* in batch assays or semi-continuous digesters co-digesting wastewater sludge and FOG (Kurade et al. 2019; Deaver et al. 2021). The feeding regime and reactor acetate concentrations may ultimately determine which acetoclastic methanogen thrives. *Methanosarcina* have a high half saturation coefficient and maximum specific growth rate allowing them to dominate in high acetate concentrations, while *Methanosaeta* have a low half saturation coefficient and maximum specific growth rate allowing them to dominate in low acetate concentration conditions (Conklin et al. 2006).

Microbial acclimatation is one suggested strategy for ensuring successful FOG co-digestion. Amha et al. (2017) demonstrated that a substantial lag preceding methane production in early FOG co-digestion runs was reduced in subsequent runs. Additionally, the relative activity of *Syntrophomonas* increased in conjunction with methane production. Ziels et al. (2016) also demonstrated that stepwise increases in FOG loading rates maintain digester function while slowly increasing the methane production rate. The associated microbial community shifted as the FOG loading increased. *Syntrophomonas* relative abundance increased from 1.2% to 9%, and the FOG loading rate relative to *Syntrophomonas* abundance was positively correlated with reactor LCFA concentrations. In an acidogenic fermentation reactor, microbial acclimatation was shown to play an important role in lipid conversion processes (Saha et al. 2019).

Microbial processes are vital for other biological FOG conversion processes including composting and co-composting processes. Oils and fats present a challenge to composting organic waste because the degradation rate is slower than that of carbohydrates and proteins. Consequently, the feeding rate per day must be lower than the oil and fat degradation rate to prevent accumulation of fats and oils that impedes organic conversion (Nakasaki et al. 2004). Fats and oils accumulation increases compost viscosity and interferes with the transport of heat and water to decrease the decomposition efficiency. Gea et al. (2007) demonstrated that moisture is vital for microbial activity during co-composting of fats with sewage sludge. Over 40% moisture was considered necessary for key microbial community members and for maintaining thermophilic temperatures. Microorganisms also degrade fats better during the thermophilic phase so maintaining a thermophilic phase is important for composting lipid-rich wastes. Detailed studies on the microbial communities during composting of high FOG wastes are lacking. However, microbial communities studied in fed-batch aerobic composters fed varying ratios of food waste demonstrated that microbial communities change from mesophilic to thermophilic to mature compost phases with temperature being the most influential factor for community succession (Wang et al. 2017). Fats and oils present in the food waste were degraded best at a 5% food waste feed ratio. Composting may perform better with lower loads of FOG. Further research is necessary to determine the effect of high-lipid content wastes on the microbial communities acting in composting processes.

10.4 Economic Implications for a Circular Economy

To effectively incorporate FOG waste into a circular economy, renewable energy production from FOG waste must be economically and environmentally beneficial. Life cycle assessments (LCA) are a common method for examining the impact of a process or product over its entire life. The life for FOG waste begins at collection and transportation and ends with the final product (biodiesel, methane gas). The steps in between can include pretreatment, processing (transesterification, anaerobic digestion, et cetera), and refinement of the biogas or biofuel product (Foteinis et al. 2020). Various studies have examined LCA for UCO, GTW, and FOG re-purposing in biodiesel production and anaerobic co-digestion. At half the price of vegetable oils, waste lipids are an economically attractive, low-cost feedstock for biodiesel production (Macombe et al. 2013). Hums et al. (2016) performed an LCA examining the use of GTW for biodiesel production. Their study demonstrated potential economic and environmental benefits for using brown grease derived from GTW as an energy product. The main findings conclude that lipid content is an important sensitivity factor, with brown grease lipid contents over 10% yielding lower greenhouse gas emissions (GHG), 20 gCO_2-eq/MJ-fuel, than that with less than 10% lipid content. The authors compared brown grease GHG emissions with those from production of low-sulfur diesel and soybean biodiesel, which yield an estimated 93 and 25 gCO_2-eq/MJ-fuel, respectively. If biodiesel derived from brown grease displaced low-sulfur diesel, it could reduce GHG by 20–75%. It also performed comparably to soybean biodiesel but provides the additional benefit of diverting GTW from landfills. Additionally, in a follow-up study, Hums et al. (2018) performed a longitudinal study tracking the characteristics of brown grease in GTW and sewage-scum grease demonstrating that though the waste streams were highly variable over time, they consistently contained substantial amounts of brown grease that can be used for biodiesel production using similar processing methods. Because these waste lipids are often underutilized, the combination of well-described grease content over time with LCA demonstrating benefits of brown grease biodiesel emphasizes the role FOG waste can have in producing renewable energy.

Foteinis et al. (2020) performed an LCA for production of biodiesel from UCO in Greece. This study collected data from an actual biodiesel plant that uses UCO and animal fats to inform their life cycle impact assessment (LCIA). The plant pretreats the UCO to dehydrate the feedstock. Then, acid catalyzed esterification followed by alkaline catalyzed transesterification is used to produce a biodiesel that is further refined to meet European Union standard EN14214 for biodiesel. The authors demonstrated that the carbon and environmental footprint for biodiesel production using UCO was 40% lower than that of the first-generation biodiesel using vegetable oils, an order of magnitude lower than that of the third-generation microalgae biodiesel, and three times lower than that of traditional petrodiesel. Transportation means and distance were important factors influencing overall sustainability. The assessment performed highlights the potential of UCO to improve biofuel representation in the transportation sector.

Economic assessment of FOG co-digestion has also demonstrated the advantages and necessary requirements for implementing economically beneficial FOG co-digestion. Parry and Fillmore (2016) evaluated barriers to co-digestion to determine the scenarios where implementation is most logical. The results of the authors' analysis demonstrated that negative tipping fee is associated with FOG co-digestion using existing reactors. A negative tipping fee ultimately indicates that the benefits of receiving FOG outweigh its cost. The negative tipping fee is derived from the lower cost of residual disposal and the higher offset electricity cost. Compared to other co-substrates, such as cow manure, which has greater residual production due to its lower volatile solids content, the economics of FOG co-digestion is more favorable. The ability to use existing infrastructure increases the economic feasibility. The need to build new infrastructure can ultimately be a barrier to co-digestion implementation for biogas capture that runs combined heat and power processes.

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Chapter 11
Food Waste Biorefineries: Developments, Current Advances and Future Outlook

Thomas I. J. Dugmore

Abstract Food wastes are simultaneously a promising and challenging feedstock for biorefineries, as they are extremely varied by nature. This results in a wide range of potential applications and outputs in the biorefinery context, yet at the same time presents problems in designing processes adaptable to this variation.

Food wastes can generally be divided into two types: avoidable and unavoidable. Avoidable wastes generally comprise of inefficiencies in the supply through overproduction, spillages, etc., whilst unavoidable wastes are generated through discarding inedible portions.

As reducing avoidable food waste can be achieved through awareness and reduction of bad practices, resulting in more food being available for the population, this should be encouraged where possible. Therefore, this chapter will largely focus on unavoidable food wastes for biorefinery feedstocks.

The primary reason for items being rendered inedible is the presence of large amounts of indigestible polymers such as cellulose and lignin. Strategies for dealing with these materials in a biorefinery concept therefore typically involve separation of these polymers from the rest of the matrix, before further processing of both fractions for use in food, fuel, materials and chemical production.

This chapter will cover these strategies and how they can be applied throughout the food industry from supply and manufacture at one end, to catering and consumption at the other. The different nature of feedstock produced and the unique challenges therefore presented at each stage will be discussed to examine how these diverse materials can be deployed most effectively as biorefinery feedstocks.

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11.1 Introduction

The concept of the biorefinery has been covered increasingly since the turn of the millennium with many studies and reviews setting out the requirements and challenges for the transition from a petroleum economy to a bio-based one (Kamm and Kamm 2004; Fernando et al. 2006; Cherubini 2010). Yet the principle of using biomass for our energy, fuels and materials pre-dates the rise of the oil refinery even for applications that would largely be considered modern day. For instance, the largest application of crude oil is for fuel for the transport—particularly automotive—industry yet Rudolf Diesel famously first demonstrated his eponymous engine using peanut oil as the fuel, envisaging a large market for it due to the different plant oils that could be found globally (Bryant 1976). Whilst the heavier hydrocarbon fraction from crude oil distillation would end up superseding the plant oils Diesel had originally intended throughout the twentieth century, there is somewhat of an irony that, due to the depletion of oil reserves and increasing costs over the environmental impact of the industry, the plant oils Diesel originally envisaged are returning to fuel his engine in the form of Biodiesel.

The development of using plant oils, such as rapeseed, sunflower and soybean, to produce biodiesel, or fermentation of high-sugar crops, such as corn, to produce bioethanol in a modern context is generally seen as one of the first major applications of the biorefinery in action. However, this development also highlighted two major issues that are important learning points for future biorefinery developments. The first is that a simple return to vegetable oils to fuel diesel engines has simply not been possible as the demands from consumers (speed, miles per gallon of fuel, etc.) and legislation (emissions) cannot be achieved from raw vegetable oils (Shay 1993). Subsequently, the triglyceride components of vegetable oils are nowadays converted with methanol into fatty acid methyl esters (FAME) in a process known as transesterification (see Fig. 11.1), prior to being used as biodiesel generating glycerol as a by-product.

The rise in production of biodiesel therefore also coincided with a production of glycerol which far outstripped its demand. Fortunately in this instance there have been numerous studies for further valorisation of glycerol into a range of other products, such as fuels, polymers and solvents to help ensure the utilisation of all parts of the oils in the biorefining process (Kaur et al. 2020). However, this is not a unique situation—the change in consumer demands and legislation on materials and products mean that the requirements of biorefineries will constantly need to adapt to fit these. Similarly, this will also mean that as further downstream processing of biorefinery feedstocks occurs to meet these demands, more by-products will be produced which will in turn need valorising to ensure the full potential of the biorefinery is met.

The second issue concerns the diversion of crops and products to fuel that would otherwise be used for food. With the global population rising nearly four-fold from approx. 2 billion at the start of the twentieth century to 7.8 billion in 2021 and still expected to rise further, the demand for food and water has similarly increased (Ezeh

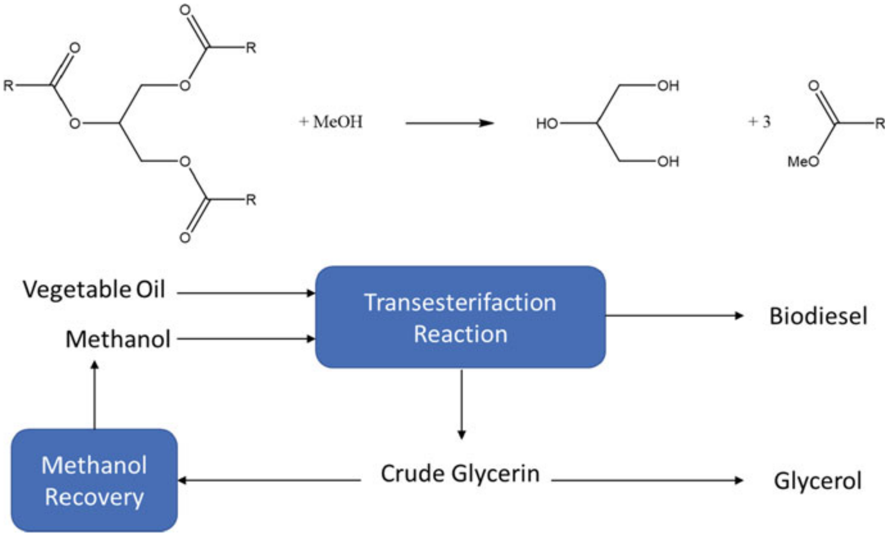

Fig. 11.1 A simplified schematic overview of the biodiesel production process

et al. 2012). This therefore raised considerable ethical concerns about diverting edible crops and their land to fuel production due to the impact on food prices and availability in what became popularly known as the 'food vs fuel debate' (Srinivasan 2009). As a result, there has been a shift in focus away from the use of food crops for biofuels and other materials towards the use of non-edible or waste biomass as an alternative in what has commonly become known as second or third generation biorefineries (Clark 2007; Scoma et al. 2016).

Within the context of these biorefineries, food wastes have become a popular target to develop as a feedstock for a number of reasons. The first being the inevitable production of wastes through the food supply processing chain through the discarding of edible portions (orange peels, spent coffee grounds, avocado stones, etc.) and the need to deal with them in a sustainable manner.

The second is the fact that, as they are generated from food crops in the first place, the land used to produce them does not directly compete with food production.

The third is the large volumes of food waste produced annually and the impact this has environmentally, economically and societally. Whilst this amount varies from type to country, it was estimated in 2011 that, on average, 1/3 of all food produced for human consumption, totalling 1.3 billion tonnes annually was lost, or wasted (Gustavsson et al. 2011). This has a direct environmental impact due to the fact that most food waste decomposes, either in a controlled (composting, anaerobic digestion) or uncontrolled (landfill, left on fields) manner, to form CH_4 and CO_2—both potent greenhouse gases. There is also an indirect effect on the environment as it means excess irrigation water, fertilisers, etc. are needed to produce resources that are never used, which also translates as an economic loss to farmers and producers through resource inefficiency. Societally, the impacts can be seen wider as this loss of food means that valuable nutrients never make it to consumption in a world where huge numbers die of malnutrition daily. Some estimates of the scale of the problem include that:

- 186 Mt. CO_2-eq, 1.7 Mt. SO_2-eq. and 0.7 Mt. PO_4-eq can be attributed to food waste in Europe (Scherhaufer et al. 2018),
- Wasted food crops accounts for 24% of total freshwater resources used in food crop production (27 m^3/cap/year)and 23% of total global fertiliser use (4.3 kg/cap/year) (Kummu et al. 2012)
- The average annual per capita food waste can provide a healthy diet to one person for 18 days (Chen et al. 2020)

The reduction or utilisation of food waste clearly, therefore, has a number of potential benefits globally. This has led to food waste being specifically targeted under the United Nations Sustainable Development Goals number 12 'Ensure sustainable consumption and production patterns', as Target 12.3: By 2030, halve per capita global food waste at the retail and consumer levels and reduce food losses along production and supply chains, including post-harvest losses (SDGs 2015).

Finally, from a biorefinery perspective, food wastes are full of a rich range of chemicals that provide functions that we need to apply to other products on a daily basis—polymers, fibres, pigments, flavours, fragrances, waterproof waxes, antioxidants, surfactants and sugars being a few notable examples. Most of the molecules we currently exploit for these purposes are derived from crude oil representing a valuable opportunity to derive direct bio-based replacements.

The use of food waste as a biorefinery feedstock is not without its issues and challenges, however. One of the key issues is familiar to any process—stability and security of feedstock availability. Whilst the amount of land dedicated to the production of food (and subsequently food waste) varies from country to country at the primary agricultural production end, so too does the amount of food wasted at the consumer end on a per capita, or per meal basis (Dou and Toth 2021). As well as volumes, composition of food waste also varies from location to location as well as by season. From the agricultural end this is to be expected as different conditions suit different crops better than others and is no different from the challenges posed to the first generation biorefineries and is relatively easily addressed by simply processing close to farms, orchards, etc. as harvesting typically produces a single source of waste. However, as food is gathered, distributed, sold, cooked and eaten, the waste streams generated at each stage become more heterogeneous as more different crops and ingredients are collated in one place, with the heterogenicity and subsequent complexity increasing at each step along the supply chain.

Within the context of the principles of Green Chemistry (Anastas and Warner 1998) and the waste hierarchy, the first priority for all waste should be to prevent it being formed in the first place and food waste is no exception. Many of the post-harvest losses in the food supply chain arise through factors such as physical damage, infection and spoilage and can subsequently be addressed through increased efficiencies in handling, transporting and distribution infrastructure (Bendinelli et al. 2020). Reducing this waste therefore also increases the amount of food that can be distributed to the population which is key to helping to battle malnutrition—another one of the United Nations Sustainable Development Goals, Number 2: End hunger, achieve food security and improved nutrition and promote sustainable agriculture. Consequently, this avoidable food waste should be sought to be reduced and not targeted as a biorefinery feedstock and only the aforementioned Unavoidable Food Supply Chain Waste (UFSCW) used. Consequently, this will be the focus of discussion on food waste for biorefinery purposes.

There have been extensive treatments on how the various components, notably the 3 main macromolecules (carbohydrates, proteins and fats) can be refined or processed into a variety of chemicals and materials (Anal 2017; Dugmore et al. 2017; Teigiserova et al. 2019) alongside the wider picture of scale-up, supply chain impact, techno-economic assessments and Life Cycle Assessments (Caldeira et al. 2020; Sadhukhan et al. 2020). As such, the chemical potential of various food waste streams and the types of reactions needed for their conversions into chemicals, fuels and materials are now relatively well established. Two of the key factors needing to be considered for the development of UFSCW-based biorefineries are implementing the technologies required at a scale large enough to process the volumes for UFSCW generated each year and how to penetrate the existing market with the resulting products. In particular, with food, pharmaceuticals, cosmetics and personal care all being identified as key target markets for UFSCW applications (Sadiq et al. 2017; Gedi et al. 2020; Osorio et al. 2021), care must also be paid towards the acceptance of such products from both a regulatory and consumer perspective.

With many new products needing larger samples or prototypes as a key first step to enter the market, developing the technology beyond laboratory is a key first step. The discussion of some of the key advances will therefore be centred around the development of enabling technologies at various Technology Development Levels (TRLs) and how they can be integrated to develop a UFSCW-based biorefinery beyond laboratory scale (Héder 2017).

11.2 State-of-the-Art and Developments

11.2.1 Anaerobic Digestion

One of the most prominent solutions to the issue of food supply chain waste from a biorefinery perspective over the previous decade has been the development and implementation of Anaerobic Digestion (AD). The overall process involves exposing the biomass to anaerobic bacteria under controlled conditions to break down the macromolecules into methane, which is subsequently burned for energy, leaving behind a residue (digestate) which can be used as fertiliser (van Lier et al. 2001). This has risen in popularity due to its cheap installation and ease of use—particularly for smaller-to-medium businesses and farms as a way to recover energy costs, reduce their reliance on electricity from the grid and reduce the amount of organic waste to be disposed of. Larger enterprises have also seized on this technology to deal with

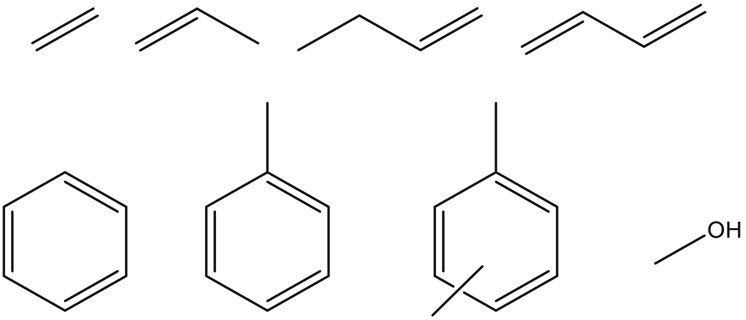

Fig. 11.2 The base chemicals from the petroleum fractionation used in the chemical industry

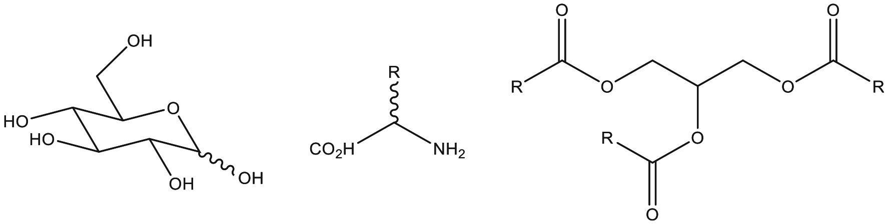

Fig. 11.3 The generic structures of the monomers for the three main biomass macromolecules. From left to right—sugars, amino acids and triglycerides

larger volumes of municipal food wastes from homes and catering to then supply energy to the grid. Both local and national authorities in many countries have been largely supportive of this as a means to meet their renewable energy targets, reduce CO_2 emissions and reduce the amount of waste going to landfill.

However, from a chemical perspective, this is highly undesirable when we consider the need of the biorefinery to provide commodities beyond fuel in order to be a viable alternative to petroleum refineries. The chemical industry is reliant upon a small amount of 2–8 carbon olefinic and aromatic ‘base’ chemicals, shown in Fig. 11.2, as the building blocks for larger, more complex chemical structures. Building up from these can require many synthetic steps to form carbon-carbon bonds, add heteroatoms and introduce functionality, each of which requires resources and generates waste.

Food waste, meanwhile, is comprised of three main macromolecules—carbohydrates, proteins and fats (generic structures shown in Fig. 11.3)—as well as many other bioactives, all of which boast already large structures rich in heteroatoms and functionality. It is therefore quite inefficient and wasteful to break these molecules back down to methane, a single carbon, non-functional molecule and miss the opportunity to exploit the rich variety of functional molecules already on offer.

However, the route to breaking down these macromolecules into their monomers, and subsequently methane, is very complex and goes via a number of intermediates,

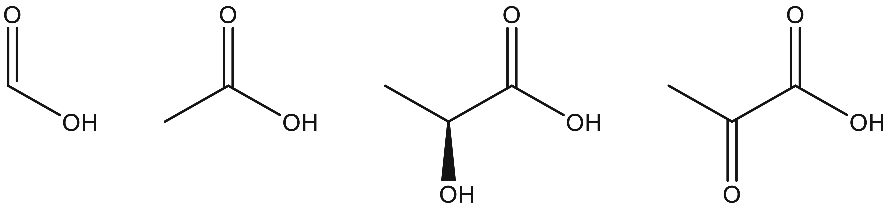

Fig. 11.4 A selection of organic acids produced during anaerobic digestion

including ammonia, sulphide and short-chain volatile fatty acids and organic acids (shown in Fig. 11.4). Many of these are valuable commodities in the chemical industry and yet their formation in large quantities can be problematic in AD due to their strong acidic/nature and the pH sensitive nature of the microbes needed to carry out the digestion. Ammonia and sulphide are also problematic as contaminants for the final methane product as they will form harmful NO_x and SO_x gases upon co-combustion.

This therefore presents the opportunity to increase the efficiency of the AD process both in terms of methane yield and as a biorefinery option to deal with food waste. Several options for in-situ removal of these components, such as membrane filters, addition of precipitators and gas scrubbers have been proposed to access these directly (Yuan and Zhu 2016), however many of these are still in development stages at the time of writing. To improve the biorefinery efficiency of AD further many researchers have investigated the potential of pre- and post-treatment of food waste destined for AD (Ren et al. 2018). Post-treatment of residues largely focuses on the fractionation of the solid and liquid phases of the digestate with the former being touted for use as soil enhancers or fuel for pyrolysis (to be discussed), whilst the latter has been looked at as a potential source of microbial oil or algal growth medium, often in conjunction with the CO_2 released from methane combustion. However, the deployment of CO_2 from emissions has also received increasing attention in biorefinery and Green Chemistry research as a chemical building block for materials such as urethanes, cyclic carbonates and fuels (Kleij et al. 2017) or as an alternative solvent to traditional petroleum-based VOCs (Nikolai et al. 2019).

Pre-treatment steps on the other hand have focussed more on pre-fractioning of the bioactives and polymers from the material to reduce their losses in the AD process. These strategies and techniques will focus largely on single-feedstock applications as this is where they can generally be deployed more efficiently. The further down the food supply chain, the more complex and heterogeneous the nature of UFSCW becomes which subsequently makes fractionation and separation more problematic. Additionally, whilst all the pre-treatment steps could potentially be considered stand-alone treatments or technologies, none are 100% efficient and will always generate waste streams such as sludges and effluents with low value, yet are still treatable via AD. Consequently, whilst not the most efficient means of valorising food waste, AD is likely to remain a key technology for food waste biorefineries for the foreseeable future.

11.2.2 Extraction and Separation

As previously stated, the three main components for biomass are the macromolecules of carbohydrates, fats and proteins. However, it is the smaller, functional molecules that, whilst minor in terms of concentration, provide plants (both edible and inedible) with their unique properties. Examples of these include volatiles to impart scent, pigments for colour, waxes for water protection and antioxidants for air protection. Some of these traits have evolved for the plant's protection against being eaten by making parts of them, e.g. poisonous—these can often comprise inedible parts of food crops that must be discarded—yet can also be deployed for other purposes. A good example of this is the chemical atropine which is found in tomato vine and potato green tops. Atropine is an alkaloid that can cause nausea, dizziness, blurred vision and extreme confusion and can be poisonous when overdosed on. However, small quantities can be used effectively to help treat several conditions and is listed on the World Health Organisation's List of Essential Medicines (World Health Organization 2019). As these are inedible and cannot be processed for food further downstream, these wastes are generally produced at the harvesting stage of the Food Supply Chain.

Other traits have evolved to encourage consumption by insects and birds as a means of spreading seeds, normally contained in the fruit, or distributing pollen, contained in the flowers. These often include pigments and fragrances to make the fruits and flowers attractive. Since the advent of agriculture, human activity has enhanced many of these traits through selective breeding. These types of compounds are therefore often found in peelings and pulps of fruits and vegetables and are therefore typically produced at the processing/catering stages of the Food Supply Chain.

The range of properties of these smaller molecules serves to illustrate the potential applications in products arising from a biorefinery and therefore why it is of interest that these are not lost in AD or other destructive processes. It is important to note that whilst these molecules may seem minor in concentration, perhaps to the point of it not being effective to pursue, the typical concentrations they are found in product formulations are not too dissimilar. For example, concentrations of antioxidants in citrus fruit juices averaging 1–2% are typically reported (Pisoschi et al. 2009), whilst the typical loadings of antioxidants in, for example, engine lubricants are 0.1–2% (Basta et al. 2017, Mu et al. 2018). Strategies for removing them prior to downstream processing should therefore be discussed.

11.2.2.1 Mechanical Extraction

One of the most straightforward ways to separate out low molecular weight molecules is to simply pass the UFSCW stream through a filter that will separate out portions of the stream via size. In fact, many of the techniques discussed in this section are already well established in industry—including the food manufacturing industry. Good examples of these in primary food production include pressing olives to extract the oil, or mashing grapes to obtain the juice (rich in flavours, fragrances) to produce wine. This therefore presents a great opportunity to deploy existing technology to a new field, particularly ones that have already had approval for use in the food industry, rather than have to develop new biorefinery technology from scratch. This section will therefore examine how and where these can best be deployed. For instance, adapting oil-seed pressing works well for streams that are rich in oil or water, where the liquid can easily pass through a mesh or cloth leaving behind the fibrous material, to extract molecules that are either very polar (and therefore hydrophilic) or non-polar (oleophilic) and therefore contained within the water and lipid fractions, respectively. Typically though, the water phase is relatively highly concentrated compared to normal aqueous streams meaning simple gravity filtration is hard to achieve and therefore other methods need to be considered.

Mechanical pressing is a popular option as it is relatively straightforward, can be done on a range of scales industrially (an example of the range of filter press sizes readily available is shown in Fig. 11.5) and is already utilised in the food manufacture industry as described above. The use of oil-seed presses, for instance, can be readily transferred to press other oil-rich food wastes, such as avocado seeds or spent coffee grounds. The major drawback to this method is the relatively low efficiency compared to other methods with the press cake still containing substantial amounts of oil, thereby needing a secondary method, such as solvent extraction (to be discussed in the next section) to extract the remaining oil.

Fig. 11.5 Two different scales of filter press

Filter presses are another common option used industrially to increase efficiency. These typically consist of a series of plates with filter clothes pushed tightly together by a mechanical press as the slurry is pumped through. By pumping the slurry against the force of the press creates a much larger pressure gradient than is typically obtained through a simple mechanical press resulting in a much drier press cake.

In a similar vein is the concept of ultrafiltration where in addition to the high pressure applied to a solution, the filter cloth is replaced by a porous membrane with a pore size on the nm scale allowing for components to be separated by molecular weight (typically $> \sim 300$ kDa being the lowest cut-off point) (Ren et al. 2006). This is especially effective for the extraction and concentration of water-soluble proteins dissolved in the filtrate emerging from the presses. As this process requires matrix to be a solution, to prevent insoluble particles from clogging the membrane, it is important to note that this is a downstream technique from bulk filtration, rather than an alternative to it.

In a similar vein, the process of extrusion can also be used as a means of pressing out oil/water content. The technique involves feeding the material along a screw or auger which presses against a mesh filter, pressing the liquid content through the pores whilst carrying the residual fibres along the channel to a separate chamber. In the food industry, this technique is already used in a variety of juicers to maximise juicing efficiency, as well as pressing food such as pasta into a fixed shape by employing a mould, as opposed to a mesh, representing a straightforward technology transfer.

For streams that are particularly concentrated, or simply low in water/oil content, another option for separation of phases is centrifugation. A number of options are available at industrial level, however the standard bucket centrifuge is limited beyond pilot scale, largely due to the power needed and friction generated for a motor needed to operate on the tonnage scale to achieve the same levels of centrifugal force seen at the lab scale. Industrial alternatives therefore typically rely on feeding material into a spinning chamber whereby solids can collect on the walls of the chamber whilst the liquid passes through. Whilst this approach loses some of the efficiency of bench-top high speed centrifuges, it offers the advantage of allowing for continuous, rather than batch processing.

As well as separating out water/oil soluble fractions and any small molecules dissolved in them, many of these techniques also offer the potential of addressing another issue with processing UFSCW—bacterial growth. A significant portion of avoidable food waste is generated through spoilage, namely through infection from bacteria or mould growths. Similarly, any UFSCW with sufficient water and sugar content can also be prone to attracting bacterial growths which can then severely limit the available applications from both a chemistry and regulatory perspective. Drying of residues is therefore often a key step to processing food residues for materials. In hot countries, this can often be done simply by sun-drying, but in more temperate areas, this is not an option, particularly in the winter months. Ovens, freeze dryers and spray dryers are all options that have been utilised, but they can all suffer from being extremely energy intensive. Overall, unless heat generated from a different site-process can be utilised, this can be a potential bottleneck to economically effective scale-up. By applying these extraction methods to utilise the inherent water in UFSCW as a solvent to remove small, active molecules prior to downstream processing, the subsequent water reduction in the press cake/pellet, etc. also aids the drying process to maintain shelf life if storage is necessary.

11.2.2.2 Solvent Extraction

Being of comparative low molecular weight compared to macromolecules and in low concentration, many of these small molecules can be extracted with relative ease into an appropriate solvent. There are several options available both in terms of technique and solvent, but they typically follow the standard steps of steeping the biomass (UFSCW in this case) in the solvent of choice allowing the molecules of interest to leach out into the solvent, the resulting solution is then filtered off and the solvent evaporated off leaving the concentrated extract behind.

Simply steeping the biomass in solvent rarely achieves complete extraction as an equilibrium is typically reached between molecules dissolved and retained that cannot be overcome simply by extending the holding time. Raising the temperature can increase the amount of extract in solution, however this is limited by the boiling point of the solvent. Increasing the amount of solvent to substrate is also effective, however this can be impractical on scale due to the size of vessels needed and the costs of using such excess amounts of solvent.

Soxhlet extraction is a popular choice in analytical chemistry. Here, the solvent and sample are kept in separate vessels—typically the solvent in a heated flask at the bottom of the setup with the sample in a porous thimble above with a condenser on top. As the solvent is heated it evaporates, then condenses upon hitting the cooling water where it rains down on the sample, dissolving the small molecules in the sample before passing through the thimble and returning to the original reservoir to boil off again and repeat the cycle. The constant re-introduction of fresh solvent to the sample helps avoid the problem of reaching equilibrium, as would happen in a standard single-batch process. It also allows the extract to become highly concentrated in the solvent, again in a way that would be difficult in single-batch extraction, therefore reducing the overall amount of solvent needed for the process. It is therefore one of the most effective means of extracting all molecules of interest and getting maximum yield. However, the large amount of cycles needed, and hence the overall time and energy requirements are problematic at larger scale.

Overall, there is no simple answer and the choice of technique, time ratios etc. will often come down to finding a balance between yield, cost and throughput. Soxhlet is still, however, a very useful tool in process development for these purposes as it can be used to obtain a theoretical maximum yield against which different conditions can be assessed for relative efficiency.

Perhaps more pertinently for these purposes is the choice of which solvent to use. Whilst, in theory, all solvent will be removed from the extract in the evaporation process, there is still the risk of residual solvent being found in the product or contaminated from elsewhere in the processing plant. For additional reasons of

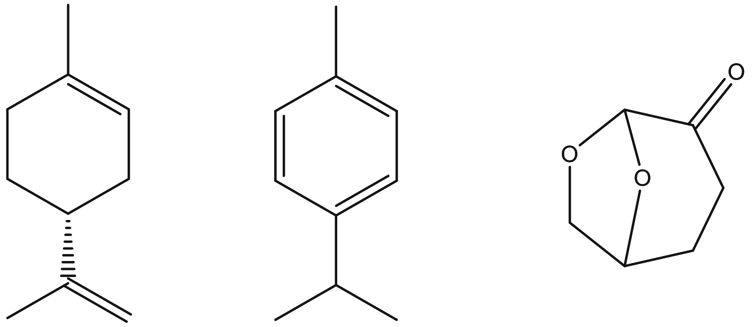

Fig. 11.6 Limonene, p-cymene and cyrene—candidate solvent to replace traditional petroleum-based ones

safety and promoting Green Chemistry, the pharmaceutical industry is becoming increasingly restrictive in the solvents it is allowing for use with some countries also now also restricting previously common solvents (such as benzene and chloroform) from use across the board (Drug 2011; Bergkamp 2013; Prat et al. 2016; FDA 2017). Solvent restrictions apply even more stringently to the food industry with EU legislation in particular recognising just 7 solvents that are free for use without specified conditions—propane, butane, ethanol, ethyl acetate, acetone, carbon dioxide and nitrous oxide (Parliament 2009). Fortunately, many small bioactives are mid-polar, therefore can often be readily extracted using ethanol and acetone. However, when low-polar materials, such as lipids and waxes are sought after, things are not as straightforward. Hexane is the standard solvent of choice for fractionation of oils and fats in the food industry, however with concerns over its health hazards towards humans and the environment its phasing out of use is highly recommended.

Additionally, in terms of looking at biorefining options—it is somewhat self-defeating to look towards petroleum-derived solvents for this purpose. Fortunately, as solvents make up the bulk of E Factors and PMIs in chemical processes, they have undergone considerable research over the past decade and a number of bio-based alternatives are now available. These include bio-derived routes to conventional solvents such as ethanol and ethyl acetate, deployment of more niche solvents, such as limonene more widely and new molecules altogether such as cyrene (Clark et al. 2015; Chemat et al. 2019), a selection is shown in Fig. 11.6.

11.2.2.3 Sub- and Supercritical Fluids

One alternative to the problem of restricted organic solvents is the use of super and sub-critical fluids. Supercritical fluids are compounds that have been elevated above their boiling point under pressure to the point where they display properties of both liquids and gases. In this context, they will expand to fill a chamber like a gas, including permeating the biomass matrix, but will maintain their ability to dissolve molecules of similar polarity. Supercritical fluids offer the advantages over conventional solvents that they are far more easily removed as they will return immediately to the gas phase upon release of pressure, thus leaving the extract instantly without the need for distillation. Additionally, varying temperature and pressure allows the user to ‘fine tune’ the solvent parameters of the fluid to help target selective extraction and fractionation of molecules of interest. However, holding and maintaining substances at the require temperature and pressure involves the use of specialist equipment which can be energy intensive and expensive.

Meanwhile, sub-critical (also called superheated) fluids are liquids that have been elevated above boiling point, but under sufficient pressure to maintain them in the liquid phase without going supercritical. The elevation of temperature above boiling points typically results in a change in polarity—with water notably seeing a reduction in polarity to that comparable with methanol at 200 °C (Smith 2006). With less temperature and pressure required, sub-critical extraction offers a less expensive option than supercritical extraction, though suffers from the disadvantage of still having the solvent in liquid form at the end, thereby requiring removal—although the most effective sub-critical extractions cause the extract to crash out of solution when the solvent is restored to its initial polarity, therefore can be simply removed by filtering.

For supercritical fluids, CO_2 is by far the most well known and applied in the food industry, being commonly used as a replacement for dichloromethane as a solvent for decaffeination of coffee. Studies have similarly shown its ability to extract other low-polar molecules, such as waxes and lipids on cereal straws (Attard 2015) with good efficiency suggesting it as a good complementary solvent to the aforementioned ethanol and acetone to deliver a range of solvent polarity for different target molecules.

11.2.2.4 Distillation

Finally, whilst not being able to achieve the same levels of separation as in the oil and gas industry, distillation remains an option for separating out volatiles from UFSCW. Depending on the moisture content, some UFSCW streams can be heated directly using the latent evaporating water as a carrier, however drier biomass can require excess water to help boil off the compounds of interest and reduce vapour pressure. This technique works well for removal of flavour and fragrance molecules as they are relatively small and have low-boiling point, such as essential oils (10–15 carbon atoms). As they are often mid to low polarity they have the additional advantage of not mixing with the water upon condensation, thereby allowing easy separation without the need for further distillation. Steam distillation in particular has an additional advantage over other aqueous extractions of UFSCW in that the resulting aqueous fraction does not contain the sugars that would normally be dissolved as they will not boil off. One potential disadvantage though is that the high temperatures and aqueous conditions can lead to hydrolysis, or other water-sensitive reactions to occur causing degradation of some of the products. An

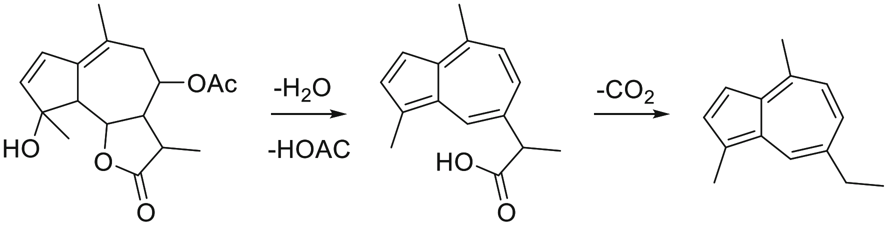

Fig. 11.7 The thermal degradation of matricin to chamazulene

example of this is on distillation of camomile oil where the key component, matricin, will undergo thermal degradation by elimination of water, acetic acid and carbon dioxide to form chamazulene—reaction shown in Fig. 11.7 (Länger et al. 1996). However, as chamazulene also has potential in the pharmaceutical industry as a profen, this is not necessarily a downside depending on what the intended application of the chamomile oil is (Ramadan et al. 2006).

11.2.3 Thermal and Microwave Treatments

Microwaves have long been used in the food industry due to their ability to reduce turnaround time and subsequently energy costs of cooking, drying and sterilisation both in the residential and commercial sectors for decades (Hager and Morawicki 2013; Guo et al. 2017). However the last 2 decades have seen a huge expansion in the use of microwaves in chemical processes and materials processing as a means of reducing the environmental impact of the respective industries (Dąbrowska et al. 2018; Horikoshi et al. 2018) and the application of this to biorefineries is no exception (Asomaning et al. 2018).

Microwave processing technologies for biorefining food wastes typically fall into two categories: pyrolysis and hydrothermal. Both of these techniques are also carried out with traditional thermal heating methods, such as fuel combustion, heating elements, heat exchangers and steam. It is important therefore to understand the difference between the two. Thermal methods typically require conduction, convection and radiation to impart heat to the sample. By contrast, microwaves interact directly with the sample with the heat being generated by the absorbance of microwaves by the molecules in the sample, being excited to higher rotational levels and then emitting heat upon relaxing back to the ground state. As such, thermal methods are said to heat ‘outside-in’, whilst microwaves heat ‘inside-out’—a schematic being shown in Fig. 11.8. This provides greater energy efficiency as energy is not wasted heating up the surroundings of the sample as well, hence the subsequent reduction in time. This also allows for greater control over the heat as the heating can be halted immediately by simply turning off the microwave generator without leaving the sample exposed to the residual heat of the surroundings (Schanche 2003).

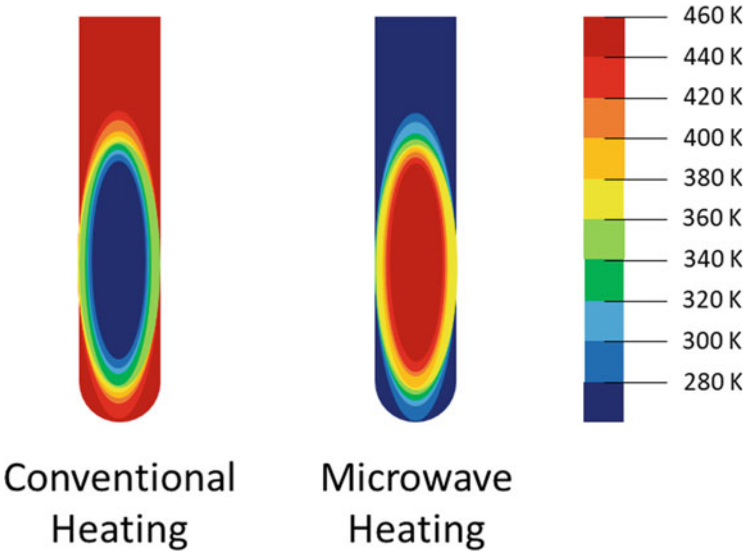

Fig. 11.8 A schematic showing the thermal profiles of a sample heated under microwave heating vs conventional heating (Schanche 2003)

11.2.3.1 Pyrolysis

To discuss this in terms of thermal treatments, pyrolysis is defined as the thermal decomposition of materials under inert atmospheres. In the case of biomass, this typically results in the production of charcoal (or activated carbons), liquids (often referred to as bio-oil) and biogas, with the ratios and nature of each being dependent upon the pyrolysis conditions and feedstock type (Demirbas and Arin 2002). This process is already deployed using thermal methods on a number of materials including lignocellulose that often comprises large parts of unavoidable food waste, but has also been applied to other plastic wastes and old tyres (Martínez et al. 2013; Anuar Sharuddin et al. 2016; Kan et al. 2016). The biogas largely comprises CO, CO, H_2O, H_2 and other small volatiles which can be fractionated, but is more often deployed as fuel, whilst the biochar is largely charcoal. From a biorefinery perspective, it is arguably the bio-oil that is the most interesting fraction as it is rich in a range of small organic molecules rich in functional groups, such as alcohols, ethers, ketones, esters and aromatics, a selection of which can be seen in Fig. 11.9 (Rezaei et al. 2014).

The range and variety of these molecules is of interest to the chemical industries as they present significant opportunities to replace the base chemicals presented in Fig. 11.2 as the key chemical building blocks for the chemical industry—as what have become known as ‘platform molecules’. The concept of these bio-based molecules for chemical synthesis feedstocks has been floated since the late twentieth century, but it was in 2004 where a full set of the most promising high-value

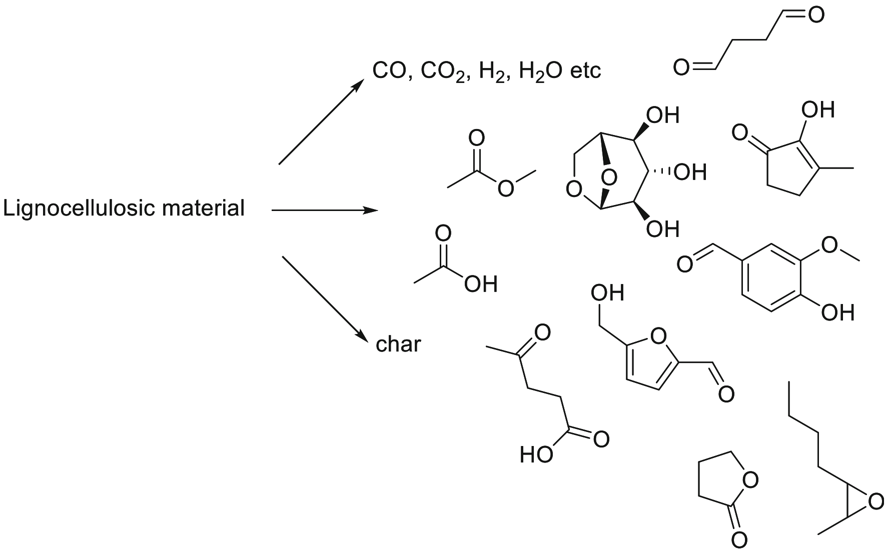

Fig. 11.9 A selection of gaseous, liquid and solid products from lignocellulose pyrolysis

bio-based molecules were established, as well as which potential applications they could act as replacement precursors to. These are what are now known more commonly as platform molecules (Werpy and Petersen 2004) and include a number of molecules commonly found in pyrolysis bio-oils such as vanillin, 5-hydroxymethylfurfural and levoglucosan (Farmer and Mascal 2015).

One of the key points of interest for platform molecules is that, whilst they are similar in size (2–8 carbon atoms) to many of the petroleum-based chemicals, unlike their petroleum counterparts, they already possess inherent heteroatoms to carry out subsequent chemical reactions on. However in practice, this also creates a problem for separating and purifying the respective compounds from the bio-oil. The presence of these heteroatoms also allows for greater intramolecular forces between the components, e.g. hydrogen bonding, meaning they cannot simply be separated via fractional distillation as is done in the petroleum industry. Instead, more complex work-up arrangements such as liquid–liquid separation or chromatographic systems must often be deployed (Luterbacher et al. 2014). Additionally recent lab scale studies are demonstrating the potential of catalysis to help improve selectivity towards different mechanisms and thereby obtain a narrower range of chemicals (Liu et al. 2020).

Microwave pyrolysis works on similar principles, but offers the advantage of much reduced holding time and temperatures due to direct heating—the offset can be as much as an 80% reduction in energy required per gram of biomass for pyrolysis (Macquarrie et al. 2012). However, it has also been noted that conventional pyrolysis gives a higher yield of biogas, whilst the yield of bio-oil remains much the same (Wu et al. 2014). The ability to tune yields according to properties presents a good option for targeting different products, depending on the desired output. However, one drawback of pyrolysis is that, much like AD, much of the other inherent, smaller, functional molecules with the biomass can be lost or destroyed within the process. Therefore, if these are still target products, then upstream processing should be considered prior to pyrolysis.

11.2.3.2 Hydrothermal

By contrast, hydrothermal processing involves processing in the presence of water in a sealed vessel above 100 °C and 1 atm of pressure (O'Hare 2001). This is not dissimilar to the concept of sub-critical water discussed earlier, although for reactions (rather than extractions and separations) the temperatures are largely kept below 200 °C. However, the ability to promote aqueous based reactions at above 100 °C is still the property under exploitation here. Hydrothermal treatments are a particularly promising technology for UFSCWs as many of them, particularly fruits and vegetables contain high amounts of water to begin with. This means hydrothermal methods can exploit the inherent water in the feedstock directly allowing for very concentrated solutions and mixtures to be processed, thereby reducing material costs and amount of runs needed and thereby increasing throughput. Hydrothermal treatments also lend themselves well to microwave processing as microwave heating works most efficiently with molecules with strong dipole moments as microwave energy excites molecules through rotational excitations which disrupt intermolecular forces (such as hydrogen bonds) keeping things in an ordered state and thereby increasing energy output through increased molecular collisions. As water has one of the strongest dipole moments known, it is an excellent microwave absorber and therefore an ideal solvent for microwave reactions (Tanaka and Sato 2007).

To explore this further, a couple of case studies will be used. One promising development for a food waste based biorefinery is the development of production of chloromethyl furfural (CMF) from sugar and cellulose-rich streams (Mascal 2019). CMF is a molecule of great interest to the biorefinery for two reasons. The first is the number of simple chemical transformations it can undergo to produce other functional molecules which can be used as monomers or other building blocks for further chemical synthesis. A selection of these is shown in Fig. 11.10.

The second is, as with lignin, it possesses an aromatic ring as its central motif, albeit a heteroaromatic ring (furan), rather than a benzene ring. Nonetheless, this does present a significant opportunity to substitute petroleum-derived aromatics with bio-based ones for applications. A good example of this is in the manufacture of plastics vs bio-plastics. One of the most common polymers on the market is polyethylene terephthalate (PET) which is used extensively in the manufacture of plastics bottles for the drinks industry. PET is synthesised via the esterification of ethylene glycol and 1,4 benzene dicarboxylic acid, or terephthalic acid as it is more commonly known—the chemical structure of the resulting polymer is shown to the left in Fig. 11.11. However, as shown in Fig. 11.10 reaction c, CMF can be easily converted into 2,5 furan dicarboxylic acid via oxidation of the chlorine group to the

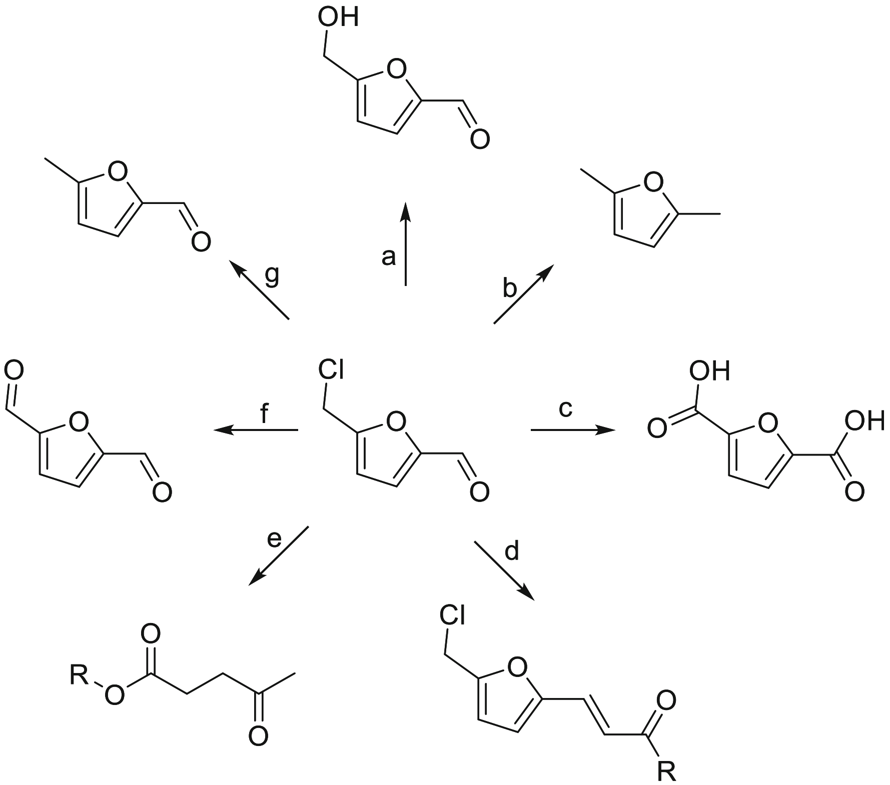

Fig. 11.10 A selection of chemical transformations that can be carried out on CMF (centre)

Fig. 11.11 The chemical structures of PET (left) and PEF (right)

corresponding aldehyde, followed by subsequent oxidation of both aldehyde groups (Anchan and Dutta 2021). The resulting diacid can then undergo esterification with ethylene glycol in the same way as terephthalic acid to afford polyethylene furanoate (PEF), the chemical structure of which can be seen to the right in Fig. 11.11.

As can be seen, the two polymers are very similar in chemical structure which results in very similar material properties making PEF suitable as direct ‘drop in’ replacement for PET in the plastics industry (Loos et al. 2020). As ethylene glycol can also be produced from catalytic conversion of cellulose (Xu et al. 2017) this represents a great opportunity for biorefineries to produce a fully bio-based material

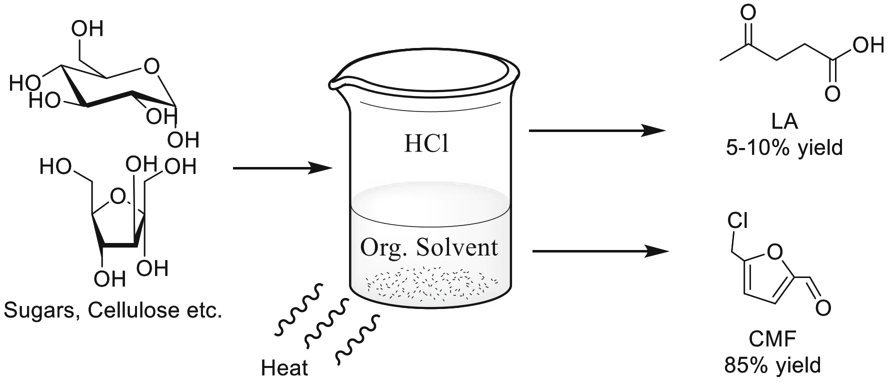

Fig. 11.12 Schematic of hydrothermal processing of carbohydrates to CMF

to replace a petroleum-based counterpart. Life Cycle Assessments have estimated that, with a market of 15 million metric tonnes per year, the total replacement of PET with PEF has the potential to reduce greenhouse gas emissions by 20–35 Mt. of CO_2eq. per year (Eerhart et al. 2012).

The method of hydrothermal CMF production from cellulose was originally reported to be carried out in a biphasic system consisting of aqueous HCl and an organic, water immiscible solvent, initially dichloromethane (DCM) (Mascal and Nikitin 2008). The subsequent dehydration reactions of the glucose monomer produced CMF which also being water immiscible was extracted into the organic phase from which it is easily recovered. The only major by-product of this reaction is levulinic acid (LA)—formed via the ring-opening of CMF, or its 5-hydroxymethyl furfural (HMF) precursor. However, from a biorefinery perspective, this is not an issue as LA remains in the aqueous phase (where it can also be extracted with relative ease) and also has great potential as a valuable platform molecule (Pileidis and Titirici 2016; Yan et al. 2017). An overview of this reaction scheme is shown in Fig. 11.12.

Over the past decade, this technology has since been demonstrated to be applicable to a range of carbohydrate-rich UFSCW streams such as corn stover and chitin (from seafood shells) (Mascal and Nikitin 2009) using both conventional and microwave heating (Breeden et al. 2013) and whilst it may seem familiar to the more established route of dehydrating glucose to HMF, the key advantage of conversion to CMF is the increased stability. HMF is known to be relatively unstable and capable of decomposing to LA or, more problematically, undergoing self-polymerisation reactions making yields as high as 85% comparatively difficult to achieve (Nikolov and Yaylayan 2011).

The use of microwaves in hydrothermal treatments can bring other advantages beyond time and energy reductions. For instance, the use of microwave technology to heat biomass can result in the increased friction between water molecules rupturing cell walls. This allows for the release of materials bound within the cell wall structure. A notable example being pectin from citrus fruits. Currently, the standard method of releasing pectin involves heating the citrus peels in acidic conditions (usually HCl) in order to break down the cell walls (May 1990). As the microwave heating can achieve this directly through generation of friction, this removes the need for the addition of acid, reducing the amount of resources needed for pectin production as well as eliminating an acidic wastewater stream to deal with. Combined with the reduction in time and improvement in heating efficiency, LCA studies have estimated that the use of microwave technology for this sector could reduce the environmental impact (in terms of factors such as greenhouse gas emissions, etc.) per gram of pectin by up to ~75% (Garcia-Garcia et al. 2019).

11.2.4 Combining Techniques

Several techniques have been discussed that can be applied to different UFSCW (and other) streams depending on composition and desired outputs. When seeking to valorise waste streams a common first question can be which technique would be the best to achieve maximum value or returns, however it is important that no technique should be seen as a 'silver bullet' and that the true maximum value for food waste-based biorefineries will be achieved instead by the deployment of several techniques in tandem—particularly for single-stream wastes where more valuable smaller molecules are present in higher concentrations than for mixed streams.

It has already been discussed how techniques such as AD and pyrolysis can destroy smaller, more valuable molecules during the procedure and thereby the need for pre-treatment steps to maximise the outputs. However, even discussing pre- and post-treatments leads to an oversimplification of the reality of how a full biorefinery may operate as it suggests somewhat of a linear process. It is worth noting that as each step of the process will generate by-products and streams, if a zero-waste strategy is targeted, all of these streams will require processing. As a result, a real-world biorefinery is likely to be a far more complex affair with several side-processes taking place.

To illustrate this, a case study of a proposed biorefinery for citrus waste, specifically oranges, will be examined. Oranges are a good example to look at for several reasons. To start with, the large volume of oranges produced per year; the Food and Agricultural Organisation of the United Nations estimates that global annual production of oranges alone has exceeded 70 million tonnes for the last 10 years, peaking at 79 million tonnes in 2019 (2016). The majority of orange production is for the juicing industry, which subsequently leaves behind large volumes of peel and pulp; even with the most efficient juicing processes, it is estimated that, by mass, 50% of the orange is left behind as waste (Pfaltzgraff 2014). However, the pulp and peel contain many components such as pectin, cellulose, flavours, fragrances, antioxidants.

Due to these factors, citrus peel as a biorefinery feedstock has been studied extensively over the past decade at various potential stages to obtain the different components. From this, the following biorefinery for citrus waste can be proposed (summarised in Fig. 11.13):

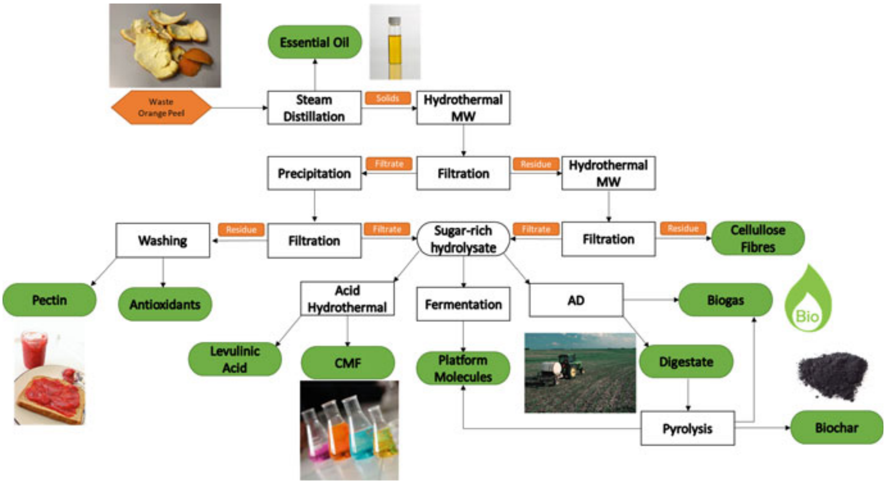

Fig. 11.13 A proposed biorefinery for waste citrus peel

Firstly, to preserve the inherent fragrance and flavour molecules, the citrus peel can undergo steam distillation to produce the essential oil as a product. Essential oils from many different plants are prominently used as an additive to impart scent or flavour in many products—however orange essential oil is of particular interest as it is comprised mainly of a single component, limonene. This is already an important ingredient in many products, from confectionary to cleaning materials due to the fact that it is not only a fragrant molecule, but has good solvation properties, making it a good candidate as a green solvent to replace traditional petroleum-based hydrocarbon solvents (Ciriminna et al. 2014).

From here, the remaining orange peel can undergo hydrothermal microwave treatment to extract pectin as described previously. The work-up stage for pectin production requires separating out the pectin-rich water from the cellulosic residues via filtration or centrifugation. The resulting filtrate/supernatant then has an alcohol (typically ethanol or iso-propanol) added as an antisolvent to precipitate out the pectin. The pectin is then removed (again via filtration or centrifugation) and subsequently washed with hot solvent to remove the impurities and obtain the pure product—however the impurities include many polyphenols, such as hesperidin and naringenin, which are antioxidants in the fruit, but can also act as natural pigment molecules (May 1990; Pfaltzgraff et al. 2013).

The aqueous/alcohol filtrate at this point primarily contains the dissolved sugars. Once the alcohol is distilled off for recovery, there are several options for the sugar-rich water. It can then be used for CMF production via acid hydrothermal treatment. It can also be fermented to produce bioethanol and bio-butanol fuels, or platform molecules such as succinic acid. Or, as a low-value resort if other options aren't available, there is still the option of AD. From here, the resulting digestate can be used as fertiliser, or alternatively can be subject to pyrolysis to yield further amounts of biogas for energy, as well as the biochar and bio-oil, the latter of which can be refined to other platform molecules.

Meanwhile, the cellulosic residues that are left behind in the pectin extraction can then undergo further hydrothermal microwave processing to hydrolyse the hemicellulose chains and leave behind the purer cellulose fibres. Again, the cellulose fibres can be separated out via filtration or centrifugation leaving behind the sugar-rich hydrolysate which can then undergo the CMF/fermentation/AD routes as described above (De Melo et al. 2017; Matharu et al. 2018).

The overall process therefore utilises several of the techniques described to help achieve a full, zero-waste biorefinery strategy where no part of the citrus peel is consigned to waste. Crucially, it also involves refining of the side streams of each process (filtrates, residues, etc.) to either feed back into the process through processes such as solvent recycling. Furthermore, by only using techniques such as microwaves and filters and chemicals such as water and ethanol, the process conforms to the regulatory requirements of many industries. These crucially include those for food and pharmaceutical applications for products such as the pectin, cellulose and essential oils.

This vision therefore not only sets out to achieve a biorefinery strategy that maximises efficiency of resource utilisation, but one that can help supply as wide a range of industries as possible as a means to help convert as many processes as possible from petroleum-derived to bio-derived.

11.3 Outlook

Overall there have been many advances in both techniques that can be used in more wider biorefinery strategies and knowledge of some of the more specific opportunities for food waste as a biorefinery feedstock over the previous 5–10 years. However, the TRL for these vary considerably. For instance, anaerobic digestion is already used extensively for food waste both in-house with companies involved in the food supply chain, as well as with the third party companies offering wider services to municipal and commercial waste. Thermal pyrolysis plants are also now in operation in several countries as a waste treatment option alternative to landfill and incineration, whilst supercritical CO_2 is already deployed in the food industry for applications such as decaffeinated coffee.

However, some of the more high-value applications discussed remain more niche opportunities. Despite the serious reductions in energy and time offered by the use of microwaves to replace conventional heating methods, this is still at pilot scale at the time of writing. As this is still a relatively niche area there is still no ‘standard’ for reactor design at pilot or industrial scale and therefore high capital costs are a major barrier for commercialisation (Asomaning et al. 2018).

In more positive developments however, the development of CMF production from sugar-rich wastes has now resulted in a spin-out company. Several new industrial partnerships have been announced for various applications over the previous year (2020–21) representing a large opportunity for bio-based materials to enter the market to displace their crude-oil based counterparts.

Another key factor to consider is the area of deployment for many of these processing technologies depending on the choice of UFSCW stream. It has already been noted that many of the target industries, such as food and pharma, are heavily regulated globally with regulation set to tighten, rather than relax, particularly in developing countries (Pezzola and Sweet 2016). Many of these regulations centre around what chemicals can be included in processing to avoid trace contaminants in the final products. The technologies discussed here have largely avoided this by relying primarily on mechanical techniques, or methods and chemicals that are already largely approved in these industries, such as microwaves, water, ethanol and mineral acids and alkalis.

However, in light of consumer safety, the issue of the feedstock is also important. Whilst this work discusses food wastes, the reality is that as soon as these materials are consigned as 'wastes' it will become extremely challenging to get any products arising from them through End of Waste regulations to be able to be used in these industries—notably in the EU (Brown 2013; De Luis and Palacios 2013). This is partly due to the fact that they will likely enter non-food grade/sterile environments upon being moved through the waste processing stages but also due to degradation. Some UFSCW streams such as eggshells or wheat straw can remain relatively stable for a long time, depending on storage conditions. However many such as apple pomace or pea vine will begin undergoing enzymatic browning or enzyme-knock out almost as soon as they are juiced, peeled, harvested, etc. Additionally, nearly all UFSCW, particularly wet, sugar-rich streams, are ideal growth media for bacteria, moulds and fungi. In order to avoid the need for consignment as waste, reduce the risk of spoilage and maximise the efficiency of the processes UFSCW biorefineries should aim to integrate alongside the processes and locations where the streams are being produced in the first place to minimise transport and storage time.

Consideration of which techniques to deploy is also of importance when considering location and the impact on the local environment. For instance—when considering hydrothermal techniques, water is considered an ideal solvent across much of Europe and North America due to its safety and ease of availability, but this is not the case across areas of Africa and the Middle East where water is much scarcer. Also, the generation of biogas through pyrolysis requires careful emission controls due to the composition and odour at lab scale alone—large amounts being generated would be unlikely to be readily accepted in locations close to residential, or environmentally sensitive areas.

Also important is the consideration of heterogenicity. Single source feedstocks such as citrus peels, wheat straw and pea vine can easily accumulate in large volumes at source processing, allowing for effective removal of extractives in relatively high amounts. However, this does not apply further down the food supply chain in cooking and catering stages where many different UFSCW streams start to be combined. At this stage, specialist chemicals unique to a certain feedstock become far more dilute in the overall waste stream and thus specialist extraction techniques will inevitably reduce in both efficiency and economic viability. At this stage, bulk processing through measures such as AD and pyrolysis are likely to remain the best option for the near-future, unless more efficient source-separation can be deployed in commercial kitchens and processing plants.

Overall, it is important not to seek quick-wins when designing strategies for biorefining UFSCW, but to consider the whole supply chain and strategically select the best techniques not just for the feedstock, but desired output. It also requires fuller systems thinking approaches to join up different processes to target a 'zero-waste' approach. As an inevitable by-product of human society, UFSCW will always be an issue to deal with. The biorefining strategy is a promising approach to turn a problem into a valuable resource to address a number of other societal issues under a holistic, whole systems approach that does not consider dealing with UFSCW in isolation, but how the different feedstocks and strategies can be linked to address different needs of different societies appropriately.

11.4 Image Credits

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Chapter 12
The Role of Livestock Wastes in Clean Energy: A Mapping in Germany's Potential Installations

Aura Cárdenas and Harald Schernthanner

Abstract Agricultural production worldwide has been increasing in the last decades at a very fast pace and with it the waste generation. Livestock activities are one of the largest producers of residues in the agricultural sector and contribute greatly to climate change. The present chapter gives an introduction and an in-depth analysis of the waste management of livestock for the conversion in a circular agriculture and economy based on research and experience in the sector conducted in the last decades. The conversion of animal waste into energy generation is an opportunity for farmers to obtain additional economic benefits, while contributing to the environment by preventing the release of GHGs into the atmosphere. The use of animal waste for energy generation through anaerobic digestion is a progressive technique and is being widely accepted in Europe, where Germany is the leading country in the use of biogas plants for energy production among others in the European Union. Economically speaking, the livestock industry faces the challenge of converting its production into a clean and more profitable production. The goal of this chapter is to analyze the economic benefit as well as the environmental contribution and future challenges of the use of livestock waste in the biorefineries sector from different perspectives, based on an intensive literature review. This review is accompanied by a geospatial analysis component, mapping biogas reactor hotspots and clusters in Germany, by means of methods of spatial statistics as analysis methods as kernel density estimations (KDE) and K-means clustering, based on volunteer geographic data. The applied methods easily can be transferred to other regions and allow a quick macroscopic overview over existing biogas reactors; furthermore, an identification of cluster and hotspots with a high biogas potential, that in a subsequent step can be analyzed in depth in larger scales.

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12.1 Introduction

Global human population is growing and if it reaches 9.1 billion by the year 2050, the food production will have to increase by 70% (Röös et al. 2017). The consequences of this increase represent a great challenge for the agricultural and livestock industry, which is already under high pressure and has difficulties in satisfying the current demand and handling the consequences of mass production, such as waste generation (Smith2015; Murchie et al. 2009; Fróna et al. 2019).

To improve production efficiency and achieve the targets, improved farming is needed, which would demand investments that optimize the management as well as enhance the global crop production potential. According to the OECD (2020) for the next decade, the global crop production is expected to come from intensive production systems and only a small part of the food demand will be supplied by productions systems related to the expansion of cropland, regional crop production gaps are expected to be reduced over the next decade, as yields of major crops are expected to increase in India and sub-Saharan Africa due to better adapted seeds and improved crop management. Similarly, a large part of the expected livestock production will proceed from productivity improvements, notwithstanding herd expansion is also expected to contribute significantly to livestock production growth in emerging economies and low-income countries; while productivity improvements in the livestock sector will be achieved mainly through more intensive feeding methods, genetic improvements and better herd management practices are also expected to be implemented.

It is also important to mention that the increase in production to fill the future lack of food also implies an increase in production of waste; therefore, the agriculture and livestock sector face another challenge, the management of residues in an environmentally friendly direction. In the last decades, different alternatives have been presented to improve waste management, this brainstorming that has been generated over the years has led us to have viable alternatives not only environmentally viable but also economically beneficial to farms, in other words we have come to apply the concept of circular economy.

At present, the Netherlands is the leading country in the implementation of circular economy followed by France, Italy, Germany, Luxembourg, Belgium, Portugal, and Spain. Each of these countries has a different way to apply the circular economy. In this chapter, we will focus on the case of Germany as it has positioned itself as the leader in waste management on the way to the transformation toward a circular economy (Hanemaaijer et al. 2021; OECD 2020).

12.2 The Role of the Livestock Industry in Waste Generation

Agriculture residues are generated in the different stage of the production chain (Bedoic et al. 2019). Intensive production systems are principally typified by a high density of livestock stock with high productivity per hectare; however, this type of production system results in a significantly elevated output of animal manure, generating the consequent requirement for appropriate manure management strategies. In countries where these types of systems are expanding considerably, such as in Latin America and Asia, they represent a growing risk of environmental contamination, because of the legal gap regarding environmental legislation. Environmentally responsible intensive production systems demand an integrated production environment, with recycling and legislative support. In Europe, there are years of experience in waste management systems and a long tradition of recycling, with strict regulations regarding waste management (OECD 2020).

Livestock manure storage is a common practice in intensive livestock production, but it contributes greatly to GHG emissions and thus to global warming, with methane emissions being the most important. According to Caro et al. (2014), for the year 2010, methane emissions from the livestock sector globally accounted for about 57% of total GHG emissions associated with the agricultural sector. Methane being the main greenhouse gas emitted by the livestock sector.

The production and management of manure currently represents a great challenge; the GHG emissions from livestock are increasing globally due mainly to the growing herd in developing countries (Caro et al. 2014). Manure management strategies is the only way to have an integrative production system without a negative environmental impact.

12.3 Livestock Residue as for Resources for Clean Energy Production

The energetic use of agricultural waste, through the generation of biogas, makes it possible to improve production systems, thus converting them into integrated systems and clean energy generators and providing a considerable global environmental benefit. From the growth of fodder plants to the consumption of farm animals and their waste, through the production of biogas as an energy source and the reuse of digested sludge as fertilizers, the natural cycle of matter has been closed (Jäkel 2003). Using the anaerobic digestion process, it is possible to convert large amounts of waste, vegetable waste, manure, effluents from the food and fermentation industry, from the paper industry, and from certain chemical industries, into useful by-products.

According g to the German Livestock association there are approximately 12.9 million heads of cattle in total, being the country with the largest dairy herd, and the second country with the most livestock population in the European Union; (BMEL 2018; Thünen-Institut 2021; German livestock association 2022); and a high manure production with approximately 200 million tons per year, from these only one third goes to the biogas production. According to the German Federal Ministry of Food and Agriculture about 9000 biogas reactors exist in Germany, producing about 4500 megawatts of electricity. Those plants provide the power for 9 million households (BMEL 2019).

12.4 Mapping Germanies Biogas Reactors

The data input for mapping the state of existing biogas reactors in Germany was acquired by filtering the OpenStreetMap (OSM). For the data download, a short shell script was written. The code is available GitHub (https://github.com/hatschito/download_bio_reactor_locations/blob/main/download_bio_generator_data.sh.) This script downloads geo-referenced biogas reactor data by specifying corner coordinates and converts the OpenStreetMap native .osm format into the Shapefile format. The download is done by using Overpass Turbo, a web-based datamining tool for searching OpenStreetMap data (OverpassTurbo 2021). The approach is only an approximation with many uncertainties, but it offers all the advantages of the volunteered approach and is based on the object type catalog of the OSM, which in itself offers comparability. The biggest disadvantage of the volunteered dataset is that the data contains no thematic information, as for example about the produced electricity or the size of the facilities, thus only pure spatial analysis is possible. The dataset downloaded May the 17th of July 2021 holds more than 1449 locations. Based on the OpenStreetMap data, the Fig. 12.1 show the created choropleth.

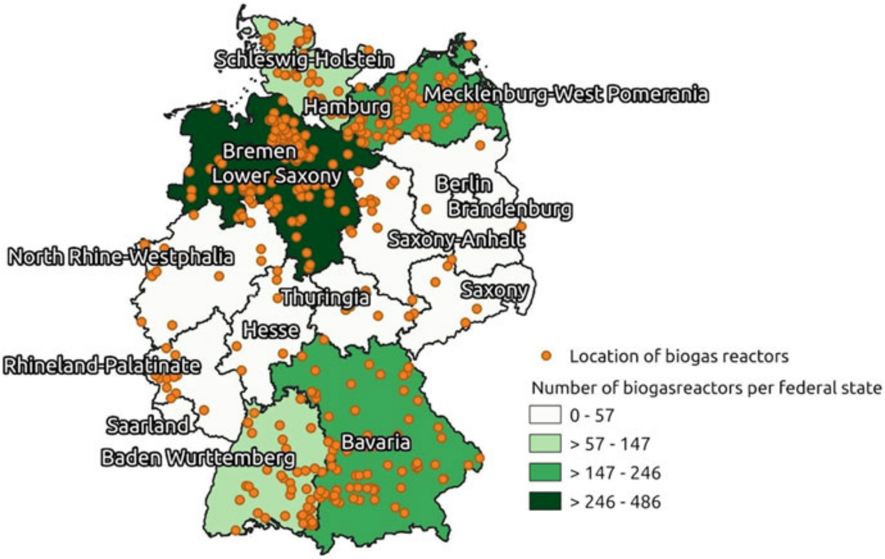

Fig. 12.1 Map of the location and number of Biogas power plants in German federal states

12.5 KDE Heatmap

Core estimation is a proven tool for identifying hotspots. The map in Fig. 12.2 shows the biogas reactor hotspot derived by means of KDE applied in the free open source geoinformation system QGIS. Core density estimation is a proven tool for identifying hotspots. A predefined grid is laid over the point dataset and the density value is than plotted into the cells (Gonschorek et al. 2016). In the visualization below, a 100 m grid was applied to the point dataset. Clearly the hotspot east of Bremen in Lower Saxony can be identified. It is a great tool to quickly derive hotspots and areas from small-scale geographical data, which are worth a more intensity look. In Lower Saxony we can find 270 biogas reactors (from 1500 in Germany), in the relatively small area of ~4000 km^2 (357,000 km^2 is the size of Germany).

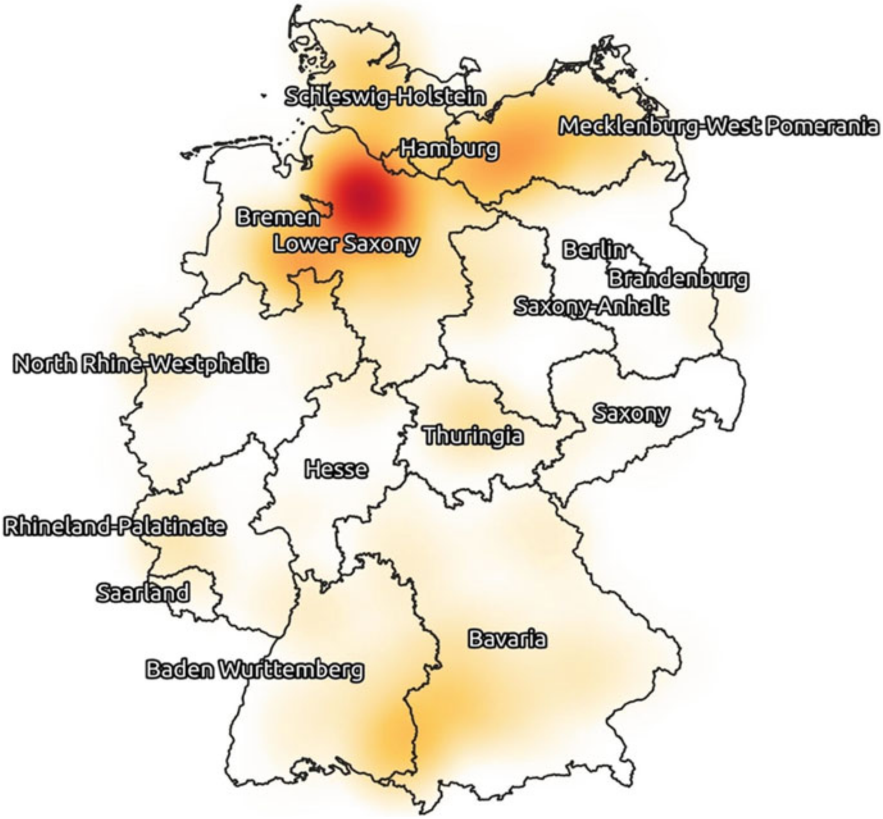

Fig. 12.2 KDE-based heatmap of German biogas reactors

12.6 K-Means Cluster

To get a deeper look on possible cluster that cannot be detected neither by spatial analysis nor by the above demonstrated hotspot analysis, K-means clustering was applied to the data. K-means clustering (Jin and Han 2011) is an iterative center-based cluster method, where n objects are clustered in k clusters, where k is a number of defined target clusters. On the Fig 12.3 is shown how by choosing a relatively

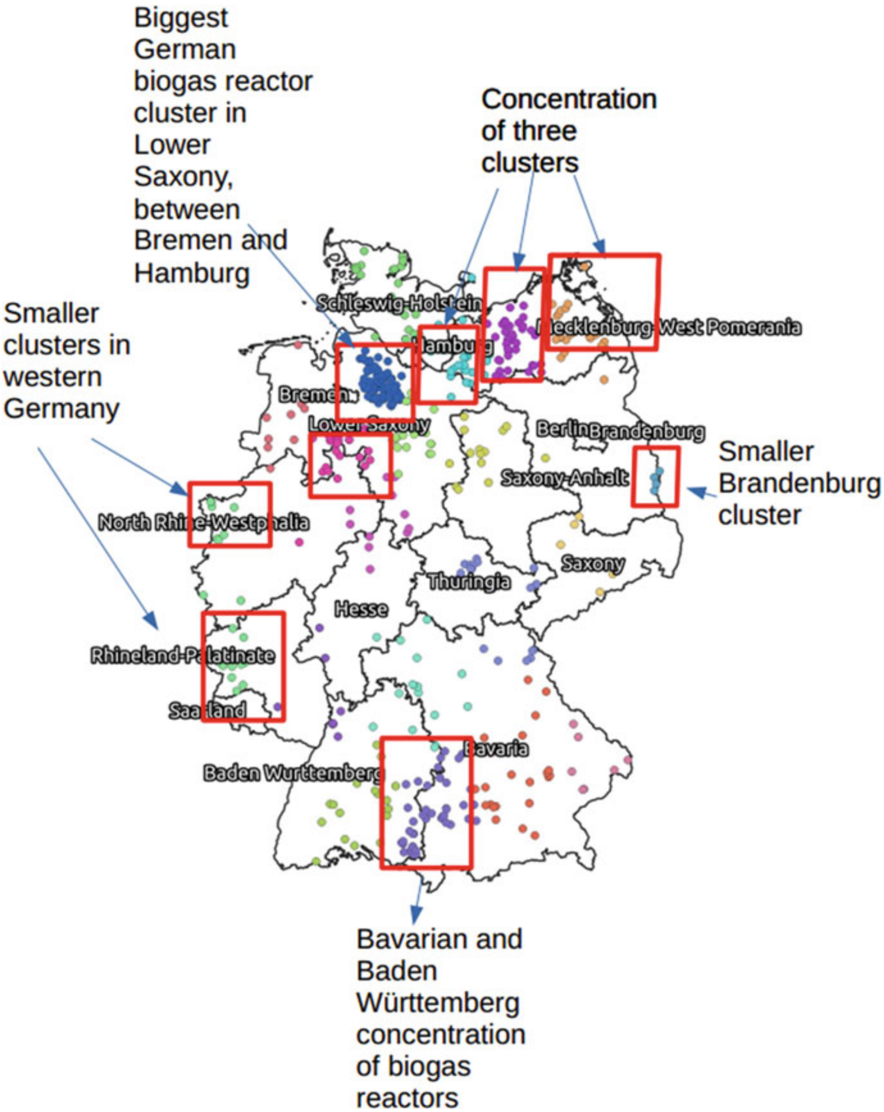

Fig. 12.3 K-means clusters: The points show the K-means cluster membership of each location. The rectangles are the authors' interpretation of clusters

high cluster number of 20 classes, singular biogas reactors could be excluded and cluster areas identified.

12.7 Conclusions

The current and future demand for food is a huge challenge for global livestock production; to achieve this goal it will be necessary to adjust along the way, so that the intensification of production systems does not place an additional burden on the environment, which is already suffering the consequences of the mistakes that have been made in the past and those that we continue to make today. Sustainable integrated production strategies are the alternative for the future of livestock production, we are working hard to meet the future challenges in an integrated and sustainable way.

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Chapter 13
Agricultural Waste-Derived Management for Bioenergy: A Paradigm Shift in the Waste Perceptions

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Abstract Waste management is a global issue facing all the economies of the world. It is estimated that 2 billion tonnes of agricultural waste is generated annually, with organic waste making up to 80% of this amount. Waste generation and its mismanagement come with severe consequences such as flooding, climate change, poor health, lost productivity, and damage to businesses and tourism; and agricultural waste is responsible for 21% of greenhouse gases, globally. Nevertheless, over the years, several approaches have been widely deployed to tackle this big issue; this includes waste reduction, reuse, recycling and reclamation for energy, with overarching benefits of food and resource security, sustainable production and consumption, poverty reduction, and sustainable energy. Therefore, this chapter focuses on how what has been tagged "waste" is being used to generate useful energy. Firstly, an outlook of the general waste management is put in perspective, touching on prevailing practices and waste handling techniques from inception to the point of disposal; this is followed by an insight into climate change, the impact of associated natural and anthropogenic factors and their correlation with waste management. Next, an assessment of the various waste-to-energy conversion technologies—exploring their suitability to individual feedstock, i.e. via direct combustion, anaerobic digestion, gasification and torrefaction. The chapter also focuses on the proper applications of waste-to-energy, which include power generation, hydrogen production, biofuel, etc. It concludes by presenting some of the advances made so far in biomass conversion technologies. The chapter tries to simplify the complexities associated with agro-waste generation, conversion and utilisation, and reiterates

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the dangers of accelerated climate change, hence, promoting a paradigm shift in the perception of waste from discarding to reuse.

13.1 General Waste Management

Waste is described as any material that is not a prime product (i.e. it is not met for market purpose), which the generator has no further use for, but with the intention of disposal. Over the years, economic growth and urbanisation have accelerated the quantities of waste being generated, and uncontrolled disposal of waste is a bane to the environment. Waste management involves the collection, transportation, treatment (conversion) and disposal of unwanted materials or by-products of human activities. It also involves the monitoring and regulation of waste-related technologies, processes, economic mechanisms and policies (UN 2017). It can be inferred that the central aim of waste management is to reduce the amount of "unusable substances" and prevent potential environmental and health hazards.

In this chapter, the waste stream in focus is agricultural wastes, which are the by-products of vegetal, livestock, poultry, forestry and agro-industrial processes. Globally, agricultural waste generation is estimated at approximately 2 billion tonnes, with forest waste put at 0.2 billion m^3 (Millati et al. 2019). Additionally, agricultural waste has been shown to increase by 5–10%, annually (Gutiérrez et al. 2020). This huge agricultural waste generation comes with several consequences, when mismanaged, for example, flooding, climate change, poor health, lost productivity, and damage to businesses and tourism (UNEP and ISWA 2020). For the past 30 years, the World Commission on Environment and Development has consistently alerted all stakeholders on the deep crisis of waste mismanagement in the environment, with agricultural waste alone responsible for 21% of greenhouse gases (Duque-Acevedo et al. 2020).

13.1.1 Waste Management Practices

Waste management practices differ around the world, for instance, it differs from the Global South and Global North divide. The total quantity of waste generated in low-income countries has been projected to increase by more than three times by 2050; with East Asia and Pacific regions generating the largest amount of waste at 23%; and the Middle East and North Africa generating the least waste at 6% (World Bank Group 2021), while the regions with the fastest growth in a waste generation are South Asia and Sub-Saharan Africa, see Fig. 13.1.

Proper waste management is necessary for the building of liveable and sustainable cities. However, this remains a challenge for many developing countries, because waste management is relatively expensive—consuming a whooping 20-50% of a municipal budget (WBG 2020) and requires modern technologies,

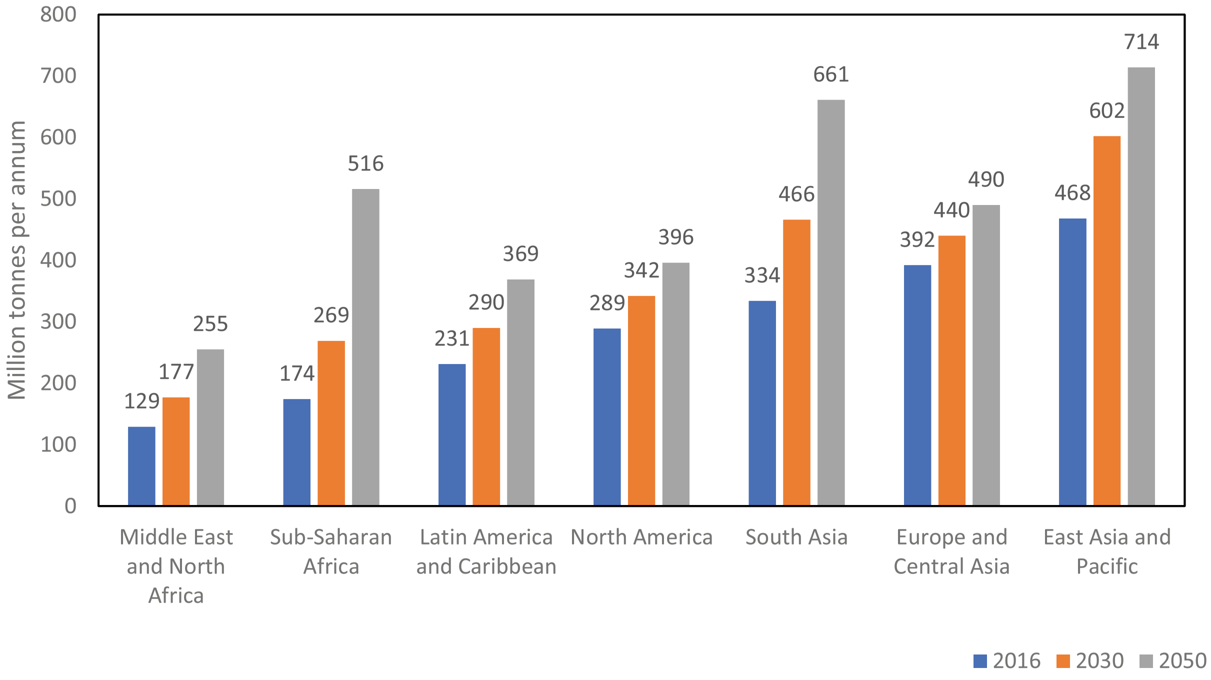

Fig. 13.1 Projected waste generation rate per region

Fig. 13.2 A typical heap of rice husk [by permission of Diemuodeke et al. 2021]

which may not be at the disposal of low-income countries. One of the oldest and most common practices for agricultural waste disposal is unregulated landfills or open dumping, see Fig. 13.2 for a typical heap of rice husk, and this has serious implications on health and the environment, because of pollution from open burning and groundwater contamination by toxic chemicals (Statistica 2019). More also, methane and carbon dioxide released from landfills have remained a major issue of global warming (Hansen and Cheong 2013). Notwithstanding, traditionally, organic wastes find use in improving the physical and chemical properties of the soil for the purpose of farming; with animal manure, food processing waste and other industrial wastes being the major sources (Westerman and Bicudo 2005). Other waste management methods and their environmental impacts are presented in Table 13.1. However, recently, waste management has included, reduction, reuse, recycling and reclamation for sustainable energy, with the latter being one of the most effective approaches to waste management (Ogorure et al. 2018; Oko and Nwachukwu 2018; Owebor et al. 2019).

The increasing energy demand has also yielded some good fruits in better managing agricultural waste. Agricultural wastes have been useful in biorefineries for the production of bioethanol, biogas and electricity which can significantly meet a substantial part of the useful energy needs of the society (Serna et al. 2016). Table 13.2 presents the major agro-waste generation in the world. These wastes include corncob, rice husk, rice straw, wheat straw, cassava peels, spent barley grains, sugarcane bagasse, potato peels, oil palm empty bunch and soybean.

Table 13.1 Possible environmental impacts of respective waste management practices

Waste management	Environmental impacts				
	Water	Air	Soil	Landscape	Climate
Landfilling	Leachate (synthetic organic compounds, heavy metals)	CO_2, CH_4, VOCs, odour, noise	Heavy metals, synthetic organic compounds	Visual effect, vermin	Worst option for GHGs[a]
Incineration	Fall-out of atmospheric pollutants	SO_2, NO_x, HCl, N_2O, HF, CO, CO_2, dioxins, furans, PAHs, VOCs, odour, noise	Fly ash, slags	Visual effect	GHGs[a]
Composting	Leachate	CO_2, CH_4, VOCs, odour, noise, bioaerosols	Minor impact	Some visual effects	Small emissions of GHGs[a]
Land spreading	Bacteria, viruses, heavy metals	Bioaerosols, dust, odour	Bacteria, viruses, heavy metals, PAHs, PCBs	Vermin, insects	Small emissions of GHGs
Recycling	Wastewater	Noise, dust	Landfilling of residues		Minor emissions
Waste transportation	Spills	CO_2, NO_x, SO_2, dust, spills, odour, noise	Spills		Significant contribution of CO_2

[a] Assuming no energy recovery; *CO_2* carbon dioxide, *CH_4* methane, *VOCs* volatile organic compounds, *SO_2* Sulphur dioxide, *NO_x* nitrogen oxides, *N_2O* nitrous oxide, *HCl* hydrochloric acid, *HF* hydrofluoric acid, *CO* carbon monoxide, *PAHs* polycyclic aromatic hydrocarbons

13.1.2 Climate Change and Waste Management

There is a steady increase in the generation of agricultural waste around the world. Improper disposal and/or utilisation of these wastes have an adverse impact on human health, either through direct handling of the waste or indirectly from contamination associated with water or the soil; the environment through pollution from burning which releases harmful gases, or in landfills or as manure which harbour pathogens, parasitic eggs and produces leachates that contribute to the emission of greenhouse gases. Waste management is thus aimed at reducing the adverse effects of waste on human health, the environment, planetary resources and aesthetics. At 1.6 billion tonnes of carbon dioxide (CO_2) equivalent greenhouse gas emissions generated from solid waste treatment and disposal in 2016, food waste accounts for 50% of these emissions (World Bank Group 2021).

Greenhouse gases are not inherently bad, as the term has been touted to sound in recent times, due to the issue of climate change currently being experienced

Table 13.2 Major producers of agricultural waste in the world

Agro-waste type	Country	Production (MMT)
Corncob[a]	USA	86.24
	China	56.54
	Brazil	20.79
	Argentina	11.22
	EU	13.42
	Global	*252.34*
Rice husk[b]	China	39.00
	India	30.00
	Indonesia	10.00
	Bangladesh	9.00
	Vietnam	8.00
	Global	*137.00*
Rice straw[b]	China	149.00
	India	114.00
	Indonesia	39.00
	Bangladesh	36.00
	Vietnam	30.00
	Global	*512.00*
Wheat straw[a]	China	106.17
	India	77.35
	Russian Federation	51.17
	USA	48.20
	France	31.88
	Global	*637.50*
	European Union	17.48
	Russian Federation	5.25
Spent barley grains[a]	Canada	2.71
	Australia	2.40
	Ukraine	2.36
	Global	*43.71*
Cassava peels[a]	Nigeria	7.02
	DR Congo	3.73
	Thailand	3.66
	Brazil	2.25
	Indonesia	2.23
	Global	*34.46*
Sugarcane bagasse[b]	Brazil	94.00
	India	93.00
	EU	55.00
	Thailand	38.00
	China	29.00
	Global	*510.00*

(continued)

Table 13.2 (continued)

Agro-waste type	Country	Production (MMT)
Potato peels[a]	China	24.83
	India	13.34
	Ukraine	6.19
	Russian Federation	6.13
	Bangladesh	5.67
	Global	*101.20*
Oil palm empty bunch[a]	Indonesia	38.17
	Malaysia	19.77
	Thailand	2.01
	Colombia	1.01
	Nigeria	0.91
	Global	*68.16*
Soybean hull[a]	Brazil	10.1
	USA	9.90
	Argentina	3.02
	Chile	1.14
	India	1.10
	Global	*27.90*

[a] An estimation based on Riaz (2016); Sadras and Calderini (2021); Vaitkevicien (2019)
[b] Millati et al. (2019); *MMT* million metric tonnes

worldwide. The original function of the earth's greenhouse gases is to make the planet livable by trapping some amount of earth's thermal energy which would otherwise have escaped into space; this heat-trapping phenomenon is what is termed the greenhouse effect. However, the presence of too few greenhouse gases makes the planet too cold and too much causes the earth to become too warm; thus, this is where the condition for "balance" is important (National Aeronautics and Space Administration 2021). Though sources of greenhouse gases in the atmosphere are both natural and anthropogenic, human activities in the past 50 years are the primary cause of their increased concentration causing global warming (Melillo et al. 2014). Natural sources include variations in the sun's output, multiple emissions from volcanic activities, methane from wetlands, the earth orbit, the carbon cycle, ice cores and thawing of permafrost; while anthropogenic sources include agriculture, land-use change, waste mismanagement and improper treatment activities and combustion of fossil fuels (United States Environmental Protection Agency 2020). The leading source of anthropogenic methane emissions is agriculture, followed by gas venting and fugitive emissions; but with regards to agricultural methane sources, livestock rearing is the largest contributor, seconded by traditional rice cultivation (International Energy Agency 2020; Reed 2020).

Major greenhouse gases include carbon dioxide (CO_2) (most commonly produced by human activities), methane, nitrous oxide and synthetic chemicals or fluorinated gases. CO_2 accounts for 64% (after increasing by 40% from the advent of industrialisation); methane is responsible for 17% and nitrous oxide contributes 6% of man-induced global warming (European Commission 2021).

13.2 Waste Conversion Technologies

Awareness of the finite nature of fossil fuel, coupled with pollution, increase in population, increasing waste generation, energy shortages and need for more competitive energy markets are aggregated factors that have in recent times influenced the behaviour of energy consumption as well as energy policies. It is estimated that potentially harvestable biomass residue worldwide has an energy content of 93 EJ, annually (Jayasuriya and Soni 2003).

Again, climate change has called for an urgent need to live more sustainably, globally, and agricultural wastes which are non-edible lignocellulosic biomass have been considered as second-generation biofuels for energy applications. Most of the agro-wastes have good heating values and can be utilised in value-added processes. Agricultural feedstock can be transformed into high-quality biomass, oils, biochar, syngas, biogas, bioethanol, biodiesel, etc., and several technologies and processes have been identified for converting agricultural waste to useful energy, these technologies are, however, dependent on the feedstock (Foster et al. 2021; Pöschl et al. 2010), see Fig. 13.3.

13.2.1 Incineration

Incineration is the oldest and most widely practised waste disposal method by direct combustion of the waste materials in the presence of excess air (Kan 2009). Incineration is high-temperature waste reductions and disposal process systems that can also be termed "thermal treatment". Incineration involves oxidation (presence of oxygen) and exothermic (release of heat) processes at temperatures beyond 850 °C. Normally, incineration involves the direct combustion of combustible waste materials in the presence of excess oxygen to produce water vapour, carbon dioxide, oxygen and oxide of Nitrogen. However, oxides of Sulphur are also produced from the Sulphur component in the fuel, which produces acid rain in the presence of water in the air that causes corrosion and other imbalances on the ecosystem. To minimise the emission of Sulphur oxides into the air (vis-à-vis acid rain), limestones are introduced into the stack of the incinerators (Tabasova et al. 2012). The incineration method of waste disposal can treat various types of combustible and non-combustible wastes (Foster et al. 2021). However, the non-combustible materials (e.g. metals, glass) form part of the Bottom Ash (residual carbon) which can easily be collected, segregated and disposed of (Department of Environment and Rural Affairs 2013). The incineration process could be classified into three fundamental types; namely, gate, rotary kilns and fluidized beds which are designed for a

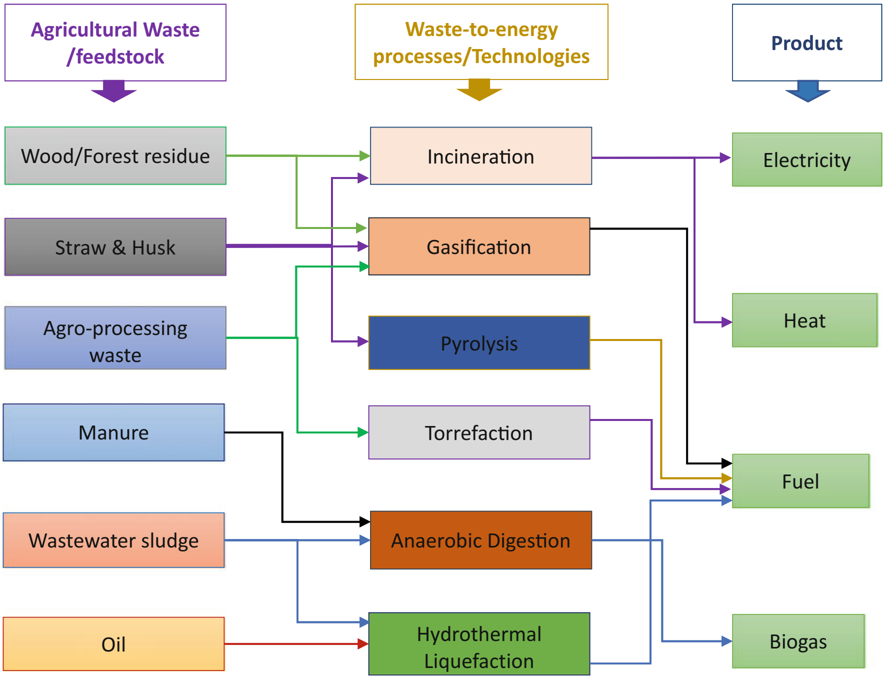

Fig. 13.3 Pictorial view of waste-to-energy pathways

specific class of feedstock; whereas there are varied designs of incineration for the purpose of useful energy recovery which include heat only boiler (HOB) for process heat, condense power (CP) for electric power generation and combined heat and power (CHP) for both electric power and process heat generation (Eriksson and Finnveden 2017).

13.2.2 Gasification

The gasification method involves the thermal treatment of wastes in the presence of limited oxygen, steam and carbon dioxide at elevated temperatures (800–1100 °C) to produce gaseous products (Alauddin et al. 2010; Devi et al. 2003; Ruiz et al. 2013). Depending on the system's configuration, the thermal treatment could be done directly or indirectly (USEPA 2014). The nitrogen in the air has the potential of lowering the heating value of the produced fuel (called syngas) from the gasification method, therefore, it requires optimal process operation (Galvagno et al. 2016). Therefore, partial oxidation is achieved by reducing the resident time of oxygen at the gasifier temperature to avoid the oxidation of the syngas before the collection and storage phase. The syngas from the gasifier process could be used to generate heat and electricity or used as a material in the production of ethanol in the chemical industries. The syngas is a combination of gases (H_2, CH_4, CO, CO_2, H_2O and N_2), with trace amounts of lower hydrocarbons; however, menthane (CH4) has the greatest composition of the produced syngas (Clarke Energy 2021; Foster et al. 2021). Because of the operating conditions of the process and composition of produced gas (syngas), gasification has found several applications in the process industry and power generation in the form of combined heat and power systems with bottoming high-temperature fuel cells (Ogorure et al. 2018; Oko and Nwachukwu 2018; Owebor et al. 2019).

In the gasification process, the feedstock to be fed into the plant is required to be of finely granulated consistency, therefore, pretreatment is required; clearly, this is a disadvantage compared to the incineration technology which also has a lower residue percentage of feedstock. However, the gasification process has the advantage of lower volumes of gases produced which translates to the use of smaller flue gas treatment systems and smaller wastewater flows from syngas cleaning; overall thermal efficiency of about 75%; the use of partial oxidation reduces the number of oxidised species such as SOx and NOx and are replaced by hydrogen sulphide, nitrogen and ammonia which are easier to scrub from the syngas than the oxidised version before syngas utilisation (Bosmans et al. 2013; Galeno et al. 2011; Soni and Naik 2016).

The gasifier could be fundamentally classified into three main types which include fluidized bed, fixed bed and entrained flow. The gasifiers can treat various sources of waste, e.g. municipal solid waste, dried effluent from anaerobic digesters, dried sewage sludge, some types of hazardous wastes and waste agri-food and process foods (Lee et al. 2019).

13.2.3 Pyrolysis

The process of pyrolysis involves the degradation of solid wastes under moderate temperatures (usually, between 300 and 700 °C) in the presence of a limited supply of oxygen similar to the gasification process (Foster et al. 2021; Lam et al. 2016). The pyrolysis of solid waste degradation process could be classified into two fundamental types depending on the speed of the process; namely, conventional pyrolysis and fast or flash pyrolysis.

For hundreds of years, conventional pyrolysis has been used to produce charcoal (primarily product) accompanied by some chemicals—methanol and acetic acid—which is the main process that drives the charcoal production space in sub-Saharan Africa. While conventional pyrolysis mainly produces a solid product, fast pyrolysis produces liquid products from biomass thermal degradation. On a dry mass basis, pyrolytic oil and char account for 40–75% and 10–20%, respectively, of the products of the biomass thermal degradation under the pyrolysis method. However, fast pyrolysis is gaining prominence because of its versatility and the liquid product, which can easily be collected, stored, transported and well-suited to support liquid-fired power (heat and electricity) generation systems (Yanik et al. 2007).

The pyrolysis waste-to-energy conversion technology is limited by technical challenges such as feedstock homogeneity, which requires a significant amount of preprocessing efforts; blockages from fly ash and tar deposition; the requirement for adequate and efficient catalysis; and choking of process pipings with the ultimate plant failure. These challenges are attributed to the limited global applications of pyrolysis even with the excellent promises (Department of Environment and Rural Affairs 2013).

13.2.4 Anaerobic Digestion

Anaerobic digestion (AD) is a biochemical degradation of wastes in the absence of air. The anaerobic digestion breaks down complex lignocellulosic materials to produce biogas (majorly methane), carbon dioxide, water vapour and hydrogen sulphide with the effluent serving as a bio-fertiliser to improve soil nutrients, which offset GHG emissions from chemical fertiliser (Labatut and Pronto 2018). Anaerobic digestion involves mainly four fundamental phases, which include hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Demirbas 2011). Some research works have established that 1 m^3 of anaerobic digestion-derived biogas could produce 21 MJ of energy that could generate 2.04 kWh of electricity at 35% energy system conversion efficiency (Murphy et al. 2004). The amount of biogas generated is dependent on the organic loading rate (OLR) which is a measure of the volatile materials in the influent substrate per unit volume and time (g/L-d). The OLR can be computed based on the knowledge of the substrate concentration and digester hydraulic retention time (HRT) using Eq. (13.1) (Labatut and Pronto 2018):

$$\mathrm{OLR} = \frac{S_0}{\mathrm{HRT}} = S_0 \frac{Q}{\forall} \tag{13.1}$$

where OLR (g/L-d), S_0 (g/L), and Q (L/d), are the organic loading rate, basis, is influent substrate concentration and is flow rate on VS or COD basis, respectively; whereas HRT (d) and $\forall$ (L) are hydraulic retention time and anaerobic digester volume, respectively.

The yield of biogas from the substrate in an anaerobic biochemical degradation process is dependent on the carbon-to-nitrogen (C/N) (Zhang et al. 2014). In general, the optimal C/N ratio for anaerobic digestion is thought of between 20 and 30 (Puyuelo et al. 2011). The anaerobic digestion system's performance (or energy output or biogas yield) is measured by substrate stabilisation efficiency and methane production. Eq. (13.2) presents the analytical relation for the computation of the substrate stabilisation (or treatment) efficiency (E) under a steady-state anaerobic digester operation (Labatut and Pronto 2018).

$$E = \frac{S_0 - S}{S_0} 100 \tag{13.2}$$

where S (g/L) is effluent substrate concentration, on VS or COD basis.

The anaerobic digestion energy conversion technology is challenged by the long time it takes for the microbial reaction to occur (about between 20 and 40 days), and, also, the presence of a high concentration of free ammonia (NH_3) obtained from nitrogen-rich protein substrate which can undermine the methanogenic bacteria supporting the anaerobic digestion process (Chen et al. 2008; Fountoulakis et al. 2008).

13.2.5 Hydrothermal Liquefaction

This involves the thermochemical degradation of wastes (biomass) into bio-crude oil that is refined into petroleum-derived fuels. Similar to anaerobic digestion, the hydrothermal liquefaction process supports wet biomass conversion without the requirement for drying as required by incineration, gasification and pyrolysis. Hydrothermal liquefaction is essentially pyrolysis in hot liquid water and, therefore, suitable for feedstock high in water content such as manure and sewage sludge (Foster et al. 2021). The major challenge faced by this bio-crude oil from hydrothermal liquefaction is the presence of a diverse range of chemical compounds in the downstream process; for instance, the high heteroatom content in the bio-crude oil can cause undesirable qualities such as acidity (Vardon et al. 2011). The hydrothermal liquefaction process occurs at pressurised environments within the range of 4–22 MPa which avoids oxygen and heats to elevated temperatures of between 250 and 374 °C; the high pressure and temperature environment facilitates the breakdown and reforming of biomass macromolecules into the desired bio-crude oil. This process has a major advantage in that at these operating conditions, water has a higher dissociation constant and lower dielectric constant which makes it less polar and a good solvent for hydrocarbon products and promotes their reactions.

13.2.6 Torrefaction

Torrefaction is a thermal pretreatment technology for biomass energy densification under temperature ranges of 200–300 °C and at atmospheric pressure in the absence of oxygen (Faaji and Bergman 2008; Zanzi et al. 2002). Torrefaction of biomass is isothermal pyrolysis at an inert and atmospheric environment to induce a series of biomass reactions which include devolatilisation, depolymerisation, and carbonisation of hemicellulose, lignin, and cellulose (Shankar et al. 2011). There are three different products from the biomass torrefaction; namely, (1) brown to black uniform solid biomass used for bioenergy applications, (2) condensable volatile organic compounds comprising water, acetic acid, aldehydes, alcohols, and ketones, and (3) non-condensable gases like CO_2, CO and small amounts of methane. The release of these condensable and non-condensable products results in changes in the physical, chemical, and thermal properties of the biomass (Bergman et al. 2005; Deng et al. 2009; Prins et al. 2006). Torrefaction increases the energy density of the torrefied product and improves its overall fuel properties. However, torrefaction is a high-energy pretreatment operation due to the high internal energy requirement of the process. The use of the excess heat generated during the process is encouraged to improve the system's overall efficiency (Shankar et al. 2011). Torrefaction of biomass alters its physical and chemical properties such as moisture content, density, grindability, pelletability, hydrophobicity, calorific value, proximate and ultimate composition, and storage behaviours such as off-gassing, spontaneous combustion, and self-heating (Sadaka and Negi 2009). Torrefaction typically achieves an equilibrium moisture content of 3% and a mass reduction of 20–30% (primarily due to the release of water, carbon oxides, and volatiles), while retaining 80–90% of the original energy content of the wood (Lipinsky et al. 2002). Due to the deep drying process of torrefaction, and depending on the torrefaction conditions, moisture content of feedstock typically within the range of 10–50% is reduced to 1–3% on a weight basis (Bergman and Kiel 2005). Moisture reduction during torrefaction has three major advantages: (1) lower moisture levels for the conversion process, (2) lower transportation costs associated with moving unwanted water, and (3) prevention of biomass decomposition and moisture absorption during storage and transportation (Shankar et al. 2011). The torrefaction process causes the biomass to be less porous due to the mass loss in the form of solids liquids and gases which results in significantly reduced volumetric density typically between 180 and 300 kg/m^3 depending on the initial biomass density and torrefaction conditions. However, despite the bulk density reduction, the energy density increases and for instance for a pine woodchip that underwent a torrefaction process, the calorific value increased from 11 to 20 MJ/kg (Bergman and Kiel 2005). This increase in calorific value after the process is because biomass loses relatively more oxygen and hydrogen than carbon during torrefaction thus increasing the calorific value of the product (Faaji and Bergman 2008).

13.3 Applications of Waste-to-Energy

Agriculture waste-derived energy finds wide application in electricity generation, biofuels for transportation purposes, hydrogen production, amongst others.

13.3.1 Electricity Production

Agricultural waste and fuel obtained from waste-to-energy have significant calorific values which can be applied more efficiently with the application of suitable technology. As a source of electricity, agro-waste-derived energy has proven useful in electrochemical processes and thermal-mechanical-electrical pathways. Studies have shown that hydrogen and methane which are obtained from the products of gasification and anaerobic digestion are very useful in fuel cell systems, as well as in high-medium-low grade thermal power systems (Galvagno et al. 2016; Ogorure et al. 2018).

Fuel cell systems convert the chemical energy stored in the gaseous fuel into electrical energy without the need for a thermal or mechanical intervention. These systems have been demonstrated to attain very high efficiency since they are not limited by the efficiency limits imposed by the Carnot benchmark on thermal conversion pathways. In fuel cell systems, the fuel reacts with air via an electrolyte which can be in solid or molten form. Several types of fuel cell technologies have emerged depending on the type of electrolyte and temperature requirement, see Table 13.3.

The thermal conversion pathways for electricity production from agro-waste-derived energy has also been demonstrated in the literature. Such systems may fire the raw biomass in an incinerator or combust the syngas or biogas obtained via gasification or digestion processes, to drive a gas turbine, or steam turbines, or other low-grade thermal power plants, such as the organic Rankine cycle, Kalina cycle, and tri-lateral flash cycle. With such systems, it is possible to attain electrical energy sufficiency, especially in low-income countries, and rural enclaves where decentralised power proves to be more economical (Diemuodeke et al. 2021).

Notwithstanding, multigeneration that produces not only electricity has been reported as well. These systems deliver multiple utilities from a single integrated unit, which could include only one or multiple inputs. For instance, the feasibility of

Table 13.3 Classification of fuel cell systems

Fuel cell type	Operating temperature (°C)	Applications
Alkaline fuel cell (AFC)	50–200	Space vehicles
Proton exchange membrane fuel cell (PEMFC)	30–100	Mobile application, combined heat and power (small power)
Direct methanol fuel cell (DMFC)	20–90	Portable electronic systems (small power generation)
Phosphoric acid fuel cell (PAFC)	180–200	Combined heat and power up to 200 kW
Molten carbonate fuel cell (MCFC)	600–700	Medium to large scale combined heat and power
Solid oxide fuel cell (SOFC)	500–1000	All sizes of combined heat and power, 2 kW to multi-MW

Sources: Larminie and Dicks (2003), Owebor et al. (2019), Rayment and Sherwin (2003) electricity, cooling, utility heat and ethanol has been demonstrated in Jana and De (2015). Such kind systems allow for optimal use of the feedstock. Multigeneration via decentralisation is very promising for the rural enclaves which are distantly located from the supply of a national grid and where the economic activities are predominantly agriculture.

13.3.2 Biohydrogen Production

Agricultural wastes have been shown to find application in the production of hydrogen. A study by Vijayaraghavan and Ahmad (2006) proposed that hydrogen-generating microflora can be isolated from cow dung in an anaerobic degradation process. However, this process requires the adjustment of the pH value, and also the application of heat treatment.

13.3.3 Ethanol Production

Agricultural waste from corn and potato peel is used for cleaner and greener compound production, such as ethanol, which has good liquid fuel properties. It is an important chemical that is used in a variety of applications ranging from the food industry (beverages and many food applications) to the petroleum industry (Kulkarni et al. 2015; Meenakshi and Kumaresan 2014).

13.3.4 Packaging Applications

Agricultural waste has emerged as a critical resource in the advancement of biotechnology, as evidenced by the use of agricultural waste (agro-waste) or by-products in the production of bioplastics, specifically polylactic acid, thermoplastics starch, and chitosan bioplastic. Bagasse, corn cob, cellulose, sago pith waste, and chitin are examples of agricultural waste that have the potential to be used as bioplastics (Chan et al. 2021).

13.3.5 Adsorption Agents

Agricultural waste is an excellent source for the adsorption of dyes produced during textile processing. Agricultural waste products are used in the adsorption process in their natural or modified form via the activation process (Rangabhashiyam et al. 2013). Agricultural waste also finds application in the adsorption of phenol from aqueous solution, via activated carbon prepared from rubber seed coat (RSCC), an agricultural waste by-product (Rengaraj et al. 2002).

13.3.6 Fertiliser and Carotene Production

In fertiliser production, the addition of palm oil mill effluent increased dry matter yield quantitatively, yielding a competent phosphorus recovery of 24.8% (Foo and Hameed 2010). According to Ahmad et al. (2008), residue from oil palm processing industries has the potential for carotenes recovery, the most important vitamin A precursor in nutrition chemistry, which protects against night blindness, skin disorders, toxins, colds, flu infections, and immunity level strengthening. The optimal extraction ratio was determined to be 0.6 (solvent/POME), resulting in a maximum recovery of 71.1%.

13.3.7 The Multiple Applications of Rice Husk/Rice Husk Ash

The ash obtained by burning rice hulls is called rice husk ash (RHA) and is a waste product generated by rice mills who use the rice hulls as fuel for their boilers and gasifiers.

Rice husks are currently widely used for pet food fibre, building and refractory materials to improve the tensile strength of materials, organic fertilisers through vermin-composting techniques, microbial nutrients for single-cell protein production, sugar reduction, and raw materials in the production of ethanol and furfural (Foo and Hameed 2009). Rice husk ash (RHA) is a residue derived from the combustion of rice husks; in some cases, the rice husks are directly used as fuel in rice mills to fire boilers and gasifiers (Malhotra et al. 2013). Risk husk ash has many applications in building materials (constituent in cement), chemical industry, mining industry, agriculture (soil ameliorant), water treatment processes and household ceramic products (tiles, glazes) (Heaton and BronzeOak Ltd 2003).

13.4 Advances in Waste-to-Energy Conversion Technologies

The utilisation of agricultural waste has become much more diversified, such as bio-kerosene, bio-gasolene, biomass molding fuel, biodiesel, bioethanol, pyrolysis gas, biogas, and electricity, in addition to a huge variety of by-products that are generated in the process of extracting useful energy from agricultural waste. Some notable advances made in the waste-to-energy conversion are presented in the following subsections.

13.4.1 Biological Hydrogen Production

The call for global climate action and the acceptability of renewable energy for environmental sustainability have induced the popularity and research interest in hydrogen production from biological methods. Microorganisms have a versatile and diverse metabolic mechanism for converting MSW to biohydrogen energy (Dimitrios-Sotirios et al. 2015). It is suggested among the comity of energy scientists that hydrogen would be the fuel of the future (Suksaman et al. 2016). Biologically derived hydrogen uses relatively low energy vis-à-vis low investment cost in its production with a high energy yield of 142 kJ/g^{-1} which is about 2.75 times superior to any hydrocarbon fuel. Biological hydrogen production is free of GHG which benefits the decarbonisation of the energy sector. It is believed that hydrogen will eventually be among the most sought-after raw materials in the chemical industry (Fountoulakis et al. 2008; Goud et al. 2014; Hernandez-Mendoza and Buitron 2013; Kumar and Lin 2014).

There are two fundamental methods of hydrogen production—physical–chemical and biological methods. Physical–chemical methods are energy-intensive processes with greenhouse gas emissions, which contribute to global warming, whereas biological methods are more environmentally friendly, use less energy, and low investment cost. Biological hydrogen production is primarily supported by anaerobic fermentation, which is divided into two categories; light-independent and light-dependent. Biohydrogen is currently attracting scientific interest as a new research area unfolding (Beyene et al. 2018; Dimitrios-Sotirios et al. 2015; Kumar and Lin 2014; Zahedi et al. 2016).

13.4.2 Dark Fermentation

Dark fermentation, as the name implies, involves the degradation of biomass (organic substrate) by bacteria in the absence of light and oxygen to produce hydrogen. The process converts complex organic compounds such as carbohydrate-rich materials by first hydrolysing them into sugar molecules which then go through a series of chemical reactions to produce biohydrogen (Martin and Michal 2009). The amount of hydrogen produced by the dark fermentation process is determined by the type of bacteria involved in the process and the formation of acids (Beyene et al. 2018).

13.4.3 Bioelectrochemical Process

13.4.3.1 Microbial Fuel Cell

Microbial fuel cells (MFCs) are bio-electrochemical devices that produce energy by generating organic phenomena from a variety of substrates using bio electrogenic microorganisms. Microbial fuel cells promise an environmentally friendly technology to meet rising energy demands by converting agro-waste into electricity and hydrogen gas. To generate electricity, the microbial fuel cells device employs electrochemically active microorganisms (EAM). Microbial fuel cells involve aerobic and anaerobic treatments with bacteria acting as a catalyst (Beyene et al. 2018).

13.4.3.2 Microbial Electrolysis Cells

Microbial electrolysis cell (MEC) is a hypothetically smart green technology that works electrochemically energetic bacteria to convert MSW into H2 and chemicals such as CH4, acetate, hydrogen peroxide, ethanol, and formic acid. This method is similar to Microbial fuel cells (MFCs), except that the cathode of Microbial electrolysis cell (MECs) is not exposed to air. Microbial electrolysis cell (MEC) has recently received increased attention as a viable means of obtaining clean and justifiable energy from waste. Furthermore, when compared to dark, photo fermentation, and Microbial fuel cells (MFC), Microbial electrolysis cell (MEC) has higher Hydrogen recovery and a broader substrate diversity (Kadier et al. 2016; Mostafa et al. 2015).

Microbial electrolysis cell (MEC) research shows more than 90% of Hydrogen retrieval compared to 33% with the dark fermentation process. With immediate wastewater treatment, the Microbial electrolysis cell demonstrated the ability to convert a variable amount of soluble organic matter to H2 or CH4 (Dimitrios-Sotirios et al. 2015). According to Lu and Zhiyong (2016), it was concluded that for future waste biorefineries, the Microbial Electrolysis Cell stage has enormous potential; they convert biodegradable waste into value-added energy carriers and bioproducts, resulting in an energy-positive and carbon-neutral system. When microbial electrolysis cell is integrated into the fermentation process, the yield and rate of microbial electrolysis cell are increased. The use of new materials, reactor configurations, and prices are frequently reduced, and system efficiency is increased.

13.5 Conclusion

The increasing population has significantly contributed to increasing global waste generation. Globally, agricultural waste generation is in the order of 2 billion tons per year, with an annual growth rate of 5–10%. With this huge waste quantity, comes the big issue of waste management and several consequences on groundwater, the soil, environment, health and the larger economy. Agricultural waste has also been reported to be responsible for 21% of greenhouse gas emissions.

Nevertheless, what constitutes a menace to society, the agricultural waste, can be widely optimised for the benefit of mankind in the form of energy. Population growth, improve the standard of living and rural-urban migration have further amplified the need for affordable and clean energy solutions. Agricultural waste has proven to be a useful source of energy that finds application in electricity generation, process heat, and cooling. If properly managed, 93 EJ per annum can be harvested from the global waste stream generation. The literature has shown that agro-waste can undergo several conversion paths depending on the quality of feedstock and the required product. The products of agricultural waste conversion can be seen in the forms of biogas and syngas which can be further utilised in electricity g; biodiesel which can be used as transportation fuel; biohydrogen; etc. Harvesting useful energy from agricultural waste will not only address the need for affordable and clean energy as proposed in the Sustainable Development Goals, SDG-7 but, also, has the potential to solve the problems associated with waste mismanagement, thereby, indirectly addressing SDG-6, SDG-11 and SDG-13. However, to adequately utilise the potentials of agrowaste-to-energy there would be a need for coordinated efforts to adequately match technology, economics and political economy of livelihood through effective energy policy pathways.

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Chapter 14
Forestry Wastes: Technical Concepts, Economic Circularity, and Sustainability Approaches

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Abstract Forestry residues include resources leftover from the handling of wood trees, including planning rejects, broken planks, old crates, barks, shavings, scrap joinery, as well as some rejects from wood processing, such as spent dyewood, tanning wood bark, unbleached screen rejects, residues from effluent treatments, wood fines from chips production, broken bleached cellulose fibers, sludges, and lignin residues. Each of these discredited resources has a particular chemical composition and variable physical properties. This chapter reviews their reuse using technical concepts on circularity and sustainability, which can be conducted through conversion processes to produce composite materials, fuels, and valuable products. Besides that, several physical, chemical, biological, and combined pre-treatments and their main technical challenges and influence on conversion processes were also addressed.

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14.1 Insights on Forestry Residues

There are no forestry wastes. In a circular economy model, there are no non-reusable wastes. That is, any material leftover from one process can be raw material to feed another system. We believe that the term waste should not be defined as often it is for different productive chains and their products. One waste should never be a retail waste. The loss should be a loss from a process, which does not occur in practice since most processes are not 100% efficient. The following terms are more closely associated with yield rather than with efficiency: (1) sidestream is any emission (product or not) different from the mainstream—failing to differentiate from a residue; (2) byproduct is something secondary generated in the process, which also has potential to be exploited as a product but is not the main one in the production chain. In pure etymological definition, waste designates uselessness, so we cannot associate it with production processes in general. Perhaps the human mentality of considering as waste (unusable) a lot of certain resources that would have the potential for at least downcycling, but possibly recycling and why not upcycling? We believe that there is no forestry waste in a circularity context, that is, taking the stratosphere as boundary conditions, there is no throwing out (Otoni et al. 2021). We complement this with Traité Élémentaire de Chimie: "Nothing is lost, nothing is created, everything is transformed" (Lavoisier 1789).

For supporting this definition, we assume that the productive forest chain presents operational aspects, which are similar to the textile, metallurgical, ceramic, glass, among other industries. In general, the production of materials has successive stages involving processes of extraction of raw materials, synthesis, and processing, manufacture of engineered materials, design,, and assembly of the product, reaching the final applications. At this stage, the consumer buys this product and uses it until be no longer useful or becomes somewhat obsolete. Then the consumer may discard this. Thus, each material from the product can be recycled, reused by returning to some production chain, or be eliminated as residue. The latter option is commonly retracting by incineration or disposal in sanitary landfills, returning to the earth to be decomposed. This ideal production chain contemplates the entire "materials cycle", having a good agreement with what we call today "circular economy" or "circularity." The importance of executing these cycles is related to the direction of the product market in recent decades, focused on the exhaustion of sources and overconsumption in a linear production/consumption chain, generating large volumes of residues, which are not properly disposed of.

Around 100 billion tons of raw materials are annually extracted from nature, including renewable and non-renewable sources (Economy 2021). However, the "renewable" terminology applied to any raw material is misunderstood because the earth's carbons are in perpetual flux. Carbon is not consumed as was no longer available in any form. Many forms of both reversible and irreversible chemical reactions occur, resulting in the transformation of all forms of carbon, including fossil carbon resources, into renewable ones in the carbon cycles. However, it is simple to think that some forms of "renewable carbon source" are widely available in relation to the necessary quantities to maintain and perhaps increase the current raw material supply. Thus, whether forestry or not, biomass is the biggest source of carbon to supply the demand.

In the same line of thought, it is increasingly evident that our planet virtually consists of a closed system with finite resources and, without safer extraction methods or correct management of their resources, combined with the intensity of production achieved in recent decades, this system is in serious danger. That is, we are in an unsustainable process. In other words, as society evolves and the population grows, some resources are becoming scarce and more attention must be paid to the materials cycle, or perhaps to the circular bioeconomy. In addition, the execution of the project for the preparation of materials requires the use of energy, which comes from different primary sources. In the United States, we know the materials manufacturing sector consumes approximately half of all produced energy (Callister Jr. and Rethwisch 2019). Thus, traditional energy sources have limited supply, and, for this reason, we must take assured steps to promote conservation and ensure their effective and efficient use. So, what is the world's energy solution? Perhaps, increasing the incentive for the use of renewable energy on a global scale, considering the potential of biomass for this use, including forest sources, supplying part of this demand in the medium term.

During all stages of the manufacture of materials, there are impacts on the environment. The conditions of the earth's atmosphere, water, and soil strongly depend on the care with which we go through the materials cycle. Some ecological damages, besides the destruction of the landscape (like deforestation), are results of the raw material extraction phase. Also, pollutants may be generated during the synthesis, processing, or use of materials, being expelled in the air and water since any generated toxic chemical need to be eliminated or disposed of. One product, device, or utensil must be designed to yield the minimum environmental impact during its production and shelf life. In addition, its residues should be reused, or in the worst case, its disposal should be associated with the minimum ecological degradation, that is, following the principle of biodegradability.

Three factors must be controlled throughout the production chain and all of them affect the cost of a product or process: (a) the project, (b) the raw materials, and (c) the manufacturing techniques. These factors are interrelated in a way that the design may affect which material will be used and, consequently, it influences the technique to be adopted in its manufacture (Callister Jr. and Rethwisch 2019). In this context, the use of recycled materials or raw materials from renewable sources can be made with adaptations in projects and manufacturing techniques. Currently, we visualize global requests from environmental organizations to adopt sustainable techniques, using renewable raw materials to maintain the natural cycle of the planet. In this way, any process or product that ally economical productivity, social viability, providing a net utility in the development of environmental and rural performance, can be considered sustainable. Furthermore, it should be in harmony with the objectives of policies for agriculture, environment, energy, and industry, contemplating the concepts of sustainability and circularity.

Sustainability can also be defined as the ability of human beings to interact with the world, preserving the environment with those natural resources that will be necessary for future generations. The concept of sustainability is complex, as it meets a set of interdependent variables, but we can say that sustainable practices may solve social, energy, economic, and environmental issues. Social issue: it is necessary to respect human beings and, thus, he can respect nature, considering that humans are the most important part of the environment. Energy issue: without energy, the economy does not develop. And if the economy does not develop, the living conditions of populations deteriorate. Environmental issue: a degraded environment yields human beings with shortening the life span. Therefore, if the economy does not develop, the future is unsustainable. In this context, new sustainable materials and chemicals must be developed, which have interconnected the concepts of long life, reuse, recycling, and biodegradability.

14.1.1 Classification for Forestry Residues

After defining forests do not generate wastes, but residues able to be re-introduced into a different, or even the same, production chain, we need to distinguish which are the main residues and where they are concentrated in the forestry material cycle. At the beginning of the chain, residues are generated from the forestry processes, *c.a.* felling of trees and their initial transportation. These rejects include treetops, stumps, branches, bark, and leaves. They can be used to produce different bio-products, as we will discuss below (Fig. 14.1a). However, the total removal of these residues from the forest or, more precisely, from its soil, harms the nutritional cycle of that area, as well as reduces the diversification of fauna (Clarke 2012; Paré and Thiffault 2016), accelerates the leaching of nutrients (Jang et al. 2015), and increases nutrient gaps (De Oliveira et al. 2018).

Besides the forestry processes, wood processing can occur in different manners, all of which result in many residues (Fig. 14.1a). The primary industry only processes the wood logs, transforming them into veneers, saw timber, and pressure-treated wood logs, in addition to charcoal and wood fragments. Conversely, the secondary industry uses products obtained from the unfolding of the raw material (primary process) to manufacture other final products, which are destined for the final consumer or other industries in the tertiary sector. The tertiary industry generates numerous highly specialized residues and several value-added products to meet the diverse needs of certain consumers. Also, we have the integrated or verticalized industry, which has two or more levels of industrial aggregation (e.g., primary and secondary or secondary and tertiary) in the manufacture of the final product. For instance, integrated pulp and paper industries comprise a primary production phase of wood chips, a secondary phase of pulp production, and a tertiary phase of paper manufacture. On the other hand, industries related to wood-based panels have a primary stage of production of wood fragments (chips, flakes, flour, among others) and their second stage is the manufacture of Medium Density Particleboard (MDP),

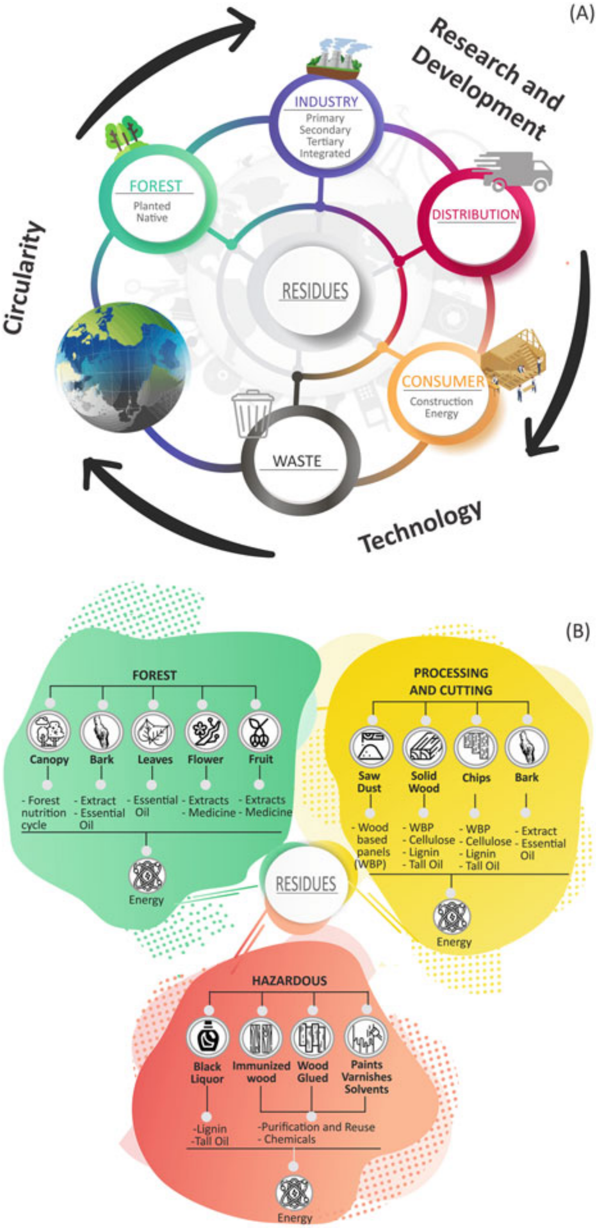

Fig. 14.1 Circularity proposed to the forestry productive chain. The waste highlighted in the center suggests that the reuse of residue can be done in the same step, or different steps of the forest chain (**a**). Subdivision into the forest, process, and cutting and, hazardous residues, and some featured applications (**b**)

Medium Density Fiberboard (MDF), High Density Fiberboard (HDF), Oriented Strand Board (OSB), or other wood panels.

Then, considering the production of residues as a whole, we propose a classification of residues as forestry residues, processing and cutting residues, and hazardous residues. Most forestry residues (bark, branches, and leaves) are left in the ground for soil protection and fertilization (Fig. 14.1b). The residues from the processing and cutting of wood comprise wood chips, sawdust, barks, and solid woods, obtained from the primary, secondary, tertiary, and integrated industries.

Black liquor is a hazardous residue that signals the application horizon for other residues in this class, which is composed of immunized/treated wooden residues and wood parts mixed with post-consumed glues (e.g., PVA, polyurethane, among others) used in the furniture industry. These residues are what we have closest to a real waste derived from the production chain. They must be sent to landfills in compliance with specific environmental standards (CONAMA 2002). Treated wood residues can neither be in contact with food, potable water, and bedding for animals, nor be burned in opened or low-temperature stoves, barbecue grills, ovens, or boilers. Procedures for obtaining leached and solubilized extracts from solid residues are properly regulated (NBR 2004a, b), although there are some research efforts to remove toxic chemicals from treated woods (Gezer and Cooper 2009; Mohajerani et al. 2018) and strengthen the concept of circularity in this process chain (Fig. 14.1b).

Management procedures applied to forestry residues, in a circular economy concept, may attend main aspects to promote a small or null generation of residues with hard reintroduction in some productive chain. The main challenges may be associated with the needed costs or technologies to value the residue. When it is not possible to mitigate the generation of residues, the processes may consider driving these residues toward proper sectors, which can occur either directly in the same productive chain or in a different one. However, it is utopian to think that 100% of all residues involved in all processes will be reused (Fig. 14.1a). Note that the circle is not entirely closed in our system, some small parts will always not be ready to be reused. For instance, if we use some kind of wood-based residue to generate energy through its burning, the removal of toxic gases and particles is done with water jets during evaporation. However, generated ashes, recovered water, purified chemicals, and other resources may yield a high environmental liability.

Figure 14.1a shows the main steps of the productive chain in different colors to distinguish the potential sources of residues. Note that we have a blend of colors to reproduce the effect of residues in the chain since one type of residue can either return to the same process or be used as raw material for other processes (Fig. 14.1b). Similarly, residues produced during the processing and cutting of wood correspond to a high amount and have a wide range of destinations in the productive chain. Chips, sawdust, solid wood, and bark—preferentially without chemicals—from any wood-based company have been reused as raw materials to produce wood-based panels (da Silva et al. 2021), small and wooden craft objects (da Silva et al. 2010), pulp and paper, extracts and essential oils (Meullemiestre et al. 2014; Saber et al. 2021), among others.

Regarding the hazardous residues, we can highlight the advances of the pulp and paper sector based on the possible alternatives to reuse black liquor for different applications. Differently from the past, nowadays black liquor serves as a potential source of lignin, which can be applied to develop dispersants, emulsions, and colloids for sunscreens, adhesives, coatings, paints, composites, among other products (Österberg et al. 2020). Woods containing traces of post-consumed glue or treated with chemicals have been exhaustively studied and some alternatives for purification and extraction of these hazardous chemicals were recently proposed (Gezer and Cooper 2009; Kartal et al. 2015; de Castro et al. 2021). After this step, solid wood, chips, or sawdust will be able to be reintroduced in the materials cycle in different ways, as a source for energy production (Helsen et al. 1998; Kumar et al. 2021a), wood-based panels, wood-plastic composites, or wood-cement composites (Amartey et al. 2003; Mohajerani et al. 2018). On the other hand, there is a promising trend in the development of sustainable resins and adhesives based on natural sources as lignins (Lourençon et al. 2020) and tannins (Tahir et al. 2019) to replace traditional wood glues, which are toxic to humans and the environment. Also, circular systems have been investigated to reuse these residues to produce other sustainable materials (Beran et al. 2021).

14.1.2 Chemical Characteristics of Forestry Residues

Knowledge of the composition and properties of forest-based residues has been driving their potential applications, although their thermochemical heterogeneity needs to be better understood and examined in detail to promote their proper use. Similarly, the reuse of industrial processing residues, such as tall oil and Kraft black liquor, also needs a deep examination to establish proper applications since pulp mills use an expressive number of inorganic chemicals for biomass delignification (Naqvi et al. 2010). Also, the black liquor is rich in lignin, and its recovery by different processes, like LignoBoost (Tomani 2010) or sequential liquid-lignin, and purification (Kihlman 2016) benefits the establishment of a biorefinery concept in this sector by producing high value-added bio-products.

Thus, both elemental and macromolecular chemical analyses of forest-based residues together with a techno-economic analysis of feasibility can promote better large-scale reuse of these materials. For instance, ashes from thermal processes applied to biomass may affect the overall costs related to the handling, processing, and efficiency of energy conversion processes (Cuiping et al. 2004; Zajac et al. 2019). Tables 14.1 and 14.2 summarize the thermochemical features of forest-based residues produced during forest operations and industrial processing. Then, we may comprehend and ascertain potential applications for each residue based on these properties. For instance, great HHV (higher heating value) and low ashes content drive an attractive application of the residue in the energy conversion sector. On the other hand, an abundant presence of lignin in the black liquor indicates a potential recovery of this material to be raw material or additive to produce resins and plastics. Besides that, high cellulose and hemicellulose contents indicate a promising source for the extraction of bio-based nanomaterials.

Table 14.1 Summary of macromolecular properties of forest-based residues

Material	Density (kg/m^3)	Cellulose	Hemicelluloses	Klason lignin	Extractives	Reference
Pinus elliottii bark	372	25.4	14.7	44.9	3.83	(Valentín et al. 2010; Delucis et al. 2018c)
Betula platyphylla rootwood	320	51.00	29.50	19.4	–	(Zhao et al. 2019)
Pine needles from *Pinus sylvestris* and *Picea abies* Swedish forest	–	23.50	16.00	33.00	15.00	(Moriana et al. 2015)
Pine needles	–	37.40	11.09	26.38	–	(Huang et al. 2019)
Wood chips from *Pinus sylvestris* and *Picea abies* Swedish forest	–	39.80	26.30	26.30	2.30	(Moriana et al. 2015)
Northern red oak bark	–	–	–	26.63	12.11	(Sillero et al. 2019)
Eucalyptus botryoides wood	910	42.00	16.70	28.00	2.20	(Dos Santos et al. 2014)
Branches from *Pinus sylvestris* and *Picea abies* Swedish forest	–	30.90	21.30	31.00	8.70	(Moriana et al. 2015)
Liquified wood residues	–	42.80	26.98	17.65	–	(Pan et al. 2007)
Pine residual sawdust	–	41.00	18.89	20.91	–	(Cavali et al. 2020)
Poplar branches	–	40.01	23.16	22.90	–	(Huang et al. 2019)
Green wood chips from a flooring manufacturer in eastern Canada	52.00	51.00	26.70	17.20	5.10	(Thiffault et al. 2019)
Engineered wood sawdust from a flooring manufacturer in eastern Canada	133.00	50.10	27.00	16.00	7.00	(Thiffault et al. 2019)

Table 14.2 Summary of bulk thermochemical properties of forest-based and wood-industrial processing residues

Material	Elemental composition (%)					Proximate analysis			HHV (MJ/kg)	Reference
	C	H	O	N	S	Ash (%)	VM (%)	FC (%)		
Mix of residues from timber harvesting of 80-year-old *Pinus sylvestris* trees	50.84	5.72	41.46	0.66	0.25	1.07	–	–	18.75	(Nurek et al. 2018)
Fresh Norway spruce branches	51.31	6.22	42.35	0.12	–	0.68	85.18	14.14	20.86	(Bach et al. 2016)
Pinus pinea chips	48.15	5.59	5.59	0.09	0.28	0.60	81.60	17.80	19.43	(García et al. 2012, 2014)
Pinus pinea cone leaf	47.65	5.43	46.21	0.27	0.44	1.30	80.00	18.70	18.63	(García et al. 2012, 2014)
Populus nigra bark	43.25	6.33	49.66	0.42	0.34	8.00	71.00	20.76	17.41	(García et al. 2012, 2014)
Fresh Norway spruce branches	51.31	6.22	42.35	0.12	–	0.68	85.18	14.14	20.86	(Bach et al. 2016)
Fresh Norway birch branches	48.55	6.19	45.09	0.17	–	0.64	89.74	9.63	19.56	(Bach et al. 2016)
Eucalyptus grandis forest residues	48.00	6.36	45.46	0.12	0.06	0.95	75.71	15.06	19.33	(van Schalkwyk et al. 2020)
Ficus benghalensis leaves	44.15	5.10	45.83	1.19	–	17.00	57.00	18.00	15.82	(Samal et al. 2016)
Eucalyptus globulus bark	45.80	5.70	42.30	0.80	0.05	5.00	77.90	17.10	18.40	(Neiva et al. 2018)
Pine needles	48.70	–	–	0.96	–	6.11	80.09	48.70	–	(Huang et al. 2019)
Poplar branches	45.30	–	–	1.13	–	2.67	80.50	45.30	–	(Huang et al. 2019)
Red oak wood	48.70	6.80	44.00	0.07	0.00	1.70	81.90	12.60	18.70	(Zhang et al. 2013)
Commercial softwood lignin	66.10	6.37	25.30	0.67	1.57	4.25	–	–	–	(Sameni et al. 2016)
Pinus pinaster wood (mix of chips and sawdust)	48.22	6.15	45.46	0.11	0.00	0.20	–	–	20.26	(Enes et al. 2019)
Pinus pinaster residues (mix of bark, branches and leaves)	48.62	6.89	39.91	1.24	0.094	3.20			19.43	(Enes et al. 2019)
Kraft black liquor from *European beech* wood pulping	31.45	4.42	–	0.11	3.68	51.69	–	–	–	(Ház et al. 2019)
Lignin isolated from *European beech* Kraft black liquor	55.68	4.62	31.66	0.28	3.91	3.85	–	–	22.60	(Ház et al. 2019)
Kraft Tall oil lignin of softwood	53.70	4.80	34.10	0.10	7.30	2.60	–	–	19.60	(Diaz-Baca and Fatehi 2021)
Black liquor of recycled paper	38.30	4.74	42.25	0.39	0.00	23.27	66.19	10.54	15.71	(Al-Kaabi et al. 2017)
Kraft black liquor from pine and spruce woods	30.67	3.74	64.92	0.67	0.00	35.93	56.92	7.15	14.51	(Al-Kaabi et al. 2017)

C Carbon, *H* Hydrogen, *O* Oxygen, *N* Nitrogen, *S* Sulfur, *VM* Volatile matter, *FC* Fixed carbon, *HHV* Higher heating value

14.2 Pre-Treatments Applied to Forestry Residues

Those processes needed to produce certain fuels, materials, and other valuable products are normally divided into two steps, namely pre-treatments and conversion processes. Pre-treatments are performed to qualify and/or enable the transformation of one raw material into a workable product and, therefore, must be associated with the subsequent processes. According to (Lomovskiy et al. 2020), a method for pre-treating plant raw materials should ally an optimal combination with the subsequent activation processes, taking into account the consumption of energy and reagents, as well as the amount of generated inhibitory agents or side products. In general, methane yield, process time, process cost, surface area, and inhibitors generation are the main factors to be taken into account in the selection of the most suitable pre-treatment (Ghosh et al. 2017; Kalyani et al. 2017; Kumar et al. 2021b). All these steps/procedures may significantly impact the final quality and cost of the final product. Figure 14.2 shows a schematic illustration of how these pre-treatments can be classified into: physical, chemical, biological, and combined ones.

Among the physical pre-treatments, the grinding process aims at changing the substrate geometry by mechanical impacts. The most common effects conferred by these methods include: increase in surface area, enhancement in subsequent degradation by the conversion process, change in the degree of polymerization, and

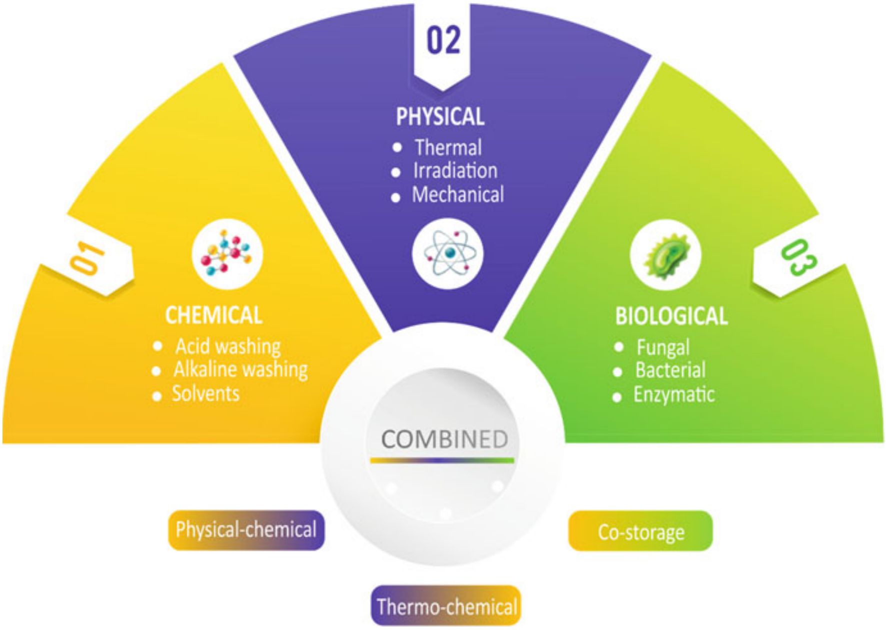

Fig. 14.2 Schematic illustration for the classification of pre-treatments for biofuel production

decrease in cellulose crystallinity (Socha et al. 2013; Da Silva Perez et al. 2015; Song et al. 2020). These processes do not require chemicals and do not generate effluents, although represent a high-energy penalty and the needed equipment may yield expensive costs. Decreases in biomass viscosity were also extensively reported, which is important for biogas production (Kalyani et al. 2017). According to (Lomovskiy et al. 2020), although most studies on mechanical grinding addressed laboratory-scale equipment, some modern approaches have been showing promising results for the deconstruction of plant-based raw materials, allowing energetically and economically sound enhancements. These authors presented a comparative review, encompassing disc mills, attritors and bead mills, ball mills, planetary mills, vibration and vibrocentrifugal mills, roller and centrifugal roller mills, extruders, hammer mills, knife mills, pin mills, disintegrators, and jet mills. They concluded that roller and centrifugal roller mills had the highest capacity/energy consumption ratio. On the other hand, they highlighted that free-impact mills must be selected when only grinding needs to be performed.

Similarly, irradiation processes do not require chemicals and yield both high-energy demand and expensive investments in the needed infrastructure. In general, these methods induce increases in heat and pressure, which facilitates the further degradation of the lignocellulosic network. Microwave irradiation, ultrasound irradiation, and pressurized water are the main irradiation processes. The former method consists of propagating microwaves through water molecules from the biomass. Then, the vibratory movement from energized water molecules generates friction and, consequently, heat, which vaporizes the moisture inside the biomass cell wall, which may collapse due to the high internal pressures developed. This also leads to increases in porosity and decreases in cellulose crystallinity, even in large particles since the heating takes place from inside to outside.

The ultrasound irradiation works with mechanical waves above 16 kHz, which propagate in the liquid medium, generating numerous cavitation bubbles, depending on the intensity of the sonication in relation to the frequency of the wave (Yang et al. 2021). These bubbles collapse and that raw material on their surroundings are projected to their interior, causing high levels of both pressure (up to 200 atm) and temperature (up to 5000 °C). Also, there are sonochemical effects, in which homolytic ruptures of O-H bonds from the water occur due to collisions between molecules, generating free radicals, which depolymerize the biomass. Besides that, mechano-acoustic effects also may occur when jets from the disrupted bubbles erode the biomass cell wall, which is also called the sononocapillarity effect. Increases in porosity and cleavage of β-O-4 and α-O-4 bonds from lignin are the main positive effects ascribed to ultrasound irradiation (Yang et al. 2021). Beyond the main disadvantages related to irradiation processes, such as high-energy demand and high equipment costs. Furthermore, even a small biomass concentration demands a large volume of solvent (water).

In the pressurized water process, the water is heated above 100 °C and pressurized, becoming sub or supercritical vapor. The water also acquires the diffusibility of a gas and the solubilization capacity of a liquid. Although this method demands a high amount of energy to the water heating and pressurizing, the solvent (water) is highly available, unexpansive, non-flammable, and non-toxic. Also, high sugar yield, lignin depolymerization, and increased porosity can be reached (Cantero et al. 2015).

Thermal processes applied to forestry residues may solubilize hemicelluloses and amorphous regions from cellulose in exchange for a high-energy demand and high investment in equipment. When the amorphous polysaccharides are decomposed, some of their aldehydes, acetic, and uronic groups may be transformed into side groups, such as acetic acid, formic acid, CH_4, CO, CO_2, among others (Clauser et al. 2018). Although decreases in viscosity may occur, which is important for biogas reactors, certain compounds that inhibit biodegradation may be also generated, such as polyphenols from lignin. Torrefaction is the main thermal pre-treatment and can be defined as a mild pyrolysis. This process can also be used to improve the combustion properties of manufactured forest products, such as pellets. Torrefied products derived from forestry residues are produced under temperatures between 200 and 300 °C for short times, which do not lead to a charcoal formation (Chen et al. 2017). Compared to pristine wood parts, torrefaction-treated ones have higher carbon content, smaller oxygen content, higher calorific value, higher energetic density, easier milling, smaller hygroscopicity, and higher biodegradation resistance (Chen et al. 2017; Chaturvedi et al. 2021). Thermal treatments can also be conducted by steam explosion and the called liquid hot water (LHW) pre-treatment. The former process consists of "explode" the biomass by the decompression of the steam, which is previously prepared at high levels of temperature (160–260 °C) and pressure (0.7–4.8 MPa) and permeate the biomass for short times (1–30 min) into an autoclave or a jacketed reaction (Clauser et al. 2018). This process is also called "autohydrolysis" since organic acids from the lignocellulose itself act as catalysts in the hydrolysis process, which is mainly focused on acetyl groups from hemicelluloses (Sidiras et al. 2011). On the other hand, LHW consists of soaking the biomass in liquid water, which is heated at 50–200 °C for 1–4 h.

Chemical processes can be alkaline or acid washes, which are efficient to solubilize hemicelluloses and even selectively remove cellulose and lignin. In certain cases, these methods do not require heating and the chemical solutions can also be somewhat reused, although toxic effluents are inevitably generated. H_2SO_4, HCl, HNO_3, H_3PO_4, and CH_3COOH are the main acid solutions used to pre-treat forestry residues. These acid solutions may majorly attack carbohydrates, especially hemicelluloses. Concentrated and diluted acids can also be used in combination. High polysaccharides degradation rates, increased porosity, increased surface area, removal of metals (catalytic metallic cations, such as sodium and potassium) can be considered as main advantages (Frederick et al. 2014; Mesa et al. 2017). However, as the main disadvantages, these solutions may also yield the formation of inhibitors, acid residues, as well as demand for the high cost of reagents endowed with high corrosiveness, which may require increase costs related to the necessary equipment. (Frederick et al. 2014) pre-treated a woody biomass from Eastern Cottonwood using a diluted solution of H_2SO_4 at 140 °C for 40 min and reported increases in gallic, vanillic, ferulic, and salicylic acid concentrations, which may inhibit further enzymatic hydrolysis.

NaOH, KOH, NH_3, $Ca(OH)_2$ are the main alkaline solutions applied to pre-treat forestry residues. They may focus on depolymerizing the lignin, although polysaccharides can be attacked in later stages. Compared to acid methods, milder treatment conditions, lower inhibitors generation, smaller polysaccharides removal, higher lignin removal, lower treatment temperature, and lower treatment pressure are considered as the main advantages of alkaline washings (Wei et al. 2009; Barcelos et al. 2021). Side groups, such as acetyl and uronyl groups, may bind the lignin to hemicelluloses and cellulose crystallinity may also be decreased (Sidiras et al. 2011). These methods can eventually be unfeasible due to the long treatment times (from hours to days), low efficiency for highly lignified biomasses, and need for remediation techniques for the generated residues (Wei et al. 2009).

Organosolv is a cellulose pulping process and thus consists of fractioning lignocellulosic materials to produce value-added products, such as lignin, hemicelluloses, and cellulose (Dos Santos et al. 2014). It consists of cooking the biomass in the presence of an organic solvent, usually short-chain alcohol (ethanol, methanol, butanol, and so on) and a catalyst. Different process temperatures can be applied, yielding low molecular lignins (contained in the liquid fraction) and high purity cellulosic fibers (the solid fraction). For García et al. (2011), the organosolv is considered the most environmental-friendly pulping process, since is sulfur-free and presents a yield of about 78% of low-molecular-weight lignin, mainly depending on the process temperature. This process is suitable to induce severe biomass fractionations and obtain less cellulose crystallinity (Yang et al. 2021). However, high-energy demand, and catalysts, generation of inhibitors, high operational risks (fire, explosions, and unhealthy environments) may be involved (García et al. 2011; Yang et al. 2021). Pre-treatments with ionic liquids are promising processes, although they exist only at a laboratory scale. Selective solubility of biomass macromolecules, amorphous cellulose, low-treatment temperatures can be reached by using these non-flammable solvents (Socha et al. 2013; Barcelos et al. 2021). However, high levels of corrosivity, toxicity, and overall costs may be involved (Liu et al. 2018; Barcelos et al. 2021).

Biological pre-treatments are those in which certain enzymes (including proteases, laccases, peroxidases, among others) are secreted from fungi and react with the lignocellulosic cell wall, yielding depolymerization of its main macromolecules. Although side products can be generated in minor amounts, these pre-treatments are energy-sufficient manners of producing glucose, xylose, lignin, and other valuable products (Wei et al. 2009; Song et al. 2020). These processes require a low-energy demand, low cost in equipment, and the generated effluents are non-toxic. On the other hand, these pre-treatments can take weeks and even months and demands a large space. There are white-rot, brown-rot, and soft-rot fungi. Increases in surface area may allow further degradation of macromolecules and even a total consumption of polysaccharides by subsequent processes, which can be operationally difficult due to the necessary previous fungal decontamination (Lomovskiy et al. 2020). According to Song et al. (2020), the use of fungi as biocatalysts will be engineered and optimized in a near future, which may ensure really promising results.

Table 14.3 Main pre-treatment processes and respective effects conferred to forestry residues

Effect	Mechanical	Thermal	Physical	Chemical	Biological
Increase in surface area	High	High	High	High	High
Cellulose solubilization	Negligible	Moderate	Moderate	High	Negligible
Hemicellulose solubilization	Negligible	High	Moderate	High	Negligible
Lignin solubilization	Negligible	Moderate	Negligible	High	Negligible
Increase in viscosity	High	High	Negligible	High	High
Removal of pathogens	Negligible	High	High	High	High
Generation of inhibitors	Negligible	High	Moderate	High	Negligible

Table 14.3 summarizes the main pre-treatment processes and the main effects ascribed to each of them. Besides that, there are combined methods, which can be divided into physical-chemicals, thermo-chemicals, and co-storage. Briefly, the physical-chemical methods consist of adding a chemical solution to catalyze an irradiation process, whereas thermochemical processes are those in which the temperature acts as a catalyst to those chemical reactions induced by a chemical solution. Co-storage is conducted into an opened reactor, in which the lignocellulose and acid/alkaline residues are kept before the aerobic digestion process.

14.3 Composite Materials from Forestry Residues

All the already extensively explained forestry residues can be combined with other resources to produce eco-friendly composites. One pre-treated woody biomass normally acts as reinforcement or even as a filler for a polymeric or cement-based matrix. Forestry residues can be broken down into small elements, removing or redistributing some growing defects, such as knots, cracks, and checks to reduce their effect on the final properties, which leads to more uniform composites.

14.3.1 Wood Plastic Composites (WPC)

Most thermoplastic polymers are based on non-biodegradable polymers obtained from petrochemical products, such as polythene (PE), polypropylene (PP), polyvinyl chloride (PVC), and polystyrene (PS). These materials are designed and manufactured to resist against environmental degradation and, due to this reason, yielded the current huge amount of plastic residues, which are strongly responsible for worldwide environmental pollution. In this context, wood-plastic composites (WPC) are a promising alternative to avoid the consumption of oil-based polymers and retain the suitable performances of neat plastics. Furthermore, even post-consumed plastics can be incorporated in certain cases, reducing this environmental liability.

WPC can be defined as a mixture of wood and polymer with a plastic content >50% by weight. Normally, wood fibers or wood flour and some additives are incorporated into thermoplastic matrixes, which are processed by thermomechanical extrusion or injection. This material appeared for the first time in the 1920s and was further developed after World War II by independent studies conducted by American and Soviet researchers. The first industries emerged in the 70s in Europe and 90s in the United States. Their use relieves pressure on virgin forests since they can replace solid woods, as well as neat plastics, cementitious composites, among other engineering materials. Their wide range of applications include construction, automotive, industrial and consumer goods, and other indoor and outdoor products (Treinyte et al. 2018; Wang et al. 2021; Treinyte et al. 2018).

Regarding the forestry residues used to manufacture WPC, post-industrial residues are normally selected, including sawmill trimmings and logging slash (Nguyen et al. 2020), sawdust (Martinez Lopez et al. 2020; Yang et al. 2010), wood chips (Razi et al. 1997), wood pellets (Moreno and Saron 2017), pine nutshell (Treinyte et al. 2018), cupula chestnut (Boran Torun et al. 2019), among other. In this study area, the hydrophilic nature of most woody biomasses is the main drawback since generates a chemical incompatibility with most polymeric matrixes and limits the amount of wood-based residues added to the matrixes. This can be overcome by certain pre-treatments, which goals to block or even degrade polar chemical groups belonging to the lignocellulose, such as hydroxyls and methoxyls (Wang et al. 2021) or using natural extracts/polymers as surfactants like condensed tannins (Missio et al. 2018) and lignins (Lee et al. 2015). The most common pre-treatments include mechanical, chemical, and biological methods.

Zhou and Wang (2020) produced thermally stable and less hydrophilic wood fibers using a chemical treatment called esterification, which increased their host compatibility with high-density polyethylene (HDPP) used as a matrix. Hosseinaei et al. (2012) extracted hemicelluloses using hot water heated at three different temperatures (*c.a.* 140 °C, 155 °C, and 170 °C) from pine wood flakes and reported that this degradation in hemicelluloses increased the whole wood hydrophobicity and conferred increases in tensile strength and water resistance to the composites. Wang et al. (2021) studied a chemical compatibilizer prepared by the reactions between a polyol (prepared with maleic anhydride and ethylene glycol) and diisocyanate. They reported that this chemical coupling agent increased some properties of forestry pine nutshell/PP composites, such as tensile strength, flexural strength, thermal stability, and water retardation capacity. Dominkovics et al. (2007) reported the reinforcement in PP/wood flour composites by modification of the wood surface by benzoylation using a diluted benzyl chloride solution heated at 105 °C.

14.3.2 Polyurethane Foams

Polyurethane foams are versatile engineering materials and have a wide range of applications, such as industrial and domestic insulation, mattresses, upholstery, and structural pieces. These cellular polymers can be classified into flexible, semi-rigid, and rigid foams. Briefly, polyurethane foams are obtained by a polyaddition reaction of a polyisocyanate with a polyalcohol (polyol). These foams can also be reinforced or filled with vegetable resources due to the aforementioned environmental concerns related to the use of petrochemicals. Furthermore, significant increases in mechanical and thermal properties were ascribed to the insertion of forest-based fibers or particles (Delucis et al. 2018a). Unlike other synthetic resins, the higher the filler hydrophilicity, the higher its host compatibility with the polyurethane matrix since the hydroxyl groups from the biomass may crosslink with urethane groups from the isocyanate instead of the hydroxyl groups from the polyol.

In their work, Delucis et al. (2018b) used wood flour, bark slices, lignin powder, and paper sludge as fillers in rigid polyurethane foams. All these forestry residues were firstly oven-dried at 50 °C and milled. In another research, these authors ascribed decreases in cell size and closed-cells content to the inserted fillers. Also, increases in mechanical, hygroscopic, thermal, colorimetric features were reached using certain filler contents and NCO/OH ratios (de Avila Delucis et al. 2018).

Similarly to conventional WPC, improvements in interfacial adhesion can be reached through chemical treatments, such as alkalinization, silanization, and acetylation (Neto et al. 2019; Kalia et al. 2009). All these surface chemical treatments also influence the stability, stiffness, and thermal conductivity of the whole composite (Kuranchie et al. 2021). Besides the use of forestry residues as fillers in PU foams, numerous studies have been aimed at replacing petroleum-based polyols with polyols from renewable resources, such as sorbitol or liquefied lignin (da Silva et al. 2017a, b, 2019). Conversion processes used to transform forestry residues into polyols will be further discussed in this chapter.

14.3.3 Cement Composites

The use of woody particles or fibers in the manufacture of building cement composites began in the early 1900s. These composites have been applied as substitutes for asbestos in fiber-cement panels. The insertion of forestry residues into cement composites has a great ecological appeal since they can partly replace Portland cement, which has an enormous carbon footprint since around 7–10% of the entire anthropogenic CO_2 generation is associated with its use and manufacture, including limestone decomposition, burning of fossil fuels and clinker foundry. Sand can also be replaced, which is of great interest aiming to avoid unwanted geomorphological changes caused by the extraction of sand from beds of rivers or underground tunnels. Guo et al. (2019) produced mortars and partially replaced the sand with a heat-treated wood flour. They reported that hygroscopic and mechanical properties of the hardened mortars remain similar with the addition of the thermally-treated wood flour. Therefore, forest residues are very versatile in their use in cementitious materials and can be used as cement replacement (Cheah and Ramli 2011), fine aggregate (Sojobi 2016), coarse aggregate (Thandavamoorthy 2016; Usman et al. 2018), and fiber addition (Ojo et al. 2019).

Furthermore, recent research has been focused on the production and use of nanocellulose in cementitious composites, thus this has become one of the most promising materials in several areas due to its mechanical and ecological characteristics (Guo et al. 2020). Currently, nanocelluloses can be produced by using various methods of mechanical fibrillation, such as high-speed blending, grinding, high-pressure homogenization, and high-intensity ultrasonication (Zhao et al. 2021). In some recent studies, nanocellulose fibers and particles were extracted from forest residues, such as sawdust (Vallejos et al. 2016), pine cone (Rambabu et al. 2016), pine needles (Xiao et al. 2015), and logging residues (Moriana et al. 2016). These nanomaterials were then incorporated into cement composites.

When inserted into the alkaline cement matrix, the vegetable resource may undergo a mercerization effect, also called mineralization, which consists of alkaline hydrolyses and leads to the dissolution of hemicelluloses and lignin, depolymerization of cellulose chains, and deposition of lime in the lumen and middle lamella from the forest-based fiber (Wei et al. 2016). A mineralized wood fiber becomes brittle, which is an issue since these fibers should confer flexibility to the cement (Ashori et al. 2011). These detrimental effects can be mitigated by a chemical treatment on the fiber surface or to add a cement additive with high pozzolanic activity to mitigate the alkaline pH of the cement solution due to their high contents of silicates and aluminates. Slag, silica fume, fly ashes, rice husk ashes, and even wood ashes can be considered as the most used pozzolanic additives. These two strategies can be combined, conjugating the effects, as in the work of da Silva et al. (2017b), who produced cement-based composites reinforced silica fume, metakaolin, and coconut fibers coated in natural latex and obtained improved mechanical performance and durability.

14.4 Fuels from Forestry Residues

Biomass can be considered all that organic matter derived from plants, animals, or microorganisms, which can be somewhat transformed into energy. This also includes residues from several origins, such as agriculture, urban areas, animal husbandry, industries, and forests. Currently, from both economic and environmental standpoints, food residues are the most relevant organic biomasses, although there are severe concerns related to the use of edible matrixes for energy production. Furthermore, forestry residues are already considered as traditional energy sources and there is a promised expectation of growth in their consumption. Some recent estimates indicate that biomass may be responsible for about half of the global energy matrix in the next decades (Li et al. 2021a).

Biofuels are biomass-based chemicals endowed with high energetic properties. Although the term biofuel has diverse meanings in the literature, the most accepted classification is based on the number of needed steps to transform an *in natura*

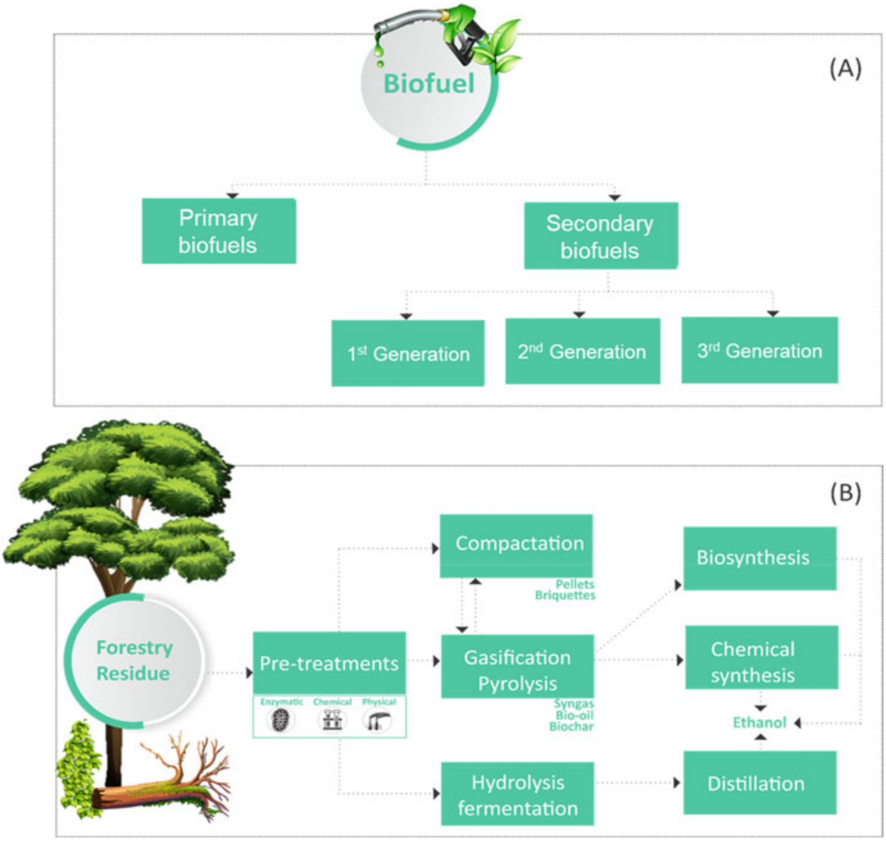

Fig. 14.3 Classification for forest-based fuels (**a**) and the possible routes for obtaining secondary fuels (**b**)

biomass into a workable fuel (Song et al. 2020). Based on that, there are primary and secondary biofuels. The primary fuels are directly converted into heat and gases by simple burning or fermentation. The latter category includes first-, second-, and third-generation fuels, depending on the number of chemical processes needed to one biomass becomes a final fuel. Nevertheless, even primary fuels can undergo a pre-treatment before being utilized. Figure 14.3a shows a schematic representation of the possible fuels derived from forestry residues and how they can be classified. Conversely, Fig. 14.3b presents physical and chemical pathways to convert ligno-cellulosic matrixes from forestry residues into secondary fuels. It is important to consider that there are certain less important fuels, which were not encompassed by Fig. 14.3b.

Fine chemicals and materials can be considered more noble applications if compared to biofuels. However, the production of biomass-based fuels is aligned to the need for feasible applications to the huge amount of residues, which are annually generated around the world. Considering moisture content of 30% in all cases, forestry biomasses have an estimated potential for energy production of 101.036.323 MWh, which encompasses both electricity and heat (Altamirano et al. 2015).

The growing demand for woody biomass is somewhat pressing forested ecosystems, which already enlarged negative nutrient budget areas (De Oliveira et al. 2018). Furthermore, according to (Delucis et al. 2018b), heavy equipment used to collect that biomass left on the ground of harvested areas may cause soil compaction. Therefore, if these forestry residues leftover from felling procedures are needed to the biofuels production, strategies to counterbalance these deleterious effects should be considered, such as: prepare harvested areas with rock products designed to replenish growth-limiting nutrients, implement forest management techniques to minimize nutrient export, and transport trees to sawmill together with their barks, leaves, and branches.

The typical energy transformation processes, which have been performed with gasoline, diesel oil, natural gas, and coal, can be partly or even totally performed using respective fuels derived from renewable resources. Regarding their possible substitutes, biochar, bio-oil, bioethanol, and biodiesel are the most common green fuels produced from forestry residues. In general, these renewable fuels are cheaper than their respective oil-based ones and, unlike other renewable energy forms (like wind and solar), products from the biomass refining can be collected, stored, transported, and even be consumed using the same infrastructure consolidated for fossil fuels (Hernández et al. 2019).

Biofuels also have been attracting attention due to the population growth and the increasing of mechanization and automation of processes, which contribute to the increase in the energy demand. China, for instance, has a great environmental crisis related to the increase in its energy consumption since this country has been experiencing enormous economic growth in recent decades (Fu et al. 2020). In this sense, the use of biomasses for energy production may strengthen its energy security.

All of these factors are also accompanied by concerns related to the need for reducing the anthropogenic CO_2 generation since the current global energy chain is majorly (up to 80%) supported by fossil fuels (Boukherroub et al. 2017). This growing pollution also charges human lives since several known diseases are associated with air pollution, especially lung and heart disorders (Yang et al. 2021). Recent cradle-to-cradle results obtained through life-cycle assessment (LCA) indicated that biomass-based fuels designed for the transportation sector yielded more favorable carbon footprints if compared to similar oil-based ones (Song et al. 2020).

Nevertheless, to the best of our knowledge, a realistic perspective indicates that a full replacement of fossil fuels in a near future does not seem plausible based on the current science and technology advances since, in most cases, those energetic properties of bio- and oil-based fuels are not comparable yet. Regarding the transportation sector, producing fuels with enough energy density for long-distance transportation is one of the main technical challenges. Yacout et al. (2021) reported that there are promised future projections regarding a partial transition from fossil fuels to biofuels in the marine sector until 2030. According to them, biodiesel and bioethanol can be blended with fossil fuels to be used in different marine engines, which may demand only minor modifications to the current infrastructure. At the same time, significant decreases in the generation of CO_2, NOx, and SOx emissions could be reached. For Song et al. (2020), although there are many factors, costs related to biomass acquisition, biomass yield, separation, and purification may determine if one biofuel is really feasible. Hernández et al. (2019) pointed out that other sustainable energy sources may also gain importance in the future, including hydroelectric, solar, wind, and tidal power plants.

According to Lapuerta et al. (2004), biomasses have been used to produce some kind of energy since ancient times. However, biomass-based fuels were relegated to a limited number of uses since the post-World War II economic expansion, which occurred in the 1960s. The consumption of oil-based fuels underwent a huge growth during this historical event to ensure industrial and social developments, mainly in the United States and Europe. More recently, government incentives around the world have been encouraging the generation of all kinds of bio-energies. These worldwide efforts can be explained by three reasons: (1) creation of livelihood sources for rural workers to avoid a massive migration to urban areas; (2) control the disposal of residues in sanitary landfills, controlled landfills, and dumps; (3) reduction of the emissions of CO_2 and other greenhouse gases.

Biomasses destined for energy production have an eminently environmental motivation in developed countries (like North America, Western Europe, and Oceania) and a social one in poorly developed countries, which are in South America, Africa, and Southern Asia. Furthermore, rich countries may need large energy sources to sustain their standard of living. In a comparison between Europe and North America, several researchers reported that the former community is at the forefront in terms of current efforts since the European Union has decided to produce 20% of its energy from renewable sources by 2020 (Barrette et al. 2017; Boukherroub et al. 2017). According to the 2015 UN climate agreement, different European countries aim to limit global warming to within the 1.5–2° targets, which is mostly supported by biomass-based fuels (De Oliveira et al. 2018). Some Nordic countries, like Sweden and Finland, defined an ambitious climate goal of zero greenhouse gases emissions by 2045. On the other hand, according to Hernández et al. (2019), underdeveloped countries are economically dependent on their agriculture and agro-industry. This context provides a large availability of biomasses with potential for energy production in these countries, in which sustainable economic growth may be accompanied by increasing energy consumption.

14.4.1 Primary Fuels from Forestry Residues

Direct incineration is the most common way of using forestry residues for energy production since these resources have a proven potential for producing heat and, consequently, electricity (Castro et al. 2017). Barrette et al. (2017) affirmed that financial subsidies could make feasible energy production through the direct burning of some non-conventional forestry residues, such as small trees and large dead trees.

Although most of the economically feasible manners of using primary fuels from forestry residues do not involve their pre-drying, their common high moisture contents restrict their energetic properties, especially their gross calorific value. According to Lu et al. (2017), moisture in wood-based fragments slows their combustion and leads to non-predictable pyrolysis, which may reduce their efficiency. Aside from highly variable energetic properties, high moisture contents are associated with low densities and low biodegradation resistances, which trigger other troubling problems related to their storage and transportation. According to Puy et al. (2011), logistic issues may impair the thermal conversion of forestry residues since it is difficult to move high volumes of low-density raw materials, like small trees and bushes, which may lead to expensive costs. Fortunately, most woody biomasses can be collected throughout the year, which reduces their long-term storage (Barcelos et al. 2021).

Therefore, thermal conversion and even previous treatments needed to transform forestry residues into workable fuels must be performed near to the original forests or industries (Fu et al. 2020). A possible solution to these problems was examined by Gautam et al. (2017), who studied the effects of a terminal built near to a forest, which was idealized in order to improve the biofuels supply chain network. Their case study demonstrated that the terminal allowed the delivery of raw materials with moisture content within 4–11%, which would yield decreases in transportation and operating costs of 11–32%. These low moisture contents may yield more predictable pyrolysis processes, which is crucial to the production of many biofuels. According to Lapuerta et al. (2004), a devolatilization kinetic study may yield valuable mathematical models, which can predict the biomass behavior when it is subjected to a heating process into a furnace or a gasifier.

The thermal decomposition profile of a pinewood sawdust can be divided into three clear stages (Hu et al. 2017). According to Lapuerta et al. (2004), these three non-interacting mass-loss events can be represented by three parallel first-order reactions to simulate the decomposition phenomenon of a pine sawdust. The first one occurs at a low-temperature range (20–100 °C) and is attributed to the evaporation of adsorbed and absorbed water molecules and volatile compounds (Hu et al. 2017). The second stage is marked by a high mass loss (around 70%) ascribed to devolatilization processes in wood polysaccharides at 300–400 °C (Hu et al. 2017). Finally, there is a slow mass loss in the third stage, which occurs in the 250–500 °C temperature range due to the decomposition of the lignin (Hu et al. 2017). Figure 14.4 illustrates the main thermal events that take place during a pyrolytic process and the main generated biofuels, which will be further addressed.

Experiments on variable heating rate only show shifted peaks and the overall decomposition profile remain similar due to combined effects from heat transfer and mass transfer (Hu et al. 2017). In general, as the heating rate is increased, the mass-loss kinetics are delayed in relation to the equilibrium (Lapuerta et al. 2004). These kinetic analyses can be classified into integral methods and differential methods. Among the integral ones, Coats-Redfern model, Ozawa model, Satava-Sestak

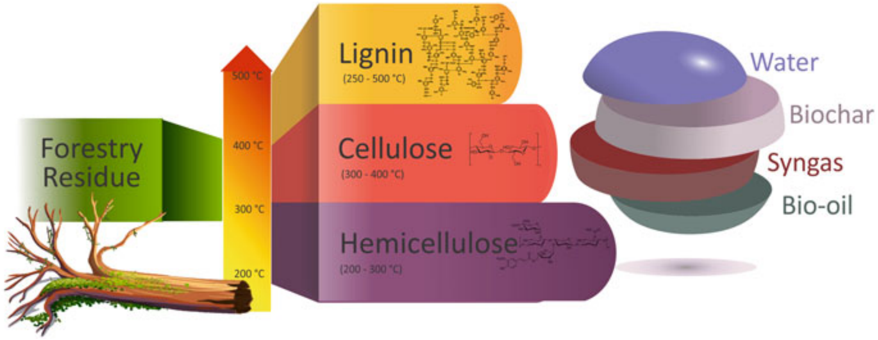

Fig. 14.4 Main thermal events from pyrolysis and main biofuels generated during this process

model, and Phaadnis model are the most common kinetic models. On the other hand, the most used differential kinetic models include Kissinger model, Network model, Friedman model, among others. There are several in-depth studies on the Kinect reactions that occur in lignocellulosic matrixes under heating (Lapuerta et al. 2004; Hu et al. 2017; Rezaei et al. 2017; Yang et al. 2021). Activated energy, pre-exponential factor, and reaction order are the main thermal properties required for a complete thermal analysis, aiming to understand how a raw material may behave under pyrolysis (Li et al. 2021a). However, this book chapter did not deal with details on these findings.

Besides that, there are pyrolytic and combustion volatiles (e.g., CO_2, CO, NOX, polycyclic aromatic hydrocarbons, and particulates) that may act as air pollutants and contribute to a hazardous impact on air quality and global warming. Volatiles from the burning of lignin is reported to contain certain free radicals, which could induce the formation of reactive oxygen species and further lead to severe cancer, heart, and lung diseases (Yang et al. 2021). The production of biofuels through thermochemical liquefaction processes (like pyrolysis and gasification) could mitigate these detrimental effects attributed to primary fuels derived from forestry residues.

14.4.2 Biofuels Produced from Forestry Residues by Densification

According to Barrette et al. (2017), most stakeholders do not recognize current technological advances on solid, liquid, and gaseous biofuels, which explains why there are no effective efforts toward the improvement of logistical aspects in the biofuels supply chain. Compaction (or densification) is a promising way to improve the storage, handling, and transportation features of forestry residues destined to direct combustion. Also, increases in energy density and homogeneity can be reached in a comparison with pristine wood parts. In this sense, pellets and briquettes are the main wooden products. The main difference between them is that the former product is manufactured using milled dead trees, wood chips, and other wood residues, while briquettes come from solid and liquid by-products derived from pyrolysis processes.

These compacted solid fuels already contribute to households, industries, and agricultural sector. Wood pellets are one of the most important wood-based commodities in the world since their trade volume is comparable to those from biodiesel and bioethanol and their production overcame 30 M tons per year (Boukherroub et al. 2017). The United States, Canada, Germany, Sweden, and Latvia are the main pellets producers and respond to about a half of the worldwide production (Hernández et al. 2019). Besides that, there is a growing expectation for the next decades, especially due to the consumption in Europe.

The prices of industrial wood pellets are relatively stable along with their history and have been keeping below those prices of similar fossil fuels (Boukherroub et al. 2017). According to Hernández et al. (2019), whenever environmental features and their easy transportation, use, and storage are taken into account, wood pellets can compete against firewood, paraffin, electricity, liquefied gas, and natural gas. Beyond physical-mechanical and energetic properties, the fossil energy required for its manufacturing, logistical costs, and transport costs must be counted to ensure the feasibility of this product. In a comparison between countries, many researchers highlighted financial governmental support as the main factor to make the pellets production really feasible (Barrette et al. 2017; Boukherroub et al. 2017; Hernández et al. 2019). Another important point is to integrate the pellets production with traditional forest products manufacturing (especially lumber) to use residues as raw materials.

According to Emadi et al. (2017), the limitation of raw materials is one of the main challenges of the wood pellet industry. Other biomasses can be blended with forestry residues to make feasible the production of pellets and briquettes. For instance, wood pulp, corn stover, wheat straw, miscanthus, and switchgrass have been used as raw materials to produce pellets, especially in the United States (Hernández et al. 2019). Hernández et al. (2019) produced pellets from orujo and alperujo, which are olive oil processing residues endowed with high energy potentials. These resources were mixed with forest residues, more specifically sawdust from *Pinus radiata* and *Populus* spp. (Emadi et al. 2017) used recycled low-density polyethylene recovered from municipal residues as a low-cost additive and binder for torrefied biomass pellets. Increases in tensile strength and heating value accompanied by a decrease in ashes content were ascribed to the incorporated plastic. Therefore, the choice of the most appropriated raw materials to the pellets production must be aligned to the local generation and the production of pellet blends using different organic materials should be encouraged.

14.4.3 Biofuels Produced from Forestry Residues by Pyrolysis

Forestry residues have a recalcitrant nature, which can be explained by their tightly lignocellulosic network. Because of that, these feedstocks can be converted into valuable chemicals by pyrolytic processes, although some of them may be technical challenges (Yang et al. 2021). According to Puy et al. (2011), pyrolysis is an alternative to avoid logistic problems related to the use of forestry residues as primary fuels. Normally, many pyrolytic products can come from the same pyrolysis process, which can be recovered, stored, and transported.

There are several subsequent and concomitant chemical reactions during biomass pyrolysis, which include dehydration, depolymerization, isomerization, aromatization, decarboxylation, and charring (Hu et al. 2017). Final temperature, pressure, heating rate, and residence time are the main process parameters that may be controlled to ensure the quality of pyrolytic products, including biochar, bio-oil, and syngas (Yuan et al. 2019). The pyrolysis processes are classified into slow, fast, and flash depending on the adjusted heating rate and residence time, which may favor the production of each pyrolytic product (Yuan et al. 2019). The proportion and composition of pyrolytic products are also dependent on endogenous factors, such as biomass source and pre-treatment (Hu et al. 2017).

According to Li et al. (2021a), pyrolysis is the most important method for the production of biofuels and consists of the decomposition of biomass under heating in an atmosphere with controlled oxygen content. In general, atmospheres rich (almost 100 wt%) in O_2 are more suitable to burn primary fuels (Puy et al. 2011). Pyrolysis in absence of O_2 may maximize the production of biochar and bio-oil, as well as organic acids (Yuan et al. 2019). And, whenever the syngas is targeted, the atmosphere must be adjusted for an O_2 content of 15–40 wt% (Hu et al. 2017; Wang et al. 2020). Normally, some kind of catalyst also may be added, especially to produce bio-oil and syngas, as discussed below (Hu et al. 2017).

Biochar is the main pyrolytic fuel produced from biomass and is considered the main renewable substitute for coal. It is normally produced from firewood by heating at a temperature range from 300 °C to 400 °C under an atmosphere endowed with low levels of O_2, which may result in a yield of 30–35 wt% and carbon retention of about 50% (Billa et al. 2019; Vendra Singh et al. 2020; Chaturvedi et al. 2021). Beyond the solid biochar, slow pyrolysis also may transform the volatile matter from the biomass into non-condensable gases, liquid pyroligneous acid, and liquid tar, which normally have yields of about 25 wt%, 33 wt%, and 7 wt%, respectively. Some of these by-products are used as fertilizers, since they are rich in K, Ca, Mg, and Na-based compounds (Billa et al. 2019). Milled forestry residues and small solid fragments leftover from the biochar production (often 15–20 wt% in yield) can be reused in further processes, like densification to produce briquettes (Castro et al. 2017). Beyond the solid fragments leftover from the biochar production, tar and other liquid by-products can also be used as binders in the production of briquettes.

Chaturvedi et al. (2021) produced biochars using different biomasses, including crop residues (rice straw, sugarcane trash, and maize stover), a processing residue (rice husk), forest litter (pine needle), semi-woody weed (lantana), and hardwood (eucalyptus). The reached thermal properties, especially heating values, revealed that those biochars derived from forestry residues presented the highest combustible features due to their lignin-rich and ash-poor compositions.

Bio-oil is the second most important biofuel obtained by pyrolysis and its production is maximized by using fast or flash processes. This biomass-based oil is composed of a series of value-added platform chemicals, including thousands of hydrocarbons, levoglucosan, phenols, furans, alcohols, and ketones (Puy et al. 2011; Yang et al. 2021), which can be controllably formed by adjusting process parameters, especially heating rate and residence time. Issues on bio-oil yield can also be solved by adjusting process parameters. Yang et al. (2021) investigated different process parameters applied to optimize the fast pyrolysis of pine sawdust and achieved high raw bio-oil yields of 60–75 wt% at a temperature range of 500–600 °C and a residence time below 2 s. On the other hand, (Xiang et al. 2018) reported that the bio-oil quality also depends on biomass characteristics, such as oxygen and moisture contents, in a manner that: the higher the oxygen content, the higher the moisture content, and the poorer the oil quality.

Puy et al. (2011) reported several compounds endowed with boiling points close to those of gasoline and diesel, which were present in pyrolytic liquids extracted from forestry residues. Compared to coal, hydrocarbons are more promisingly extracted from bio-oil using thermochemical liquefaction processes due to their low sulfur content and almost carbon-neutral content. Bio-oil production has been upgraded and high-quality hydrocarbon fuels have been successfully produced. The aforementioned valuable chemicals belonging to bio-oil are potential alternatives for numbers energy applications, including diesel-like fuels that drive engines, turbines, and boilers (Li et al. 2021a), and ethanol, which can be produced from levoglucosan (a pyrolytic product derived from cellulose) by acid hydrolysis (Yang et al. 2021).

Results reported by Hu et al. (2017) indicated that pine sawdust also has a strong potential for syngas production and inexpensive char/char-supported catalysts can be used to accomplish that. Metal oxides, transition metals, and zeolites are the most used catalysts during fast pyrolysis to reach increased yields of bio-oil and syngas. These catalysts can also be devalued residues endowed with high contents of CaO or $CaCO_3$. Recently, Yuan et al. (2019) analyzed the effects of eggshells in the catalytic pyrolysis of three pellets, which were produced using different residues, namely rice husk, herb, and wood sawdust. They reported that the CaO from the eggshells helped to absorb the CO_2 generated from the biomass-based pellets and yielded an increase in the CO production at low temperatures (below 400 °C). At high temperatures (above 400 °C), that $CaCO_3$ from the eggshells was thermally decomposed and became CO_2.

Yang et al. (2021) also investigated pine sawdust and applied fast pyrolysis under glycerolysis (heating in a glycerol medium) using alkaline and alkaline earth metals (also extracted from the studied forestry residues) as catalysts. First, they deconstructed the softwood waste into three phases, namely cellulose-rich fraction, hemicellulose-derived sugars, and organosolv lignin. Each of these phases allowed different results in terms of catalyst extraction and that lignin fraction produced by organosolv extraction stood out since this pre-treatment was effective to break cellulose-hemicellulose-lignin bonds, even using low boiling organic acids, reducing the known recalcitrant character ascribed to this biomass compound.

The heating rate can also be improved using microwaves to maximize the production of certain fuels, especially bio-oil and syngas. According to Yang et al. (2021), microwave heating is a more efficient pre-treatment than conventional oil bath heating due to its rapid heat transfer. Several studies already pointed out that microwave-assisted pyrolysis can be energetically and economically feasible (Bashir et al. 2018; Zhou et al. 2020; Li et al. 2021a, b). Most results revealed that the pyrolysis process can be successfully enhanced if microwave heating and metal catalysts are synergically used, especially in the heating rate and residence time, which may favor bio-oil production. According to Yang et al. (2021), biomass recalcitrance can be significantly reduced by the effects of metal catalysts and ultrasonic radiation integrated with the microwave heating process, which resulted in increased levoglucosan content, accompanied by decreases in aldehydes, ketones, acids, and phenols yields.

Nevertheless, most locations have several kinds of residues, and, because of that, the pyrolysis of forestry residues must be conducted together with other organic residues. Co-pyrolysis processes are common in large-scale plants and these processes can even yield better fuels than those obtained with isolated forest-based feedstock. Carbonaceous compounds are chosen to be blended with forestry residues in most cases, which is a unified solution to transform residues into fuels by pyrolysis or gasification, ensuring high process efficiency. In their study, Wang et al. (2020) investigated the co-pyrolysis of tire residues and pine barks using a fixed bed adjusted for a temperature of 900 °C. They reported that the higher was the pine bark content, the higher was the syngas yield. Also, high H_2 and CO contents and low CmHn hydrocarbons content were associated with high pine bark contents.

Paradela et al. (2009) studied the pyrolysis of tri-component blends made with variable percentages of pine sawdust, plastic residues (mixture of polyethylene, polypropylene, and polystyrene), and scrap tires. They reported that the plastics acted as H-donors, which increased the conversion of aromatic compounds into alkanes and alkene, and increased the bio-oil yield from 33 wt% to 92 wt% since several pyrolysis reactions were improved. Increases in energetic properties of the produced syngas were also ascribed to high plastics contents due to the release of gaseous hydrocarbons. The plastics also yielded decreases in aromatic compounds (liquid) and CO_2 (gas) contents from 52 wt% to 28 wt% and from 67 wt% to 2 wt%, respectively.

14.4.4 Biofuels Produced from Forestry Residues by Gasification

Gasification, also called indirect liquefaction, is nothing more than a pyrolysis process, which aims at maximizing gaseous products, especially syngas (also called producer gas). According to Sikarwar et al. (2016), H_2 and CH_4 are the main targeted feedstock in biomass gasification. Nevertheless, agricultural and forest industry residues, such as crop straw, forestry scrap, and sawdust, can react with the gasifying medium (such as air, oxygen, and/or steam) to produce numbers of gases, containing CO, H_2, CO_2, CH_4, and N_2 in variable proportions (Song et al. 2020). Several valuable liquid and gaseous fuels are extracted from syngas, especially under two different commercial processes, namely Fischer-Tropsch synthesis and methanol/dimethyl ether synthesis.

Oil biodiesel produced from syngas is considered a potential fuel for automotive compression ignition engines. Yacout et al. (2021) prepared life-cycle inventories to compare the estimated environmental impacts of the production and use of biodiesel derived from forestry resources instead of heavy fuel oil in a case study of marine shipping industry. They concluded that the replacement of fossil fuel by biofuel yielded a decrease in acidification potential of 55%. Furthermore, lower impacts on climate change, particulate matter, photochemical ozone formation, terrestrial eutrophication, marine eutrophication, and freshwater ecotoxicity were ascribed to the production and use of biofuels instead of oil-based fuel.

The gasification process is a complex mechanism, which involves a combination of chemical reactions (mostly endothermic) in the solid, liquid, and gas phases, including oxidation, drying, pyrolysis, and reduction. The required thermal energy comes from an exothermic combustion reaction or even from an external source. Normally, temperatures within 200–700 °C are adjusted to achieve decreases in molecular weight by the depolymerization of polysaccharides (hemicelluloses and cellulose) and aromatic polymers (lignin) from the forestry residue, which become the aforementioned medium-size molecules, such as CO, CO_2, H_2, and CH_4 (Wei et al. 2009; Song et al. 2020). Compared to coal, the gasification of forestry residues can occur at low-temperature ranges from 400 °C to 1000 °C since these later feedstocks are more reactive under heating. According to Wei et al. (2009), depending on the gasifier and the feedstock, the syngas produced under oxygen-starved conditions is composed of 15–30% H_2, 10–65% CO, 1–20% CO_2, 0–7% CH_4, and trace amounts of other gases.

Briefly, the reduction of amorphous regions from polysaccharides occurs at temperatures around 300 °C and generates free radicals, such as carbonyl and carboxyl groups. The crystalline cellulose decomposition occurs above 300 °C, leading to the formation of charcoal, tar, black carbon, and gaseous products. The lignin is decomposed at high temperatures, ranging from 300 to 500 °C, and forms CH_4, acetic acid, water, and acetone (Zhou et al. 2020). Volatile compounds, like organic extractives, are oxidized, yielding the aforementioned gaseous fuels.

Beyond the useful gaseous products, NOx, SO_2, and tar are the most undesirable by-products from gasification. The tar is mostly composed of condensable hydrocarbons, including aromatic compounds with up to five rings (which can be oxygenated) and polycyclic aromatic hydrocarbons (Valderrama Rios et al. 2018). Thus, this liquid by-product is considered one of the biggest obstacles in the utilization of syngas. According to Hu et al. (2017), tar is harmful to human health, and its generation may impair the syngas quality and block pipelines since it is majorly composed of volatile matter. Process parameters may avoid the tar formation, especially high temperatures (around 1000 °C) in the reduction zone that increase the oxidation of the solid residue (Valderrama Rios et al. 2018). When the tar content surpasses 5 g Nm^{-3}, this must be removed from syngas, which can be performed by catalytic reforming, transforming it into a combustible gas (Sikarwar et al. 2016).

According to Lapuerta et al. (2004), the gas produced by gasification processes can be directly used for producing kinetic energy in internal combustion engines, such as spark ignition mechanisms and gas turbines. In fact, gasification seems to be a promising technology in rural areas, when the large amounts of leftover biomasses can be in situ converted using small and low-cost gasifiers. Also, efficient engines can be coupled to the gasifiers, avoiding costs related to storage and transportation. Therefore, gasification may be encouraged aiming at reducing environmental pollution, ensuring energy security, and favoring economic development. The most commonly used gasifiers are fixed bed gasifiers, fluidized bed gasifiers, and entrained flow gasifiers (Sikarwar et al. 2016). This equipment can be divided into updraft (fuel enters from the top, gasifying agent from the bottom) and downdraft (both fuel and gasification agent enter from the top) depending on the biomass way inside the gasifier (Fig. 14.5).

The overall quality of gasification products is strongly related to the moisture content of the biomass feedstock, which varies according to features of the environment and/or the gasifier type, such as temperature and relative humidity, as well as endogenous factors from the raw material, like anatomical structure and chemical

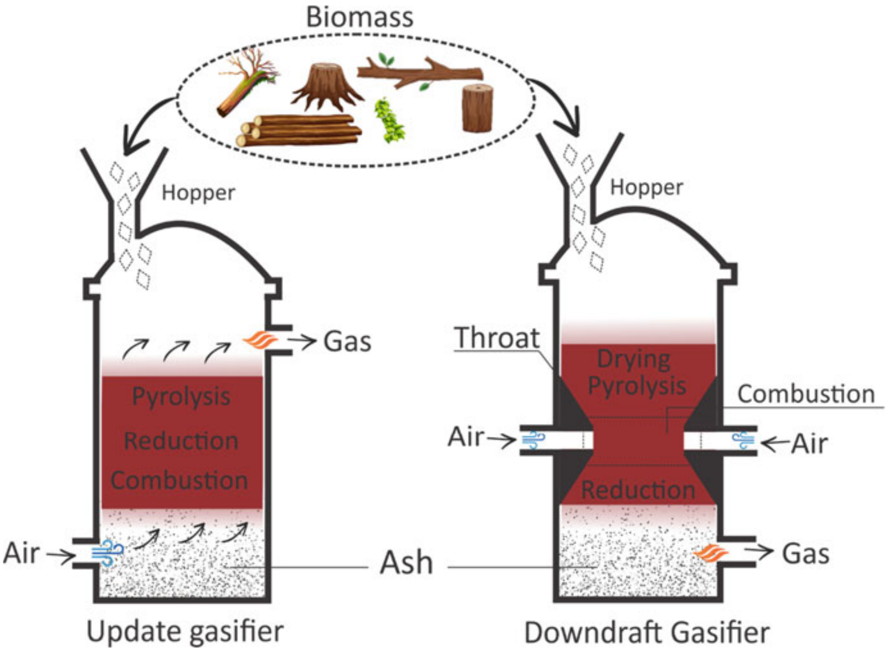

Fig. 14.5 Schematic illustration of updraft and downdraft gasifiers

composition. Some forestry residues are processed by gasification at moisture contents up to 40%. This moisture becomes vapor at 100 °C and also generates CO and CO_2, conferring deleterious effects to certain targeted gaseous products, which indicates that moist resources may demand a high energy penalty to be dried before the process (Da Silva Perez et al. 2015). Because of that, softwood sawdust and other low-density resources are normally preferred over wood bark and hardwood sawdust for gasification.

Weaknesses of certain forestry residues can also be compensated by other residues by using co-gasification processes, which has been receiving much attention in recent years. According to Peng et al. (2012), compared to other vegetable matrixes, forestry residues contain high contents of volatile matter and fixed carbon accompanied by low ashes and moisture contents. They proposed a way to mitigate these unfavorable characteristics of forestry residues by blending them with a by-product from a wastewater treatment plant (*c.a.* a sewage sludge) using a lab-scale fixed bed gasifier. The blend presented an intermediate moisture content, which generated steam in situ and increased the production of H_2 and CO. They also reported that an optimal wet sewage sludge content of 30 wt% and an optimal reactor temperature of 900 °C yielded a dry gas yield of 0.70 N m^3 kg^{-1} and this gas contained an H_2 yield of 11.67 $mol{\cdot}kg^{-1}$ and a lower heating value of 11.89 MJ Nm^{-3}. Nevertheless, there are several technological efforts for developing gasifiers capable of process moist biomasses. Even though, the high moisture content of certain biomasses can be an insurmountable drawback from an economic standpoint. In these cases, fermentation could be chosen instead of gasification.

14.4.5 Production of Ethanol from Syngas

Ethanol is the main biofuel used for transportation since can also act as a gasoline extender. Besides the transport sector, the food industry is also responsible for significant consumption. According to Barcelos et al. (2021), several forestry residues and even standing trees can be used to produce ethanol, although it is difficult to affirm if ethanol production can compete against other purposes since the lumber industry is normally more feasible to produce value-added products. For Mesa et al. (2017), the low cost of forestry residues and enzymes may allow a feasible ethanol production using these raw materials.

Although ethanol can be produced by oil cracking, most (over 90%) of ethanol production comes from biomass resources (Wei et al. 2009). This valuable fuel can be obtained by biomass refining using three pathways: direct fermentation, hydrolysis fermentation (hydrolysis followed by fermentation of polysaccharides), and syngas conversion. The former one is the simplest process although it is only possible by using food sources as raw materials.

The ethanol can be produced from syngas by two routes: biosynthesis and chemical synthesis. The former one is called syngas fermentation and consists of microbe mediated reactions performed using microorganisms endowed with the ability to metabolically convert CO, CO_2, H_2O, and H_2 from syngas into ethanol, as well as minor amounts of acetic acid, water, a liquid stream (Wei et al. 2009; Socha et al. 2013; Song et al. 2020). A further purification process can also be conducted to separate each targeted compound. The overall process is directly dependent on environmental conditions since the syngas (gaseous phase) are inserted into the bacteria medium (liquid phase) and there is a poor chemical interaction between them. Because of that, the CO dissolution into the produced ethanol may be a challenge, especially aiming at a scale-up. Normally, temperature ranges around 30–40 °C are applied at atmospheric pressure, yielding a low rate of ethanol production, which may take weeks and even months. Also, it can be hard to isolate that microorganism able to consistently produce ethanol from syngas at considerable concentrations (over 25 $g \cdot L^{-1}$) (Wei et al. 2009; Kumar et al. 2021b). There are several bacteria able to produce ethanol from syngas by anaerobic fermentation, although few of them are really available (Wei et al. 2009; Wang et al. 2018).

The chemical pathway consists of a catalytic process at high levels of temperature (between 200 and 350 °C) and pressure (around 7 MPa). The chemical products yielded throughout this process are similar to those produced via biosynthesis. Briefly, syngas, catalysis, temperature, and pressure are feed into a reactor and undergo quick reaction, which may take minutes or even seconds, yielding a final biofuel with an ethanol content around 70% associated with CO-to-ethanol conversion rates over than 40 wt% (Wei et al. 2009).

14.4.6 Biofuels Produced from Forestry Residues by Fermentation Hydrolysis

Bioethanol is mostly produced using organic residues, non-edible vegetables, and poorly lignified agricultural crops, which grow on marginal lands and prevent soil erosion, such as corn, sugarcane, and seed oils (Barcelos et al. 2021). These vegetables do not demand pre-treatments before the needed conversion processes and, because of that, they yield the called first-generation ethanol. On the other hand, the lignocellulosic nature of the forestry residues made them recalcitrant to ethanol production using those chemical reactions that occur in a fermentation hydrolysis process.

Hydrolysis fermentation is a process in which cellulose becomes glucose and xylose due to the action of specialized microorganisms, steam, and catalysts. This process occurs at a temperature range of 120–250 °C and atmospheric pressure (Wei et al. 2009). For that, a series of steps may be overcome, including hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Kumar et al. 2021b).

High energy consumption, sugar loss during intermediate separations, cellulose decrystallization ineffectiveness, efficient recovery of pre-treatment chemicals, wastewater treatment, generation of inhibitors, and presence of toxic extractives can be considered the main endogenous features that hinder the deconstruction of wood polysaccharides into alcohol mixtures (Wei et al. 2009; Socha et al. 2013; Lomovskiy et al. 2020; Barcelos et al. 2021). The glucose yield can increase from 20% to 90% in certain cases due to the applied pre-treatment (Wei et al. 2009).

Due to this reason, the protective lignin wrapper must be removed from the cellulosic fibers to allow the access of the enzymes onto the surface area of the wood polysaccharides, which may become monomeric and oligomeric sugars. Weak acids, furan derivates, and phenolics can also be generated, which may potentially inhibit later fermentation (Mesa et al. 2017; Kumar et al. 2021b). For that, the previous pre-treatment must be selected accordingly, as discussed above. Organosolv, steam-explosion, and acid washing are the most important pre-treatments used to allow the biofuels production by fermentation of woody biomasses. Less frequently, alkaline washing and sulfite pulping processes are also applied (Barcelos et al. 2021). Before any of these thermal and chemical pre-treatments, wood chipping, grinding, and milling are commonly applied to achieve suitable surface areas (Wei et al. 2009; Lomovskiy et al. 2020).

The pre-treated wood sugars are fermented at 20–40 °C and atmospheric pressure by the action of specialized microorganisms, such as enzymes and bacteria, which yield a liquid fraction of ethanol, cell mass, and water, as well as a gaseous phase called biogas, which is rich in CO_2 and CH_4, and a disposable solid phase. This solid fraction is called digestate and normally is used as fertilizer. This process can take few days or even some days and has a low efficiency since the final ethanol content of the liquid fraction is close to 10 wt% (Frederick et al. 2014; Barcelos et al. 2021). The fermentation product stream must then be purified by cycling through a number of distillation and dehydration operations to get fuel-grade ethanol, which may be endowed with a purity of 99.9%.

Regarding biogas production, the greater the bacteria diversity, the greater the biogas yield (Kalyani et al. 2017). This biofuel is a promising alternative to natural gas, especially when biomethane is obtained by further processes. This is mostly produced in landfills from urban areas or biodigesters installed on farms. Several limiting factors must be overcome in order to reach increased biogas yields from forestry residues, including redox imbalance, the concentration of inhibitors, and retention time (Kumar et al. 2021b). In this sense, the pre-hydrolysis process, two-stage processes, bioaugmentation, buffering control, and activated carbon addition are the most promising solutions in the literature (Mehariya et al. 2018; Alavi-borazjani et al. 2020).

14.5 Main Valuable Products Derived from Forestry Residues

In addition to the processing of biofuels and composites, there are several valuable products that can be obtained through conversion processes using forestry residues. According to Stafford et al. (2020), all those chemicals traditionally obtained from fossil resources have similar ones that can be extracted from plants or other sustainable raw materials. As discussed above, the biorefinery concept focuses on isolate one targeted valuable compound from plants, which is similar to what refineries make with petrochemicals. For instance, Stafford et al. (2020) reported 129 chemical compounds and 78 of them can be considered unique products. All these compounds could be extracted through cost-effective methods and further destined to different applications, such as biopolyols, film formers, sorbents, furans, and carboxylic acids. As already discussed, forestry residues have a recalcitrant chemical structure, which normally demands physical, biological, chemical, or combined pre-treatments in order to make feasible their subsequent fractionation into valuable chemical components. In this section, the most important chemicals that can be extracted from forestry residues will be discussed.

14.5.1 Sugar Alcohols

Biopolyols are mostly composed of alcohols, phenols, and some of their derivatives, which can be extracted from forestry residues. All these compounds are rich in polar chemical groups, such as hydroxyls and methoxyls. Forest-based polyols are mostly produced using lignin from pulp and paper mills (Lee et al. 2002), sawdust (Wang et al. 2013), and barks (D'Souza and Yan 2013). Liquefaction, including hydrolysis, decomposition, and polycondensation are some of the recently studied processing routes to produce polyols from forestry residues (Li et al. 2020a, b). Most biopolyols are derived from hydrothermal liquefaction processes, which are carried out at a 250–290 °C temperature range for 30–120 min using alkali catalysts, such as Na_2CO_3, K_2CO_3, NaOH, and KOH (Li et al. 2020a, b; D'Souza et al. 2017). Forestry residues can also be converted into biopolyols by fast-pyrolysis at temperatures above 400 °C and short residence times below 5 s (Li et al. 2020a, b; Torri et al. 2016). After that, the superheated steam is cooled down, forming the liquid biopolyol (Butler et al. 2011). These biopolyols contain multiple reactive hydroxyl groups and can partially or totally replace synthetic polyols to produce several kinds of polyurethane-based products, like resin, foams, adhesives, among others.

For instance, xylitol is a polyol that has been applied by several industries, such as food, dentistry, and pharmaceutical. This can be produced either by chemical hydrogenation of xylose (C5 sugar) or by biotechnological processes (de Albuquerque et al. 2014; Ur-Rehman et al. 2015). The chemical pathway is considered a difficult, expensive, and energy-intensive process (de Albuquerque et al. 2014). This occurs by acid hydrolysis of a xylan-rich feedstock yielding a solid fraction composed of pure xylose. Then, this pure xylose undergoes a hydrogenation process using a Ni-Al2 alloy as a catalyst. On the other hand, the bioconversion route is performed using microorganisms able to somewhat metabolize the biomass, such as those from the Candida genus (Ur-Rehman et al. 2015). This process route is more economically feasible than the chemical one due to its smaller demand for energy, although certain inhibitors may be generated by the acid-pretreatment, impairing the whole conversion process.

Sorbitol is obtained from a cellulose-based fraction, which undergoes a hydrolysis process that breaks D-glucose bonds and there is further hydrogenation of glucose macromolecules (Ochoa-Gómez and Roncal 2017). Normally, selective degradation of certain chemical groups to produce sorbitol is neither simple nor inexpensive since further purification processed may be needed in order to reach a high purity compound. This high-value-added compound has many industrial applications, especially surfactants, which are applied as wetting agents, foaming agents, dispersants, detergents, emulsifiers, and so on. In their study, Ribeiro et al. (2015) performed single step hydrolysis using a carbon-supported ruthenium catalyst and hydrogenation by ball milling, reaching a selectivity to sorbitol of 40 wt%. Yamaguchi et al. (2014) directly converted wood chips into sugar alcohols. Their catalytic hydrolysis process was conducted at 190 °C and a pressure of 5 MPa, using a carbon-supported platinum catalyst, and a total conversion to sorbitol of 36% was reported.

Ethylene glycol is one of the most targeted products in the conversion of lignocellulosic biomass into valuable products since it can be used as a precursor in many industrial applications, such as the manufacture of plastics, foods, antifreeze and liquid refrigerants for automobiles, among many others. Besides its synthesis from non-renewable resources, ethylene glycol can be obtained from cellulose or glycerol using chemical conversion processes. The production of ethylene glycol from cellulose starts with a hydrolytic conversion to obtain glucose, which is followed by hydrogenolysis, in which the glucose is transformed into the product of interest. However, some drawbacks must be overcome in a near future in order to create more efficient catalytic systems able to convert lignocellulosic biomasses into ethylene glycol, especially regarding the applied catalyst, which is not a renewable compound in most cases (Xiao et al. 2018). Ribeiro et al. (2021) investigated various forestry residues (including wooden fragments from pine, oak, eucalyptus, platanus, as well as cork, pine cones, and paper residues) and achieved ethylene glycol yields up to 24–41% using catalytic systems based on tungsten, ruthenium, and commercial carbon nanotubes. Xiao et al. (2018) demonstrated that a hybrid catalyst of niobium (15%) and tungsten (20%) favored the ethylene glycol production from hardwood pulp and a final yield of 42% was reported. Ji et al. (2008) reported the direct conversion of cellulose into ethylene glycol using a one-pot process, in which a carbon-supported niobium/tungsten catalyst was used and a final yield of 61% was reached. Finally, Zheng et al. (2010) investigated nickel/tungsten catalysts and up to 76.1% in yield was reached.

14.5.2 Films

Among those compounds that can be extracted from forestry residues, hemicelluloses have been attracting attention due to their high film-forming properties, which have been yielding films with high oxygen barrier properties (Edlund et al. 2010). In this sense, xylans from hardwood have been explored as film constituents for potential packaging applications (Gröndahl et al. 2004). Hemicelluloses can be extracted from lignocellulosic biomasses by a series of filtration steps, in which monosaccharides, extractives, and lignin are removed from a polysaccharide fraction. The hydrothermal treatment of wood chips generates a hydrolyzed wood fraction in form of wastewater, which often contains a minor amount of lignin and is economically feasible to the barrier film production by simple membrane filtration (Edlund et al. 2010; Zhang et al. 2021; Lindblad et al. 2009). In this sense, Edlund et al. (2010) developed a thin film based on a hydrolyzed wood fraction produced at 150–170 °C for 60 min, which was recovered from a wastewater phase and was then processed by ultrafiltration to produce free-standing smooth and transparent films. As main results, they reported oxygen permeabilities below 1 cm^3 μm m^{-2} day^{-1} kPa^{-1} and tensile strengths above 50 MPa in some cases. Bufalino et al. (2016) successfully conducted alkali and bleaching treatments in *Cordia goeldiana* veneer residues to produce nanocellulose films. For the alkali treatment, a digester was filled with a solution of 5% of NaOH, a temperature of 150 °C, and a pressure of 0.7–1.2 MPa were adjusted. The NaOH-treated material was then bleached under mechanical stirring at 3000 rpm using a $NaOH/H_2O_2$ solution. They also reported cellulose cristalinities above 60% and that the ground nanocellulose fibers interacted with each other by hydrogen bonds.

14.5.3 Biosorbents

Synthetic dyes and heavy metals can be removed from water bodies or other contaminated environments using biomass-based adsorbents. These valuable compounds can be considered as efficient and inexpensive alternatives to traditional adsorbents and may yield a low secondary pollution risk (Deniz and Kepekci 2017; Semerjian 2010). These conventional methods have some remarkable disadvantages, such as incomplete removal, high requirements of both reagents and energy, and generation of toxic slurry or other effluents that require disposal (Deniz and Kepekci 2017). These pollutants are encountered in wastewater streams from many industries, such as textile, paper, dyeing, tannery and paint manufactures (Sidiras et al. 2011),

Semerjian (2010) reported that an *in natura* pine sawdust acted as an efficient adsorbent for the removal of cadmium from aqueous solutions. For this purpose, the used forestry residue normally may undergo an acid and/or alkali pre-treatment before being used as an adsorbent since its sorption characteristics may be controlled by the types and numbers of functional groups on its surface. This also depends on chemical features of the contaminant that must be removed (Zhao et al. 2012). Deniz and Kepekci (2017) used cetyltrimethylammonium bromide as a modification agent for a multi-component biosorbent composed of pine, oak, hornbeam, and fir sawdust biomasses. This biomass-based compound yielded promising results for removing

Malachite green, which is a known dye contaminant. Xu et al. (2020) studied residues from camphor leaves prepared by a mechanical pre-treatment. This milled biomass was then treated by alkalinization using a NaOH solution, which was followed by grafting of a 1,2,3,4-butane tetracarboxylic acid. Genevois et al. (2017) reported bioadsorbents derived from Douglas fir bark, which were subjected to a 2,2,6,6-etramethylpiperidine-1-oxy radical (TEMPO)-mediated oxidation, which improved its cesium (Cs+) adsorption capacity. The authors showed that and incorporation of nickel-metal hexacyanoferrate successfully created carboxyl groups onto the bark's surface and enabled an increased Cs removal from the water solutions.

14.5.4 Furans

Any sugar fraction obtained by chemical hydrolysis may contain furfural, hydroxymethyl furfural (HMF), phenolic compounds, and aliphatic acids (Ur-Rehman et al. 2015). Furfural and HMF are dehydration products from C5 (xylose) and C6 (glucose) monomers, respectively. They can be obtained from hemicellulose, cellulose, or starch-rich biomasses. The hydrolysis of either hemicellulose into furfural or cellulose into 5-HMF (and subsequent levulinic acid) to co-produce platform compounds is still limited (Chen et al. 2020). The furfural derived from hemicelluloses is used to produce furfuryl alcohol, tetrahydro furfuryl alcohol, acetyl furane, furoic acid, methyl furane, and tetrahydrofuran (THF). This is a key renewable chemical platform in the commercial exploitation of chemicals, biofuels, renewable additive fuels, and integrated biorefinery products (Cai et al. 2014; Pogaku 2019), such as lubricants, adhesives, and polymers (Clauser et al. 2018). For instance, Nylon 6,6 and Nylon 6 are two of the main polymers derived from furfural and have a huge market (Kamm and Kamm 2004).

The transformation of forestry residues into furfural involves acid washing at moderate levels of temperature (ranging from 150 °C to 170 °C) and pressure (around 1 MPa) (Pogaku 2019; Li et al. 2020a, b). Currently, commercial production of furfural uses mineral acid catalysts (such as hydrochloric acid and sulfuric acid) and superheated steam that catalyzes the reaction by heating. However, there are some disadvantages ascribed to the process, such as the generation of acidic effluents, unwanted side reactions, and high corrosiveness (Liu et al. 2020). The use of solid acid catalysts is a promising manner to mitigate the corrosiveness of this process, avoiding a high cost related to the involved equipment, although other environmentally friendly, easy to recovery, and highly stable compounds may be generated, such as molecular sieves, carbon-based solid acids, and sulfamic acid (Li et al. 2020a, b).

5-HMF is recognized as a valuable and versatile platform chemical for the synthesis of key materials, such as pharmaceuticals, plastics, and fine chemicals (Feng et al. 2015). However, that hydrothermal process needed for the HMF production has the main drawback related to the generation of an unstable HMF in most cases. This can be explained by the low reactivity of the cellulose throughout the conversion process, which may lead to unwanted generations of levulinic acid and humins (Chen et al. 2020). Ching et al. (2017) investigated a microwave conversion of microcrystalline cellulose using water and a diluted acid was used as a catalyst. Both HMF and levulinic acid were produced at the end of the process and the authors affirmed that the adjusted temperature strongly affected the efficiency of the conversion of cellulose into HMF. Seri et al. (2002), who reported a final yield of 19%, extracted HMF from a cellulose fraction using an acid catalyst ($LaCl_3$) and water heated at 250 °C for 150 s. (Wu et al. 2019) used a niobium-doped carbon microspheres catalyst and a Brønsted acid heated at 200 °C for 60 min to convert cellulose into 5-HMF and a maximum 5-HMF yield was 85% was reported.

Hydration of HMF leads to an unstable tricarbonyl intermediate which can be transformed into levulinic acid and/or formic acid (Hayes et al. 2006). Levulinic acid can be produced from carbohydrates through hydrothermal processes using mineral catalysts, such as hydrochloric acid and sulfuric acid (Liu et al. 2018). The oxidation of levulinic acid can also lead to the production of succinic acid, which is a precursor for certain products, such tetrahydrofuran, 1,4-butanediol, and c-butyrolactone (Hayes et al. 2006). These high value-added chemicals have been applied by several industries to the manufacture of polymers, resins, pesticides, and fuel additives (Clauser et al. 2018; Liu et al. 2018).

Regarding the formic acid, which is a by-product from the levulinic acid extraction from cellulose, it can be reacted with alcohols and alkenes to produce formate esters (HCO–OR). These chemicals can be applied as solvents, chemicals, or fuel additives. Also, they can be purified by distillation, which yields this valuable commodity chemical. The production of formic acid originated from forestry residues by hydrothermal reactions is receiving significant attention with respect to thermal degradation, oxidation, hydrolysis, and other reactions. Yun et al. (2016) used NaOH heated at 150 °C for 15–20 min and reached a high selectivity, as well as remarkable yields of 80–85% from monosaccharides and disaccharides.

Lactic acid is one of the main platform chemicals that can be extracted from glucose (C6 sugar). Several bio-degradable polymers, solvents, metal pickling, and food additives can be obtained through the conversion of lactic acids (Oh et al. 2005). This valuable carboxylic acid can be produced by hydrothermal reactions from carbohydrates and high yields have been reported in recent studies. For instance, Yan et al. (2010) achieved lactic acid yields of 20–27% from the hydrothermal conversion of a carbohydrate fraction from woody biomass using NaOH and $Ca(OH)_2$ as alkaline catalysts. Their results showed the highest lactic acid yield of 27% in terms of carbon percent at an optimal reaction temperature of 300 °C and reaction time of 60 s using 2.5 M NaOH. For the $Ca(OH)_2$, the highest yield was 20%, which was obtained using 0.32 M $Ca(OH)_2$ and the same conditions of temperature and time adjusted for the NaOH case.

14.6 Concluding Remarks

Forestry residues are widely available in different formats, although the literature lacks proper classification to them, as well as a concise and deep review on their variable composition and possible applications. There is a perception that the environmental impact caused by forestry residues is not so high as that of industry residues, although there are several hazardous residues associated with the forest-based productive chain. Furthermore, even the reuse of dead trees, timbers endowed with growth defects, and other wood-based by-products should be encouraged to strengthen a concept of circular economy in the entire forestry supply chain.

These resources are promising alternatives to fulfill several different markets, such as fuels, materials, and other valuable products described in the chapter. These niches are traditionally dominated by oil-based products, although there are important research, technological, and governmental efforts toward the replacement of these ecologically unfriendly resources. More results obtained through life-cycle assessment, life-cycle costing, and carbon accounting methodologies are needed for ascertaining which bio-based product may suitably replace its respective petrochemical one.

In the coming decades, the use of modern processes applied to the production of bio-based products may help to ensure energy security, economic development, increases in the standard of living, decreases in emissions of greenhouse gases, and decreases in global warming. These advances come up against certain difficulties, such as the low conversion of biomass into some biofuels, limited supply of key enzymes for fermentation processes, large energy penalty demanded by thermochemical pathways, high capital investments necessary to implement large-scale biorefineries. It is expected that optimized integrated biorefinery processes will maximize the use of all compounds from biomasses, meeting both economic and ecological requirements. In this sense, environmental preservation may be reached together with the use of the current idle productive capacity.

However, some biofuels may negatively impact the environment due to the emission of particulate contaminants, the implementation of monocultures, and the consumption of pesticides. Therefore, biofuels that favor family farming, social development, and the use of residues should be prioritized, which also leads to a reduction in logistical costs. The planet's energy matrix in the future will probably has a consolidated consumption of seasonal renewable technologies, such as solar energy and wind energy, in addition to hydrogen fuel cells and electricity produced by nuclear plants.

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Chapter 15
Panoramic View about Microalgae Biomass as Waste-to-Energy: A Biorefinery Concept

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Abstract Biorefining is an alternative and a sustainable biomass processing and transformation method that yields bioenergy, biofuel along with other valorized products through different processes and equipments. The idea of biorefinery has been identified as a potent and promising way to establish a biomass-based industry. A promising and dominant candidate in biorefinery processes that are employed for obtaining multiple products is microalgae, as it contains various beneficial biologically active components. Biodiesel extracted from microalgae has been extensively analyzed and examined since the last 20 years. Alongside biodiesel, other high-value products can also be extracted from microalgae, which include pigments, long-chain polyunsaturated fatty acids, and antioxidants due to the occurrence of proteins and carbohydrates. The obtained products are beneficial in cosmetic, nutraceutical, and pharmaceutical industries. Valued compounds can be extracted either concomitantly or batch-wise post biodiesel production in order to minimize the gross disbursement. Biorefinery concept is utilized to make use of the vital components housed by microalgae. They are also beneficial in decreasing the harmful greenhouse gas emission while using simply saline or wastewater. These advantages and multi-uses render microalgae a potent source in terms of biorefinery approach. This review paper aims to highlight beneficial components of microalgae and throws light on the current and future prospects as well as enhancing bio-processing viability for microalgae-based biorefinery.

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15.1 Introduction

Energy plays a crucial role in social and economic development. With the increment of global economy through rapid urbanization and industrialization, the worldwide global energy consumption and supplement has also been increasing rapidly. As per the International Energy Agency (IEA), the worldwide energy consumption is likely to observe an increment of approximately 53% by 2030 (Ong et al. 2011), as well as the overall energy consumption will be higher in developing countries in comparison to developed countries by 2030 (Saito 2010). Researchers say that issues related to energy crisis are extremely evident and foreseen and therefore it is doubtful whether there will exist enough fossil fuel reserves for people to consume in the future. Burning of fossil fuels due to anthropogenic activities along with other serious issues such as climate change and its adverse effects and global warming has altogether received a special focus on CO_2 emission mitigation (Zhu 2015). This can be achieved by replacing fossil fuels with clean and renewable energy (Hejazi and Wijffels 2004). Environmental policies have thereby supported and favored increased research and development in the use of biofuels all over the world, with a primary focus on the replacement of fossil fuels used in transportation (Demirbas 2008). The use of biofuels provides several advantages such as energy security, environmental sustainability, economic stability, and reduction of greenhouse gases (González-Delgado and Kafarov 2011). In this regard, the third-generation feedstock, microalgae have received an increased attention and are recognized as an alternative to remove CO_2 from the atmosphere (Trivedi et al. 2015). Microalgae consist of many bioactive components such as carbohydrates, lipids, and proteins that have become the limelight of research with respect to biofuel production for sustainable development. Hence, microalgae usage is mainly focused on biofuel production along with value-added products in comparison to the traditional functions (Zhu et al. 2013).

The biorefinery and traditional petroleum refinery concepts are quite similar where the raw material is transformed into valuable commercial products (Pérez et al. 2017), but the key variation exists with raw materials (biomass or crude oil) and conversion technology applied (González-Delgado and Kafarov 2011). Biorefineries are widely applied in the industrial sector at a large scale and that helps to focus on the production of various bioproducts. In biorefineries, integration of the production configurations can be applied, which would result in maximum product output and profit from a single raw material, even with the problems of raw material scarcity and environmental impact (Moncada et al. 2015).

The production of different products from microalgae is considered an economical process since the microalgae can be cultured using water and atmospheric CO_2 only. Microalgae grow easily in waste land without creating any obstacles against land as well as food crops. This is also possible to cultivate using a medium containing heavy nutrients and salts (Baicha et al. 2016). Furthermore, the high photosynthetic efficiency of microalgae is the quality that gives it the potential to pave way toward gaining of renewable energy sources in near future (Khoo et al.

2013). Another quality of microalgae is that it has the ability to biosequester CO_2 from flue gases generated from power plants which will contribute toward a decrease in greenhouse gas emissions (Cheah et al. 2015).

This review targets to provide updated information about the principles of biorefinery related to the conversion of microalgae into different high-value products such as proteins, carbohydrates, lipids, pigments, etc. A detailed investigation was performed about the principles and fundamentals of microalgae biorefinery along with the benefits associated with these methods. Furthermore, analyses of the economic potential and sustainability of microalgae biorefinery have also been performed in this review.

15.2 Biorefinery of Microalgae

15.2.1 Lipids Fraction

Lipids from microalgae are of significant interest in the field of biodiesel production and energy storage. Microalgae produce lipids are usually classified into two main groups namely polar lipids, i.e., glycerophospholipids and non-polar lipids, i.e., triacylglycerols (TAGs). The production of lipids from microalgae, preferably triacylglycerols, is receiving the most attention to produce biodiesel. Triacylglycerols (TAGs) can be easily converted into fatty acid methyl esters (FAME) through the well-adopted technique of transesterification in the presence of acid and alkaline catalysts (Alishah Aratboni et al. 2019).

The lipid content in microalgae depends upon the type of microbial species, cultivation and environmental conditions (Chisti 2007). The lipid yield from microalgae can be enhanced through the strategic control of various factors such as the intensity of light, pH, temperature, and nutrient starvation. The most effective method of improving lipid accumulation in microalgae is through nitrogen starvation, which results in increased accumulation of lipids (Zhu et al. 2016).

Lipids extraction is an extremely important process for the production of biodiesel from microalgal lipids. Lipids from microalgae can be extracted by several techniques which include solvent extraction method, microwave-assisted extraction, ultrasonic extraction, and electroporation. Presently, solvent extraction methods are most used for lipid extraction as they provide the highest lipid recovery. However, lipids can also be extracted by non-solvent extraction methods, namely isotonic extraction, osmotic pressure method, electroporation, and enzyme extraction. These non-solvent extraction methods are facile and eco-friendly (Ranjith et al. 2015). However, the development of cost-effective and efficient methods is necessary to maximize the extraction of desirable lipid fractions. Different by-products of microalgal biomass are shown in Fig. 15.1.

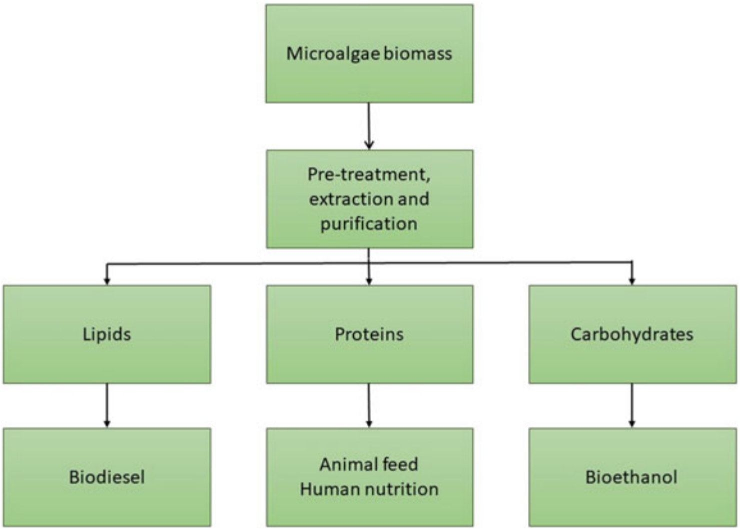

Fig. 15.1 Different by-products of microalgal biomass

15.2.2 Carbohydrate Fraction

Microalgae contain a sustainable amount of carbohydrate content due to their relatively high photo-conversion efficiency (Yen et al. 2013). Microalgae consist of a combination of various kinds of monosaccharides, polysaccharides, and other complex polymeric carbohydrates (John et al. 2011). The absence of lignin content in microalgae simplifies the process of producing bioethanol. Different microalgae species and their corresponding cultivation conditions lead to a difference in the concentration of carbohydrate and starch contents. Multiple stress conditions such as high light intensity, high salinity, and nutrient starvation conditions can be used for enhancing carbohydrate content in microalgae (Chen et al. 2013). Carbohydrates from microalgae are conventionally extracted by means of chemical hydrolysis (Chew et al. 2013) (Table 15.1).

15.2.3 Protein Fraction

Microalgae have high proportions of proteins around 50–70% depending on the species (Chew et al. 2017). The high quality of protein in microalgae can be used to substitute the traditional protein sources as an alternative protein source for human food consumption and animal feed (Bleakley and Hayes 2017). Microalgae-based proteins due to their balanced amino-acid distributions are of significant interest as an unconventional source of protein (Caporgno et al. 2018). Microalgae also contain some toxic proteins, so analytical analyses need to be performed to determine the

Table 15.1 Chemical composition of microalgal species

Sl No.	Microalgae species	Lipid content (% dry weight)	Carbohydrate content (% dry weight)	Protein content (% dry weight)	Reference
1	*S. almeriensi*	24.2	12.5	55.9	Papachristou et al. (2021)
2	*S. almeriensi*	11.2	38.7	41.8	García et al. (2012)
3	*Chlorella vulgaris*	14–22	12–17	51–58	Becker (2007)
4	*Chlamydomonas rheinhardii*	21	17	48	Becker (2007)
5	*Scenedesmus obliquus*	12–14	10–17	50–56	Becker (2007)
6	*Spirogyra sp.*	11–21	33–64	6–20	Bruton et al. (2009)
7	*Spirulina maxima*	6–7	13–16	60–71	Bruton et al. (2009)
8	*Spirulina platensis*	4–9	8–14	46–63	Bruton et al. (2009)

presence of any toxic proteins to ensure it is safe for utilization. Algal proteins are usually extracted by centrifugation, filtration, and solvent extraction methods (Chew et al. 2017).

15.3 Microalgae Biomass Conversion Technologies

Algal biomass is considered as a potential feedstock for food nutrients, pharmaceuticals, chemicals, and types of renewable energy applications. There exist different possible methods for the conversion of algae into fuels, heat, and power related to biorefinery. The major composition of microalgae viz. carbohydrates, lipids, and proteins can be transformed into different products such as bioethanol, biodiesel, biogas, etc. applying biochemical, chemical, thermochemical, and direct combustion methods (Halder and Azad 2019).

15.3.1 Thermochemical Conversion

Thermochemical conversion refers to the thermal decomposition of algal biomass into biofuels which includes liquid, gaseous, and solid fuels. It is considered the simplest way for microalgae conversion into biofuels in comparison to other existing conversion methods. Thermochemical conversion can be classified as gasification, liquefaction, pyrolysis, and direct combustion based on temperature, pressure, and heating duration (Sharma and Bhatti 2010).

15.3.1.1 Gasification

Gasification is the thermochemical conversion process that transforms the carbonaceous materials in microalgae biomass into combustible gas at elevated temperatures (800–1000 °C) and in the presence of insufficient oxygen. The combustible gas obtained from gasification contains mainly of CO and H_2 along with the traces of CO_2, N_2, and CH_4. These obtained gaseous products possess low heating value and therefore can be directly applied for burning. The gasification of microalgae takes place in four stages, i.e., drying, pyrolysis, combustion, and reduction (McKendry 2002). In an investigation, Hirano et al. (1998) studied the influence of temperature on the gasification of Spirulina sp. and found the enhancement in H_2 content and reduction of CO_2, CO, and CH_4 with the increase in temperature. Due to the high moisture content in microalgae, the drying stage of conventional gasification consumes lots of heating energy. Since supercritical water gasification can completely avoid the disadvantage of the drying stage, it is gaining attention in recent times. Supercritical water gasification can be carried out beyond the critical point of water (374 °C and 22.1 MPa) (Amin 2009). In the investigation performed by Guan et al. (2013), it was found that the production of H_2 and CH_4 from supercritical water gasification of Nannochloropsis sp. enhanced rapidly in the presence of NaOH and KOH.

15.3.1.2 Liquefaction

Liquefaction of microalgae is performed at lower temperature ranges between 300 and350 °C and high pressure (5 – 20 MPa) for 5 – 60 min in the presence of catalyst and solvent to convert the microalgae into biofuels. Microalgae contain moisture content of 80 – 90%; therefore, it is a favorable candidate for liquefaction, since this conversion process requires feedstock to be used in the reactor in slurry form. The drawbacks of the reactor used in liquefaction are its higher cost and complex form (McKendry 2002; Goyal et al. 2008). Minowa et al. (1995) used Dunaliella tertiolecta as the feedstock to produce bio-oil using liquefaction conversion process. In this investigation, a total liquid oil yield of 42% was obtained from the feedstock at 300 °C, and a higher heating value (HHV) of 34.9 MJ kg^{-1} was achieved.

15.3.1.3 Pyrolysis

Pyrolysis of microalgae is performed by heating the sample at temperature ranges between 400 and 600 °C with a pressure of 0.1 MPa for 30 – 60 min in absence of air, which gives the products liquid oil, gas, and solid char (Babich et al. 2011). Many investigations have already been performed by different researchers to observe the effect of slow and fast pyrolysis on microalgae in the presence as well as unavailability of catalysts. The bio-oils obtained from microalgae possess a higher heating value of 31 – 42 MJ $kg^{-1}$and viscosity of 0.060 Pa s, and contain hydrocarbons from lipids and nitrogenous compounds from proteins as the major components (Harman-Ware et al. 2013). In comparison to bio-oils obtained from lignocellulosic biomass, the algal bio-oil is more stable and therefore suitable for further applications (Grierson et al. 2009). The production rate of bio-oil from microalgae and its quality are highly influenced by different pyrolytic parameters viz. temperature, pressure, holding time, type of pyrolysis, and catalytic effects (Peng et al. 2000). In an investigation, Miao and Wu (2004), studied the fast pyrolysis of microalgae and lignocellulosic biomass and found that the microalgae bio-oil contains low oxygen along with high calorific value in comparison to lignocellulosic biomass. Furthermore, Pan et al. (2010) investigated the catalytic pyrolysis of Nannochloropsis sp. and observed that the application of catalyst reduced the oxygen content in bio-oils to 19 wt% from 30 wt% and heating value increased to 32.5 MJ kg^{-1} from 24.6 MJ kg^{-1}.

15.3.1.4 Direct Combustion

Direct combustion of microalgae is performed by heating the feedstock around 1000 °C in a furnace, boiler, or steam turbine in the availability of excess air to produce mainly heat energy (Fan et al. 2017). The direct combustion process requires microalgae having less than 50% moisture content (McKendry 2002). Therefore, drying and grinding of microalgae required for efficient combustion make rise in the energy demand and additional cost for the process (Goyal et al. 2008). The extra cost required for grinding and drying of microalgae is possible to reduce by effective utilization of heat produced from direct combustion (Kandiyoti et al. 2016).

15.3.2 Chemical Conversion

The chemical process of algal biofuel production includes the extraction of lipids from the microalgae and then conversion of lipids into biodiesel. The conversion of microalgae lipids into biodiesel is mostly done by either transesterification or esterification, based on the composition of the feedstock. The micro algal lipid is composed mainly of triglycerides (90 – 98%), moisture and traces of other residual materials (Naik et al. 2010). If the lipids contain a large amount of free fatty acids (FFA) or moisture, transesterification reaction is performed following the esterification, to restrict saponification (Razzak et al. 2013).

15.3.2.1 Transesterification

The production of biodiesel performing transesterification involves the reaction of microalgae lipids (triglycerides/FFA) with mono-alcohols in the availability of catalysts (Razzak et al. 2013). The transesterification reactions are equilibrium reactions that require a high alcohol/bio-oil ratio to shift the equilibrium to the right side for higher rates of reaction (Singh and Singh 2010). The transesterification reaction can be classified into three types on the basis of the catalyst applied (acid, base, or enzymes). These three types can be further subdivided into two different classes viz. homogeneous transesterification and heterogeneous transesterification. The advantages of homogenous transesterification are the low cost of catalyst and fast reaction rate; whereas the easy separation/regeneration of catalyst is the advantage of the heterogeneous one (Leung et al. 2010).

1. *Base-catalyzed transesterification.*

   Transesterification of lipids performed by using basic homogenous or heterogeneous catalyst refers to base-catalyzed transesterification. These reactions are fastest in comparison to acid and enzyme-catalyzed transesterification (Tubino et al. 2016). The transesterification where heterogeneous basic catalysts are used is eco-friendly because of the low separation cost and easy catalyst generation (del Pilar Rodriguez et al. 2016). In homogeneous basic transesterification, most commonly bases such as KOH and NaOH are used for biodiesel production on a commercial scale (Kwon et al. 2013; Schwab et al. 1987).

   Many experiments have been performed for biodiesel production by applying homogeneous base catalysts in recent times. In an experiment, the conversion of waste oil into biodiesel over homogeneous methyl alcohol and sodium hydroxide reaches 85% of FAME yield at 0.5 h (Leung and Guo 2006). Since methanol (MeOH) is the cheapest alcohol, it is widely utilized in transesterification reactions; but in some cases, ethanol and n-butanol are also applied (Andrade et al. 2011). The reaction temperature of these catalysts is usually at the boiling point of the mono-alcohol (65 °C for MeOH). In an investigation, Arzamendi et al. (2008) found that the hydroxides of lithium, cesium, and rubidium are possible to use instead of conventional KOH and NaOH; wherein the main concern is the higher cost of these catalysts.

   In some studies performed in the recent past, heterogeneous base catalysts have been incorporated in transesterification reactions for biodiesel production. The use of heterogeneous base catalyst instead of homogeneous base catalyst is of great importance due to the economically easy separation of the solid catalyst from the liquid effluent without emulsion formation and occurrence of corrosion (Hossain 2019). The heterogeneous base catalysts can be classified on the basis of Hattori's classification: single-metal oxides, multiple-metal oxides, zeolites, alkali and alkaline earth-supported metals, layered double hydroxides (LDH), and organic solid bases (Hattori 2004; Lee et al. 2009). Out of various alkaline earth metal oxides, CaO has been highly used as heterogeneous catalyst because of its easy availability and low cost. Demirbas (Demirbas 2007) mentioned that the FAME yield is dependent on the methanol-to-oil ratio along with the reaction temperature. In a transesterification reaction of sunflower oil, FAME yield reached up to 99% at a methanol/triglyceride (oil) molar ratio of 41.1:1, but have to focus on CaO catalyst as these have a smaller surface area, low reaction rate at low temperature, requirement of higher mono-alcohol/oil ratio, and chemisorption with water and carbon dioxide (Melero et al. 2009).

2. *Acid-catalyzed transesterification.*

   The transesterification reactions where acid catalysts are applied for biodiesel production are termed as acid-catalyzed transesterification and involve the same reversible steps as that of the base-catalyzed transesterification. Adopting the acidic transesterification, FAME yield of 95 – 99 % can be achieved. However, in these transesterification reactions, a higher alcohol-to-oil ratio (typically 9:1 to 166: 1) is required to move the equilibrium toward the product side (Melero et al. 2009). Generally, a higher molar ratio of alcohol to oil is used in acidic transesterification, as it is always preferable to utilize the lowest possible reaction temperature for lipids transesterification, which would reduce the selectivity to undesired products along with the reduction of material corrosion (del Pilar Rodriguez et al. 2016). Because of the higher acidity of the feed oil in acid-catalyzed reactions, there is no risk of soap formation as compared to basic transesterification reactions, which happen due to simultaneous esterification and transesterification.

Most commonly, hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) are the catalysts used in the homogeneous acid-catalyzed transesterification of microbial oil (Lee et al. 2009). Wang et al. (2006) investigated the influence of the operating conditions on the catalytic activity of H_2SO_4 in the conversion of waste cooking oil to biodiesel and found that parameters such as methanol-to-oil ratio, time, temperature, and the strength of the catalyst have a direct effect on the final FAME yield. One of the properties of acidic transesterification is that if smaller methanol/oil ratio is selected, then higher should be temperature chosen for the reaction. In another investigation, Soriano Jr et al. (2009) examined the effects of $AlCl_3$ and $ZnCl_2$ acids in the homogeneous transesterification for the production of biodiesel from vegetable oil. This study reported that the use of $AlCl_3$ has resulted in a FAME yield of 98% at a temperature of 110 °C for 18 h. The efficient catalytic performance of $AlCl_3$ is because of the higher acidity in comparison to $ZnCl_2$. The use of heterogeneous acid catalysts has higher significance as it can directly scale up if the reaction rate is possible to increase. The main advantages of the application of these catalysts include: no requirement of washing of the biodiesel, easy catalyst separation/regeneration, lower product contamination, and easy scale-up for continuous biodiesel production (Lam et al. 2010).

3. *Enzyme-catalyzed transesterification.*

   The use of enzyme as catalyst in transesterification reactions is a suitable process to mitigate the potential problems associated with basic and acidic transesterifications. The major advantages of enzyme-assisted transesterification are high-purity biodiesel formation, no saponification, low operating cost, easy separation, and recycling. So, this class of transesterification is considered as the most favorable option for biodiesel production that can replace conventional diesel (Pourzolfaghar et al. 2016). The lipases used as the enzyme is favorable for both homogeneous (free form) and heterogeneous (immobilized form) transesterification. The homogeneous enzyme transesterification possesses good mixing and holds the catalyst for a longer time, therefore showing greater catalytic activity in comparison to heterogeneous setup (Hossain 2019).

Enzyme-catalyzed transesterification reactions require alcohols such as methanol, ethanol, or butanol to function as acyl acceptors. It has been found that the availability of these alcohols reduces the workability of the lipases by denaturation. In an investigation, the lipase obtained from Pseudomonas cepacia showed only a FAME yield of 54%, mainly due to the presence of ethanol (Encinar et al. 2010), and it has been recommended to use ethanol in stages or as a co-solvent like n-hexane and tert-butanol (Rodrigues et al. 2016). But the availability of these co-solvents with the produced biodiesel enhances the separation cost, thus increasing the biodiesel price (Hossain 2019).

15.3.3 Biochemical Conversion

The biochemical conversion of microalgae includes different processes such as anaerobic digestion, fermentation, photobiological technique, etc. These processes are characterized by low conversion rate and need long reaction time. The conversion of microalgae into biofuels in biochemical processes is performed by the application of microorganisms and enzymes (Naik et al. 2010).

15.3.3.1 Anaerobic Digestion

In recent times, the production of biogas from microalgae using anaerobic digestion has received greater importance. The anaerobic digestion is favorable for microalgae containing moisture content of 80–90% and high polysaccharides with no lignin. There exist some factors which affect the conversion of microalgae into biogas. These factors include recalcitrance of cell wall, carbon-nitrogen ratio (C/N), and high protein content. Biogas production from microalgae by anaerobic digestion can be enhanced by prior effective pretreatment. High protein-containing microalgae possess low C/N ratio which is not suitable for anaerobic digestion. However, biogas production from algal biomass can be increased by co-digestion of waste paper with algal biomass (McKendry 2002; Passos et al. 2014).

15.3.3.2 Production of Bioethanol

The process of bioethanol production involves pretreatment followed by enzymatic hydrolysis and then fermentation. Microalgae do not contain lignin in the cell wall which reduces the recalcitrance in comparison to lignocellulosic biomass, thus considered as a favorable candidate for enzymatic hydrolysis. On the other hand, microalgae containing lower carbohydrate content are not suitable for bioethanol production. Different pretreatment methods such as mechanical techniques, physical techniques, thermal pretreatment techniques, chemical techniques, combined techniques, etc. have already been applied for the breakdown of cell walls and removal of lipids which favors the enzymatic hydrolysis route and bioethanol production (Onumaegbu et al. 2018). Harun et al. (2010a, b) investigated the fermentation of Chlorococcum sp. and reported that 60% more ethanol had been obtained from lipids extracted from microalgae in comparison to untreated intact microalgae.

15.3.3.3 Production of Biohydrogen

Hydrogen (H_2) is an environment-friendly energy resource which possesses very high latent heat. H_2 can be produced from microalgae by applying photobiologically, which is possible because of the metabolic and enzymatic properties of microalgae (Ghirardi et al. 2000). Eukaryotic-type microalgae are able to produce H^+ ions and oxygen during CO_2 fixation under anaerobic reaction conditions. Hydrogenase enzyme can then produce the H_2 molecules in the presence of these hydrogen ions.

The productivity of H_2 is reported to be theoretically higher in acetate fermentation compared to butyrate fermentation in different literatures. Melis and Happe (2001) investigated the production of hydrogen from green algae using a two-stage photosynthesis process and obtained a maximum hydrogen yield of 200 kg H_2 $ha^{-1}d^{-1}$. Since photosynthesis is a reversible process, the movement of hydrogen in between the product and reactant side is possible, depending upon the protons that react with hydrogen. The oxygen that is released during the photosynthesis is observed to be harmful toward hydrogenase that produces the H_2 and as such, the biomass culture should be subjected to anaerobic conditions. Furthermore, the by-products (acetate and butyrate) may cause product inhibition to the microalgae activities during hydrogen fermentation. Therefore, proper attention is required to reduce product inhibition during biohydrogen production (Amin 2009).

15.4 Potential Products from Microalgal Biomass

15.4.1 Lipids and Oil

Microalgal lipids are categorized into two major groups: polar or structural lipid and non-polar lipid. Polar lipid protects the cell from the external environment by providing a selectively permeable membrane and aids to separate and maintain the distinct cell organelles. It also plays an important role in cell communication and response to alterations in the cellular environment. Polar lipid includes glycolipids and phospholipids and is basically constituted of long-chain fatty acids that can be converted to polyunsaturated fatty acid (PUFA) which has varied applications. PUFA is also important for the nutrition of aquatic animals and humans (Gopalakrishnan and Ramamurthy 2014). Microalgae are photosynthetic organisms that can utilize solar energy, atmospheric carbon dioxide, and water to convert into molecules such as lipid, pyruvate, xylose, acetate, etc. During the process of photosynthesis, neutral or non-polar lipids are stored as triacylglycerols (TAG) that can be transformed into different types of fatty acid methyl esters (FAME) that has great deal of commercial value. Neutral lipid includes free fatty acid and acylglicerids (Vitova et al. 2015). The fatty acid compositions are similar to vegetable oil thus exhibiting higher potential for biofuel production. However, some free fatty acid components such as pigments and steroids cannot be converted into biodiesel. Hence, even if some microalgae yield high lipid content, this does not necessarily signify high biodiesel production (Mata et al. 2010). Oleaginous microbes comprise of numerous families, some of which are algae, fungi, yeast, bacteria, etc. in which the lipid portion is beyond 20% with respect to the biomass content of the cell.

Microalgae and yeast are able to produce and accommodate TAG within their cell when exposed to nutrient derivation. In microalgae, the cell growth is arrested in nitrogen lacking and carbon-rich conditions due to the inhibition in protein synthesis which activates the deaminase enzyme that acts particularly on AMP. This leads to citric acid accumulation and its subsequent conversion to acetyl CoA which is the main precursor for the synthesis of fatty acids. Thus, carbon is metabolized in nitrogen-deprived conditions for lipid synthesis. The advantage of microalgae is that it can grow very fast, economic in production with high TAG content, and the oil content may surpass 80% of the dry feedstock weight, making it a best alternative source for biodiesel production (Dong et al. 2016). Microbial lipid technology can be made more efficient if the cell mass by-products such as nutrients, elements, polysaccharides, proteins, and other trace elements are recycled and reused (Subramaniam et al. 2010). Optimizing the growth determining factors such as temperature, salinity (Qin 2005), control of nitrogen level (Weldy and Huesemann 2007), CO_2 concentration (de Morais and Costa 2007), light intensity (Weldy and Huesemann 2007) and harvesting procedure (Rodolfi et al. 2008) may increase the concentration of lipid. Lipid productivity and lipid accumulation are not corresponding to each other. Lipid productivity considers both lipid concentration as well as the overall biomass production by the microalgae cell, whereas lipid accumulation takes into consideration only the lipid concentration. Hence, lipid productivity is a better indicator of biofuel production cost.

As microalgae are photoheterotrophic in nature, supplement of organic carbon is not a prerequisite for its cultivation. Soluble carbonate or inorganic CO_2 can be used as a carbon source. Ji et al. (Ji et al. 2017) obtained the lipid productivity, carbohydrate productivity, and growth rate of Scenedesmus obliquus cultivated on flue gas to be 9.9 mg/L/d, 10.3 mg/L/d, and 1/d, respectively. Kao et al. (2014) studied the lipid productivity and growth rate of Chlorella sp. MTF-15 on three individual flue gases of a steel factory located in Taiwan. It was found that the microalgal strain was able to absorb CO_2, NO_x, and SO_x from flue gas with lipid accumulation of about 35%. Lipid production and growth rate were 0.961 g/L and 0.827/d, respectively. Therefore, heterotrophic mode of microalgae culture yields high lipid and biomass productivity which is about 26% more than phototrophic culture mode. Heterotrophic microalgae that can grow in light-devoid conditions and accumulate high lipid content include *Chlorella vulgaris, Chlorella protothecoides, Schizochytrium limacinum,* and *Crypthecodinium cohnii.*

Biofuels derived from microbial lipids have similar characteristics to fossil-based fuels. Esterification, transesterification, and anaerobic digestion are the three conventional processes to produce biofuels from microbial lipids (Garay et al. 2014). The different categories of microbial lipids within oleaginous microbes include free fatty acid (FFA), polyhydroxyalkanoates (PHA), wax ester (WE), and TAG. Out of all, PHA and TAG are more preferred for biodiesel production as lipids of minimal viscosity are needed to use in IC engines (Zhu et al. 2008). WE are used in coating, printing inks, polishes, and lubricants. Occurence of FFA brings hindrance in the conversion process due to the formation of soap. Thus, pretreatment is a major step to eliminate the presence of FFA in biofuels. Two conversion routes to obtain biofuel from lipids are: One-step and Multi-stage process. One-step process eliminates the steps of cell rupture by high energy input and lipid extraction, which owes this process an economical and environment friendly. While multi-stage process demands the requirement of two or more processes to convert lipids into biofuels either sequentially or simultaneously (Chen et al. 2012).

Botryococcus braunii is considered to be one of the best microalgal lipid producers, which has a hydrocarbon content of about 75% (w/w). It produces hydrocarbons with different structures such as monounsaturated, polyunsaturated, or branched hydrocarbons that can be converted into fuel with properties equivalent to gasoline by cracking (Rao et al. 2007). Other important species having a good amount of lipid includes Botryococcus, Scenedesmus, Chlorella, Nannochloropsis, Neochloris, Schizochytrium, Dunaliella, Nitzschia, which can produce triglycerides and are characterized by the presence of monounsaturated, di-unsaturated and polyunsaturated fatty acids (Brennan and Owende 2010). Transesterification converts these oils into biodiesel and glycerol. Glycerol can further be commercialized to produce wax, candles, humectants, and cosmetic products (Knothe 2005). Glycerol as a by-product in transesterification has dropped the cost of crude glycerol from 0.5 US-$/kg to 0.1 US- $/kg (Jeong et al. 2008). Fatty acid composition is a key factor that determines biodiesel production and quality. High quantity of saturated fatty acid exhibits good combustion properties but poor outflow property, whereas high amount of PUFA negatively influences oxidative stability but positively influences the outflow property. According to EN14214, the amount of tri-unsaturated fatty acid should be at most 1% of polyunsaturated acid (Gupta and Kumar 2012). Chlorella vulgaris ESP-31 having lipid content of 63% was converted to biodiesel via transesterification with immobilized Burkholderia lipase. Biodiesel conversion efficiency reached up to 97.3% without lipid extraction with simultaneous lipase reuse for 6 continuous cycles (Tran et al. 2012).

The calorific value of crude algal lipid is about 36 kJ g^{-1}. This is attributed to the low calorific value of phospholipids and glycolipids. But the low calorific value will not have any effect on the properties of final biodiesel as these fractions will be dissociated in the transesterification process. Fatty acid composition majorly determines the biofuel characteristics. Microalgal species having long fatty acid chain length (>C20) are more applicable to use in lubricant market whereas shorter fatty acid chain length (<C16) are more amenable to producing jet fuels. Hence, lipid-rich microalgae can be cultivated and is a potent source to valorize a number of feedstock as substrates to yield multiple products for biofuel production (Williams and Laurens 2010). Lipid from Nannochloropsis oculata was transesterified using CaO supported with Al_2O_3 obtained biodiesel yield of 97.5% at methanol to lipid molar ratio of 30: 1, reaction temperature of 50 °C, and catalyst loading of 2 wt% (Umdu et al. 2009). Chlorella pyrenoidosa with lipid oil content of 56.2% yields 95% biodiesel using hexane as co-solvent with reaction temperature and time of 90 °C and 2 hours, respectively, methanol to lipid molar ratio of 165: 1 and 0.5 M H_2SO_4 (Miao et al. 2011). Algal fats and oils also contain polyunsaturated fatty acids (PUFA) that have high commercial values, which include EPA (Eicosapentaenoic acid), GLA (-γ-Linolenic acid), DHA (Docosahexaenoic acid), and AA (Arachidonic acid). PUFA falls under the category of functional food due to the occurrence of $\omega-3$ fatty acids and $\omega-6$ fatty acids and finds huge application in the therapeutic and pharmaceutical sectors. Some of its therapeutic uses include relieving anxiety, schizophrenia, and depression (Rose and Connolly 1999). As per European Food Safety Authority (EFSA), EPA has several nutritional benefits and food value. EPA is a $\omega-3$ fatty acid that synthesizes eicosanoids that is beneficial for blood pressure regulation, blood clotting, cancer prevention, and coronal heart disease (Jude et al. 2006). Microalgal EPA producer includes Eustigmatophyceae strains of Phaeodactylum tricornutum (Belarbi et al. 2000) and Nannochloropsis sp. (Zittelli et al. 1999). It also plays a vital role in aquaculture for fish farming and nutritional benefits. Microalgae such as Pavlova lutheri, Schizochytrium, and Crypthecodinium cohnii produce DHA which is the only commercialized PUFA (Yaakob et al. 2011). DHA presents a main structural component of retina, human brain cerebral cortex, testicles, and sperm. It finds importance and applications in eye and infant brain development, nervous system, development of breast milk (Malone 2011), breast cancer (Trappmann and Hawk 2011), colon cancer (Kato et al. 2007), and fetus and dietary supplement in beverages and food. Consumption of microalgal phytoplankton enriches the oceanic fish oil with DHA such as cod liver oil and train oil.

ARA is an unsaturated $\omega-6$ fatty acid used for the repair and development of skeletal muscle tissue, applied in aquaculture, major dietary component, and exhibits anti-inflammatory effects (Baynes and Dominiczak 2005). GLA or γ-Linolenic acid is an unsaturated $\omega-6$ fatty acid present in Arthrospira (Mendes et al. 2006). Food rich in GLA is helpful against diabetes, breast cancer, obesity, high blood pressure, skin allergies, heart disease, multiple sclerosis, and premenstrual syndrome. Its therapeutic uses include anti-cancerous, anti-inflammatory effects. In the human body, GLA synthesizes prostaglandins (Fan and Chapkin 1998).

15.4.2 Biodiesel

Due to the rapid depletion of fossil fuel reserves and growing concerns about global warming, biodiesel has received great attention in recent times, as it possesses carbon dioxide-neutral properties and also renewable in nature. Biodiesel is composed of fatty acid methyl esters (FAME), which are obtained from triacylglycerols (TAGs) by applying transesterification with small chain alcohols such as methanol. During this process, glycerol is also obtained as another by-product. In recent times, biodiesel is mostly produced from the available feedstocks such as waste cooking oil, animal fat, and various oleaginous species such as soybean, rapeseed, corn, sunflower, peanut, jatropha, and oil palm (Deng et al. 2009). The cost of these vegetable oils is highly expensive which in turn increases the price of the derived biodiesel and makes it less competitive with fossil fuel at today's energy prices. Furthermore, the limited supply of these raw materials would highly obstruct the further expansion of biodiesel production to a large extent. In order to overcome these feedstock problems, suitable energy crops must be explored, separately and distinctly from food.

Microalgae are an abundantly available group of photosynthetic eukaryotes with a simple cellular structure, ranging from unicellular to multicellular forms. They can be found in the places where water and sunlight co-occur, such as soils, ice, lakes, rivers, hotsprings and ocean, etc. (Chisti 2007). Microalgae possess the ability to absorb carbon dioxide and convert energy of sunlight into chemical energy. In recent times, microalgae have gained attention as an alternative non-food feedstock for biodiesel due to their high oil content and its rapid growth (Deng et al. 2009).

15.4.3 Drop-in Fuels

Drop-in fuels are alternative fuels that can be used to substitute conventional petroleum-based fuels without any significant modification in engines and fuel systems. According to IEA, "Drop-in biofuels are liquid bio-hydrocarbons that are functionally equivalent to petroleum fuels and are fully compatible with existing petroleum infrastructure."

- Microalgae are potential renewable energy source to produce drop-in biofuels as they offer many advantages such as high per-acre productivity, rapid growth rate and they can be cultivated in different types of water such as fresh, brackish, saline, and wastewater. Also, since microalgae are not a common food source, algal cultivation for fuel does not pose food security issues (Jegathese et al. 2014).

Microalgae contain high oil content, which exceeds up to 80% by weight of its dry biomass compared to other terrestrial crops due to which they are considered an ideal feedstock for producing biodiesel (Chisti 2007). Microalgae are capable of producing algal oil 58,700 L/hac which can produce 121,104 L/hac biodiesels (Khan and Kim 2018). Biodiesel production from microalgae includes several upstream and downstream operations, including microalgae cultivation, biomass harvesting, lipid extraction, and transesterification of the lipids fraction with short-chain alcohols while mediated by acid, base or enzyme catalysis. Among them, the extraction of lipids is the most challenging step. Therefore, the development of efficient lipid extraction technique is essential for industrial-scale production of microalgae-based biodiesel. However, there are some standards such as ASTM Biodiesel Standard D 6751 (United States) or Standard EN 14214 (European Union), which are required to comply with the algal-based biodiesel on the physical and chemical properties for its acceptance as a substitute to fossil fuels.

- Microalgae biomass has high content of carbohydrates which can be used to produce bioethanol through fermentation. Microalgae consist of mainly starch and cellulose and the lack of lignin makes it easier to break them down into monosaccharides to produce bioethanol. Some carbohydrates-rich microalgae like *Chlamydomonas reinhardtii* and *Chlorella vulgaris* are potential feedstock for producing bioethanol. Microalga *Chlorella vulgaris*, in particular, has been recognized as a potential feedstock for bioethanol production due to its capacity to accumulate high levels of starch (up to 37% dry weight) (Dragone et al. 2011).

Bioethanol production from microalgae biomass has three main steps:

- Microalgae biomass can be pretreated with acid, alkali.
- Fermentation of pretreated microalgae biomass to produce bioethanol.
- Purification of produced bioethanol.

Pretreatment of microalgae biomass before fermentation is a crucial step to remove undesired elements or impurities, thus, increasing bioethanol yield which subsequently results in reducing cost and energy requirement of bioethanol production (Phwan et al. 2019).

- Microalgae rich in carbohydrates can be utilized as a carbon feedstock to produce gaseous biofuels, such as biomethane and biohydrogen, through either process of aerobic fermentation or anaerobic fermentation. Anaerobic fermentation of wastes such as organic waste, wastewater to produce methane have been well investigated. Thus, microalgae biomass serves as a potential alternative for methane fermentation. Biohydrogen is a developing new energy source because of its reduced environmental impact and increased energy efficiency. Anaerobic fermentation using microalgae-based carbohydrates is a sustainable and favorable pathway to produce biohydrogen economically (Chen et al. 2013).

Microalgae has potential prospects as a sustainable feedstock to produce liquid biofuels such as biodiesel and bioethanol and gaseous fuels such as biomethane/

biohydrogen. However, several technological improvements are required to produce microalgae-based biofuels commercially on a large scale.

15.4.4 Bio-Oil and Bio-Char

Bio-oil and bio-char are the by-products that can be obtained from the pyrolysis of microalgae. The yield of these products depends on the temperature, residence time, and type of feedstock. By changing the mentioned pyrolytic parameters, the yield of bio-oil and bio-char can be varied based on the requirements. Bio-oil and bio-char are essential for the application of heat generation by combustion process. Furthermore, bio-char can be used as activated carbon, fertilizers, soil compost, and efficient catalyst for biofuel production. Among the different thermochemical processes, pyrolysis has gained more attention in recent times due to its simplicity and speed. Pyrolysis of microalgae can be classified based on the conditions into slow, fast, flash, microwave-assisted, and hydrolytic pyrolysis. The composition and yield of bio-char as well as bio-oil from microalgae are dependent on the temperature and other conditions used in pyrolysis. Furthermore, the concentration of solid and liquid products can be altered by choosing the optimized pyrolysis process and the microalgae species (Sekar et al. 2021).

A few investigations have been performed on the conversion of algae feedstock to fuel by pyrolysis in recent times. Maddi et al. (2011) studied the compositions of products (bio-oil, gas, and bio-char) obtained from pyrolysis of algae and lignocellulosic biomass and found that the percentages of bio-oil yield from these two feedstocks were similar but the bio-oil and the bio-bio-char from algae had more nitrogen content in comparison to lignocellulosic. In another investigation, Demirbaş (2006) studied the properties of extracted fuels from mosses and different types of algae (Polytrichum commune, Dicranum scoparium, Thuidium tamarascinum, Sphagnum palustre, Drepanocladus revolvens, Cladophora fracta, and Chlorella protothecoides). The study showed that bio-oils yield from algae and moss were about 34.3–55.3% at pyrolysis temperature of 775 °C with a heating rate of 10 K s^{-1}. On the other hand, the bio-oil from algae possessed higher heating value (32.5–39.7 MJ kg^{-1}) in comparison to mosses (21.5–24.8 MJ kg^{-1}).

Bio-char is a product from pyrolysis and has carbon content of over 50%. It can be applied not only as a fuel but also as an underground carbon sink. Due to its molecular structure, it is quite stable both chemically and biologically, and it can remain stable in soil for 100 or even 1000 years. Bio-char has a highly porous structure, and the addition of bio-char to soil could improve water retention and increase the surface area of the soil, increasing the efficiency of nutrient use (Bird et al. 2011).

The reported literatures show that the increase in pyrolysis temperature results in higher amount of bio-oil and lower amount of bio-char production. At high temperatures, carbon dioxide (CO_2), carbon monoxide (CO), water, and hydrogen (H_2) are released in higher concentration, and the hot combustion products (CO_2 and H_2) are further converted to a useful synthetic gas (a mixture of carbon monoxide and hydrogen), while the rest of the biomass material is converted into fused aromatic ring bio-char (Sekar et al. 2021).

15.4.5 Heat and Power

Microalgae-based biofuels can be utilized for producing power and is likely to replace petroleum products for internal combustion engines (Ullah et al. 2014). Co-firing of microalgae with coal can generate electricity that will eventually decrease the non-renewable energy consumption and mitigate greenhouse gases (GHG) (Giostri et al. 2016). Biofuels from microalgae, i.e., biodiesel and bioethanol can be used as a substitute for petrol and diesel as transportation fuels (Singh and Olsen 2011). Chemical properties of biodiesel play an important role in terms of its acceptability as a fuel, which is further based on fatty acid methyl ester (FAME) profile. The FAME content of microalgae is dependent on nutrition, light intensity, and temperature (Qin 2005; Weldy and Huesemann 2007; de Morais and Costa 2007). Higher oleic acid content enhances the fuel properties such as oxidation stability, lubricity, viscosity, ignition quality, cold filter plugging point, and combustion heat (Lucena et al. 2008). Blending petroleum products with biodiesel or bioethanol is highly recommended as they emit clean gases during combustion. Heterotrophic nature of microalgae allows it to adsorb CO_2 emitted by industries or power plants for self-cultivation and later its subsequent co-firing with coal can generate clean energy. This biological sequestration is carbon neutral in nature (Matsumoto et al. 1997).

Combustion or open burning is the most direct way to use microalgae as fuels. Gross calorific value or higher heating value (HHV) is a key parameter that indicates its industrial application. Typically, HHV of coal ranges from 25 to 35 MJ kg^{-1} (Du et al. 2010) while that of microalgae is between 14 and 24 MJ kg^{-1} (Xu et al. 2011). This is attributed to inadequate carbon content in microalgae, i.e., between 37 and 53 wt%. Hence they are inappropriate to be burned directly in industries due to low energy density. Instead, co-firing of microalgae with coal for generating power is an optimum cost-effective approach to reduce greenhouse gas emissions (Kadam 2002). Co-firing coal with microalgae cultivated in open pond system is highly promising to produce energy. The problem associated with the low calorific value of microalgae can be addressed by thermal upgradation, i.e., torrefaction. Microalgae is degraded at a temperature range of 200–300 °C, 1 atm pressure at inert atmosphere. This results in partial carbonization due to thermal decomposition of protein and carbohydrates and dehydration of microalgae. Temperature and duration of torrefaction are crucial parameters as they affect the pretreatment performance (Chen et al. 2014). Torrefied microalgae will thus have more HHV than its parent material due to an increase in carbon content. Wu et al. (2012) torrefied *Spirulina platensis* and observed that the fixed carbon content, HHV, ash content, and Hardgrove grindability index (HGI) increased with respect to time and temperature. At 300 °C and 30 minutes' time duration, the calorific value raised from 20.46 to 25.92 MJ kg^{-1} which can be used to partially replace coal in industry.

Thermochemical or hydrothermal liquefaction involves the use of hot compressed or sub-critical water to transform microalgae primarily into liquid fuels at 300–350 °C, high pressure of 5–20 MPa for 5–60 min. High pressure is required to keep the water in liquid state (Barreiro et al. 2013). Rapid heat transfer is allowed owing to the small size of microalgae (Lam and Lee 2012). In hot compressed water, the lipid, carbohydrate, and protein molecules of microalgae will undergo depolymerization and repolymerization, converting the biomass into solid, bio-oil, and gaseous products. Brown et al. (2010) converted *Nannochloropsis sp.* into crude bio-oil and gaseous by-products via thermochemical liquefaction. HHV and bio-oil yield were 30–50 MJ kg^{-1} and 30–65 wt% which was comparable to petroleum oil (43 MJ kg^{-1}), indicating that microalgae pretreated by liquefaction can be utilized as fuel to be burned. Also, the elemental oxygen content and sulfur content in bio-oil decrease upon liquefaction (Shuping et al. 2010). Aqueous phase of the bio-oil is rich in nutrients which include nitrogen, phosphorus, magnesium, calcium, sodium, and potassium that can be again recycled for microalgae cultivation while gaseous by-products from liquefaction include CO_2, CH_4, N_2, H_2, C_2H_4, C_2H_6, etc., out of which the concentration of CO_2 is maximum while that of C_2H_6 and C_2H_4 is minimum (Brown et al. 2010). Thermochemical liquefaction of Dunaliella tertiolecta and B. Braunii achieved high calorific values of 34.9 MJ kg^{-1} and 45.9 MJ kg^{-1} and positive energy balance (output by input ratio) of 2.94: 1 and 6.67: 1, respectively (Shuping et al. 2010).

Pyrolysis is a thermochemical conversion route in which microalgae is heated in the absence of air at a temperature between 400 and 600 °C. Bio-oil produced from microalgae consists of linear hydrocarbon and nitrogeneous species owing to pyrolysis of lipids and proteins (Harman-Ware et al. 2013). Also, higher concentrations of fatty acid alkyl ester, aliphatic compounds, nitriles, and alcohol are present resulting in improved HHV and decreased tar formation. Jena et al. (2011) used Spirulina platensis as feedstock for the production of bio-oil via slow pyrolysis and found the bio-oil yield ranged 23–29%, bio-char yield of 28–40%, and HHV of bio-oil to be 24 and 34 MJ kg^{-1}. Grierson et al. (2009) pyrolyzed Tetraselmis chui as feedstock to study the properties of bio-oil and found that the primary components present are alkenes, alkanes, fatty acids, aldehydes, amides, pyrrolidines, terpenes, phenol and phytol with HHV of the bio-char around 14 and 26 MJ kg^{-1}. Calorific value of the condensable gases is low, i.e., between 1.2 and 4.8 MJ kg^{-1} which limits its usage for industrial applications. Fast pyrolysis occurs at high heating rate (H.R) along with short residence duration of the vapors to obtain high calorific value of about 24–41 MJ kg^{-1} and high yield of around 18–72 weight% of bio-oil. Fast pyrolysis of microalgae yields bio-oil of lower oxygen content and higher calorific value as compared to lignocellulosic biomass, which enhances its stability without polymerization for a longer time (Belotti et al. 2014). It was found that Chlorella protothecoides yields 57.9% bio-oil of lower viscosity (0.02 Pa s), lower density (0.92 kg l^{-1}), and high calorific value (41 $MJkg^{-1}$) that is 3.4 times higher than other plant biomass (Miao and Wu 2004). Nevertheless, the oxygen content in bio-oil obtained from microalgae is high to commercialize which imparts problem in terms of polymerization, stability, energy density, and condensation reactions. To meet the above problems, the use of catalyst is favorable to upgrade the bio-oil quality. Catalysts such as H-ZSM-5, Ni-ZSM-5, Cu-ZSM-5, Fe-ZSM-5, Na_2CO_3 are commonly used for microalgae pyrolysis (Babich et al. 2011). Highest performance was obtained from HZSM-5 which enhanced the hydrocarbon fraction of the organic phase of bio-oil to 43 wt% with the least coking (1.3 wt%) (Campanella and Harold 2012). The use of catalyst aids the bio-oil quality by imparting higher aromatics, higher calorific value, and lower acidity. For industrial applications of bio-oil for fuel-based applications, microwave-assisted pyrolysis is more favorable as bio-oil yield and calorific value are 18–59 wt% and 30–42 MJ kg^{-1} (Du et al. 2011).

Gasification of microalgae produces syngas and other combustible gases that find huge industrial applications. *Nannochloropsis sp.* was gasified at 850 °C in a fixed-bed reactor producing bio-oil, char, and gas yield of 13.74 wt%, 58.18 wt%, and 28.08 wt% with a calorific value of 34.1 MJ kg^{-1}, 17.5 MJ kg^{-1}, and 32.9 MJ kg^{-1}, respectively (Khoo et al. 2013). *C. Vulgaris* was gasified with nitrogen cycling and obtained fuel rich in methane in which nitrogen components inherent from microalgae was converted into rich fertilizer. Co-gasification of *Tetraselmis sp.* with low-rank coal in a fluidized bed reactor at 830–880 °C increased the CO content while decreasing the CO_2 and H_2 content (Alghurabie et al. 2013). While in conventional gasification high energy input is needed to dry the wet microalgae, supercritical water gasification (SCWG) directly converts the microalgae into combustible gases by splitting C-C bonds to produce H_2 and CH_4 (Yeh et al. 2012). Integrated gasification and combined cycle (IGCC) is focused due to its high power generation efficiency. In IGCC with conventional gasification, a fluidized bed is used due to its high conversion rate, high gasification efficiency, and avoids reactor plugging. It produces clean syngas which is utilized as a raw material or fuel in the combustor to produce high pressure and temperature gas. This hot gas is used to superheat the exhausted syngas and rotate the turbine to produce power. Also, the heat of high-temperature flue gas is recovered in heat recovery steam generator to produce steam, thereby rotating the steam turbine. Hence, the application of microalgae for power generation will enhance its utilization as a very potential biomass resource (Aziz et al. 2015).

15.4.6 Carbohydrates

Eukaryotic microalgae and cyanobacteria are photosynthetic microorganisms that convert solar energy into chemical energy through cellular respiration by a number of complex reactions. Photosynthetic reactions are of two types: light and dark reactions. During light reaction, sunlight is captured and absorbed by photosynthetic antennae to break down water into electrons, protons, and oxygen. Electrons and protons are utilized to generate ATP and NADPH, which act as energy carriers to support the metabolism of the organism. In dark reaction, energy from NADPH and

ATP is derived to reduce carbon dioxide to carbohydrates via the Calvin cycle (Masojidek et al. 2004). Calvin cycle initiates with the assimilation of carbon dioxide that is catalyzed by Ribulose-1,5-bisphosphate carboxylase oxygenase. CO_2 is used for the carboxylation of five-carbon compound (Ribulose-1,5-bisphosphate) into three-carbon compound (3-phosphoglycerate), one of which is utilized as a substrate for carbohydrate formation. Carbohydrates are produced inside the chloroplast and cytosol which becomes either the primary component of cell wall or accumulated in plastids. Carbohydrates in microalgae act as storage compounds, i.e., they provide the energy required for metabolism and acts as structural components in cell wall. Carbohydrate encompasses sugars (monosaccharides), its polymers (disaccharide, oligosaccharide, polysaccharide). Red algae synthesize floridean starch; cyanobacteria synthesize glycogen; green algae synthesize starch (amylopectin-like polysaccharide) (Viola et al. 2001). The carbohydrate content depends on the type of microalgae species used, environmental conditions, cultivation techniques, light intensity, and temperature. Other than carbon dioxide and sunlight, phosphorus, nitrogen, potassium, and other vital nutrients are also required for its growth. Nutrient limitation strategy is a technique of enhancing the yield of carbohydrates by limiting the availability of a particular nutrient from the cultivation medium that particularly leads to lipid or carbohydrate accumulation (Dragone et al. 2011). Limitation of macroelements such as nitrogen leads to carbohydrate accumulation in *Chlorella vulgaris* from 38 to 41% and 55 to 65% in *Spirulina platensis* (Branyikova et al. 2011). With the decrease in carbon dioxide concentration, the carbohydrate content in the algal biomass increases. This is attributed to carbon dioxide concentrating mechanisms (CCM). At low carbon dioxide conditions, the microalgae are enabled to obtain and concentrate inorganic carbon from the external environment (Thyssen et al. 2001). Izumo et al. (2007) observed that with the depletion in carbon dioxide concentration from 3–0.04%, 2.5 times rise in carbohydrate concentration was found. Hence, it is foremost to choose microalgae that yield substantial carbohydrate productivity and sugar composition to produce platform chemicals or biofuel.

Several biomass conversion technologies are employed for biofuel production from the microalgal carbohydrate which include anaerobic fermentation, anaerobic digestion, and production of biohydrogen. Carbohydrates from microalgae are apt for bioethanol production, but to commercialize microalgae-based ethanol, economic cell harvesting technologies should be developed. The large amount of by-product carbon dioxide that is produced during bioethanol fermentation can be recovered and coupled to grow microalgae for carbohydrate storage. Thus, efficient CO_2 mitigation and its re-utilization can be achieved and the resulting carbohydrate enriched microalgae can be re-used as feedstock for bioethanol production. Bioethanol fermentation via enzymatic hydrolysis is the most promising method among other hydrolysis technologies (Choi et al. 2010). This is attributed to the accumulation of starch that leads to its direct conversion into bioethanol both at dark and anaerobic conditions. The carbohydrate content of microalgal biomass can be hydrolyzed into fermentable sugars for bioethanol production via chemical pretreatment methods, using acids and alkali. Nguyen et al. (2009) found that pretreatment of microalgae with 3% sulphuric acid for 30 minutes at 110 °C released 28.5 g/L glucose corresponding to a glucose yield of 95%. Harun et al. (2010a, b) used 0.75% (w/v) of NaOH for pretreatment at 120 °C for 30 minutes and obtained a highest bioethanol yield of 0.26 g bioethanol/g algae. But it has been found that the absence of lignin in microalgae eases the disruption and the degree of pretreatment for bioethanol production decreases. Bioethanol production by microalgae using anaerobic fermentation consumes less energy and is simpler. *Chlamydomonas reinhardtii* yields the highest bioethanol production of 30–40%. Biobutanol is another potent alternative fuel produced from carbohydrate-based microalgae. Its properties such as higher energy content, water solubility, less corrosive, low volatility, and better mixing properties with gasoline enhance its utilization in the present-day storage and distribution condition and infrastructure of gasoline-based transportation fuels. Advanced biofuel includes biobutanol and other significantly higher alcohols that are presumed to replace bioethanol (Zhang et al. 2011). Butanol is synthesized from conventional carbon sources as raw material. Significant by-products during biobutanol production include organic acids, acetone, and bioethanol. Theoretical highest yield of biobutanol is 1 mol/mol of glucose with controlled fermentation and only hydrogen and carbon dioxide as the by-products. Efremenko et al. (2012) studied the production of biofuels by acetone-butanol-ethanol fermentation by utilizing the pretreated biomass of different microalgae and cyanobacteria catalyzed by Clostridium acetobutylicum cells immobilized in PVA cryogel. Maximum biobutanol yield was achieved using thermolysis pretreated Arthrospira platensis and *Nannochloropsis sp.* Along with the conversion of microalgal starch components to biobutanol, the cellulose section can also be converted to the same post-appropriate hydrolysis. Wheat bran, wheat straw can be converted into biobutanol by anaerobic fermentation using *Clostridium spp* (Qureshi et al. 2008). Carbohydrate-based microalgae are used to produce gaseous fuels, such as biohydrogen, methane. Biohydrogen is a clean, highly efficient, and promising new energy carrier that can be utilized in fuel cells to generate electricity. Microorganism generates molecular hydrogen under specific conditions either by fermentation or photobiologically. Thermo-alkaline pretreatment of lipid extracted microalgal biomass residues (LMBR) at 100 °C produced the highest biohydrogen yield of 45.54 mL/g-VS (Yang et al. 2010). This is three times higher than the untreated LMBR. Starch containing green alga C. Reinhardtii and Dunaliella tertiolecta produced biohydrogen yield of 52% and 61%, respectively (Kawaguchi et al. 2001). The organic waste or wastewater can be converted into methane by anaerobic digestion in fermentation plants such as bioethanol production units. This yields maximum methane content (60%) and low sulfur content favorable to use in power generators. The cell wall of some microalgal species are difficult to break down, hence it requires disruption while certain microalgae species are devoid of cellulosic materials that leads to enhanced hydrolysis rates and thereby higher conversion efficiency. Anaerobic digestion becomes more favorable in high carbohydrate content, e.g., glucose resulting in high biogas production such as Chlamydomonas reinhrdtii. Co-digestion of microalgal residues with cellulosic biomass (e.g., Spirulina and waste paper) followed by physical pretreatment is helpful to enhance methane production by compensating for the low C/N ratio of

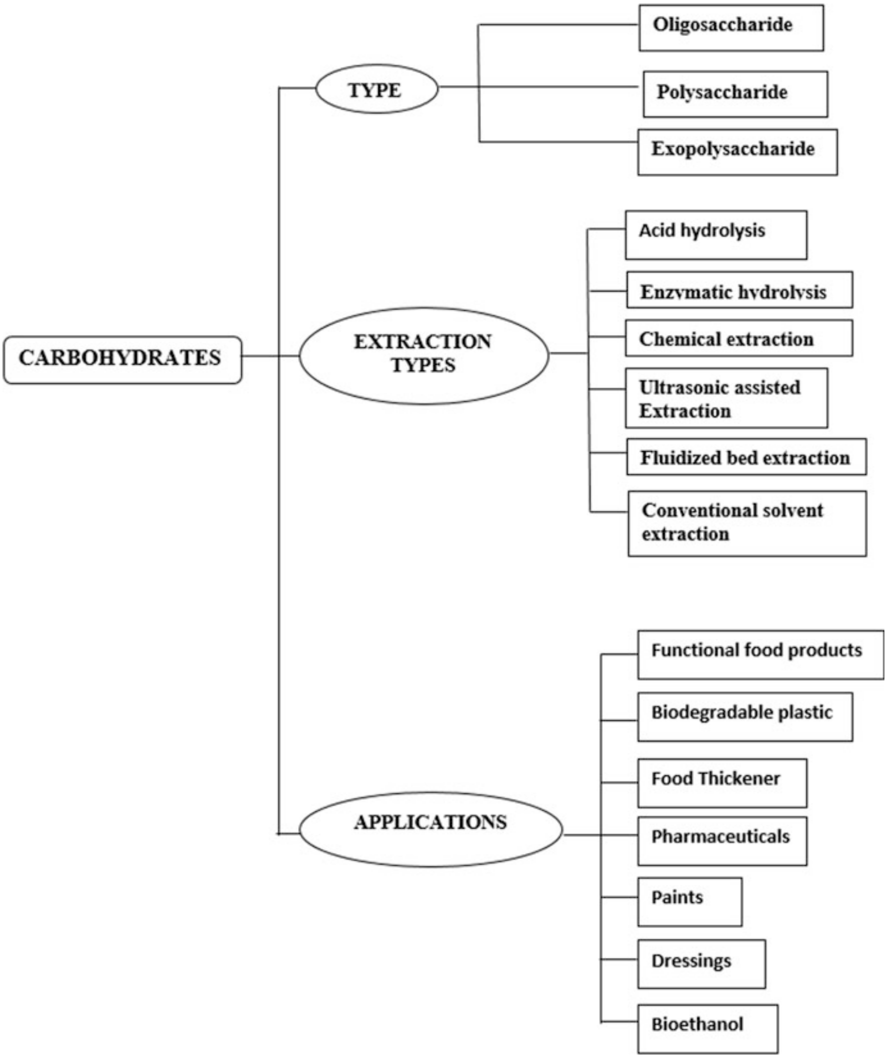

Fig. 15.2 Extraction and application of microalgae carbohydrates

original microalgae biomass (Yen and Brune 2007). The extraction process of microalgae carbohydrates and their applications are shown in Fig. 15.2.

15.4.7 Proteins

Various microalgal species have high protein content and are often considered to be an unconventional and alternate sources of protein. The pattern of amino acids of nearly all algal species is on par with other conventional protein sources (Fleurence 1999). The composition of amino acids differs with respect to species, growth condition, and growth phase. Algae are more advantageous to use than other high-protein crops in terms of their protein content and productivity. The protein content and productivity of microalgae is about 55% and 4–15 tons/Ha/year while that of conventional crops such as wheat and oats is 15–19% and 1.1 tons/Ha/year, respectively. Also, the use of microalgae for protein extraction eliminates the issue related to excessive freshwater requirement for agriculture and is also beneficial to health due to the presence of several nutritional compounds such as phlorotannins, carotenes, phycobiliproteins, etc. (van Krimpen et al. 2013). Protein production has multiple routes to yield protein isolates, purified protein, protein concentrates, defatted high-protein meals, and defatted low-protein meals. Recovery of microalgal proteins is done post biomass production and recovery from a liquid medium which is followed by microalgae cell disruption thereby releasing its intracellular components. To produce purified protein, four complex steps are required, i.e., cell lysis, soluble protein separation, isolation of protein fraction, and protein purification. During cell lysis or disruption, the intracellular contents are released to solvent or buffer. During this process, cell wall can provide a barrier to disruption efficiency. Spiden et al. (2013) found that Nannochloropsis sp. and Chlorella sp. are more difficult to rupture than T. suecica. Studies on mechanical (Lee et al. 2012), chemical (Safi et al. 2014) and enzymatic (Keris-Sen and Gurol 2017) cell disruption techniques were evaluated and observed to find an efficient disruption technique in terms of scalability and specific energy requirement. Among mechanical techniques, bead mills and high- and low-pressure homogenizers are more likely for easy cell disruption (Chisti and Moo-Young 1986). Nonmechanical disruption uses enzymes or chemicals which are less hostile than mechanical disruption and enhances the penetration of cell wall. Although enzymes operate in mild conditions with lower energy requirements, they are too expensive to commercialize. Also, enzymes may lead to selective cell disruption and release certain undesired compounds that may interfere with the protein extraction (Demuez et al. 2015). Chemical disruption involves the use of solvents, detergents, acids, alkalis, chelating agents, and antibiotics. Out of these, sodium hydroxide is often used owing to its high production, mild temperature, and greater permeability. Protein separation from the cellular residue is based on the detachment of protein-enriched aqueous phase from solid phase and its dispersion in water. Centrifugation, filtration, and ultrafiltration are commonly used separation methods. Protein isolation involves the separation of protein which exhibits similar physical characteristics, such as size, density, dispersibility using gradient centrifugation technique (Gerde et al. 2013). Purified protein is mainly needed for pharmaceutical or health-related services which require protein of high grade. Chromatography is the principal technique used in protein purification which includes ion-exchange affinity, molecular exclusion, and hydrophobic interaction. In ion-exchange chromatography, protein purification is done based on net electric charge. Molecular exclusion chromatography involves protein purification based on its size and shape using polyvinyl chloride, polyacrylamide, agarose, and silica (Walker 2010). *Arthrospira platensis* or Spirulina is a filamentous, unicellular microalga that is used as a highly nutritious food supplement, such as biscuits, pasta, noodles, drinks as it consists of all the essential amino acids. It is labeled as "super food" by the World Health Organization. It has the highest recorded protein content (about 63%) and helps in improving blood quality, resistant to viral infections, diabetes, allergic rhinitis, protects against viral infections, kidney, liver and is also capable to inhibit carcinogenesis. It is known to contain 670% more protein than bean curd, 180% more calcium than milk, 5100% more iron than spinach, and 3100% more β-carotene than carrots (Capelli and Cysewski 2010). *Chlorella vulgaris* has a protein content of 51–58% dry weight, exhibiting higher antioxidant activity and has potential applications in food industries and pharmaceuticals due to the occurrence of significant nutrients such as β-carotene, minerals (iron, magnesium, calcium, sodium, potassium), vitamins (ascorbic acid, B-complex), and chlorophyll (Becker 2007). Microalgae and seaweeds contain all the essential amino acids and high protein content and hence serve as a valuable protein intake for the athletes and players, particularly vegetarian athlete for building and repair of tissue (Koyande et al. 2019). It also plays an important role in animal husbandry, aquaculture and a rich source of dietary supplements. Hall et al. (2012) found that using 4% *Ascophyllum nodosum* into bread decreased the energy intake in hefty males in a test meal. *Ascophyllum nodosum* enriched bread may substitute normal bread as a part of breakfast meal to decrease the habitual energy intake thereby improving health conditions. The two algal proteins that have been used intensely for industrial uses are phycobiliproteins and lectins. Certain lectins act as mediators between nitrogen-fixing bacteria and leguminous plants. It also plays a role in antiviral therapy, gene therapy, and enzyme replacement therapy. Treatment with anti-lectin antibodies can reduce the growth of tumor cells in agarose and thereby retards lung colonization in vivo. Interaction of lectin with carbohydrate exhibits high specificity. This helps in cancer treatment because lectins residing on the surface of tumor cells can bind with exogenous carbohydrate molecules and internalizes by endocytosis. Other bioactivities exhibited by lectins include anti-viral, anti-adhesion, antibacterial, anti-inflammatory, anti-nociceptive, cytotoxic, and mitogenic. Bioactivities exhibited by phycobiliproteins are antitumor, liver-protecting, atherosclerosis treatment, neuroprotective, lipase-inhibition activity, serum-lipid-reducing, antioxidant, hypocholesterolemic, anti-inflammatory (Harnedy and FitzGerald 2011). Commercial applications include cosmetic such as lipstick, lip balm, eyeliner and food items such as soft drinks, chewing gum, confectionery, cakes, and dairy products. Tasco, a seaweed meal extracted from Ascophyllum nodosum, is used in animal feed that possesses the benefits of improved immune system, reduced pathogenic microbes in final meat product, enhanced quality and productivity, and resistance to stressors (Bleakley and Hayes 2017). Supplementing algal feed is highly favorable due to digestion of food containing high fiber content and had highest extraction efficiency of the algal proteins. Spirulina consumption by ruminants absorbs the proteins and nutrients in abomasum and increases digestion. Supplementing 200 g/day Spirulina along with cattle feed increases the daily milk production by 21% and body weight by 8.5–11%. Spirulina intake has increased the average daily gains and quality of meat (high GLA) in lambs and sheep (Capelli and Cysewski 2010). Abou-Zeid et al. (2015) and Al-Batshan et al. (2001) observed and evaluated the productive performance of broiler chicks fed with diets containing *Chlorella vulgaris* and *Spirulina platensis*algae. It was found that 2 g spirulina/kg diet enhanced the weight, increased viability, increased macrophage phagocytic activity, notable increase in white blood cell count, and improved immune system. *Ulva lactuca, Sarcodiotheca gaudichaudii,* and *Chondrus crispus* helped to decrease the cholesterol, serum lipid, uric acid concentration thereby improving the egg quality, chicken gut health, and productivity. Ross and Dominy (1990) observed that by addition of less than 20% dehydrated Spirulina in broiler and chicken diet content enhanced the growth, egg production, hatchability, fertility, eggshell quality, and feed efficiency was obtained. Dietary content of 1% Spirulina fed to Japanese quail intensified the yolk color due to β-carotene (Anderson et al. 1991). Spirulina further improves and valorizes eggs by replacing the saturated fatty acid content and cholesterol by omega-3 polyunsaturated fatty acids. Another prominent poultry animal includes pigs. Incorporation of *Laminaria digitata*, i.e., a brown seaweed and Ascophyllum nodosum, helped to raise the iodine concentration in pig's fresh muscle by 45%, increase its body weight by 10% and also increased the concentration of beneficial bacteria in the gut (Dierick et al. 2009). Addition of Spirulina increased sperm motility, better fertility, and storage viability. Microalgae such as red seawood is a potent protein-based food additive. Incorporating 1% and 10% of *Gracilaria chilensis* in the diet of Salmo salar increases the antiviral activity against salmon anemia virus. Similarly, adding 10% *Gracilaria chilensis* in the Salmo solar diet increased its specific growth rate by 1.51% (Lozano et al. 2016). Salmo solar was observed to have improvement in hepatitic function and the overall lipid content upon addition of 5% and 15% of Palmaria palmate (Wan et al. 2016). Bioactive peptides provide the basic nutritional value and health benefits due to its unique amino acid sequence (Hayes 2013). Its length extends from 2 to 30 amino acids and is predominantly found in egg, fish, soybean, wheat, algae, broccoli, and garlic (Miguel and Aleixandre 2006). Bioactive peptides extracted from algae exhibit a multitude of benefits, such as anti-oxidative, appetite suppression, anti-hypertensive, anti-microbial, hypocholesterolemic, antithrombotic, and opioid (Korhonen and Pihlanto 2006). Microalgae species from which antioxidant peptides are isolated include *Chlorella ellipsoidea, Chlorella Vulgaris,* and *Navicula incerta*. Anti-cancer peptide is displayed by polypeptide Y2 obtained from A. platensis and *Chlorella pyrenoidosa* antitumor polypeptide obtained from *Chlorella pyrenoidosa* (Ko et al. 2012a, b). Anti-atherosclerosis and Anti-inflammatory exhibited by peptides from A. Maxima and C. Pyrenoidosa isolated from Chlorella 11 (Shih et al. 2013). Other bioactivities exhibited by algal-based peptides are protection from ultraviolet (UV) radiation, anti-coagulant, hepatoprotective, anti-osteoporosis (Athukorala et al. 2007), and can also prevent gastrointestinal digestion with the aid of enzymes such as pepsin, trypsin, and chymotrypsin to achieve a physiological effect at the site of action (Cian et al. 2015). Angiotensin-I-converting enzyme (ACE-I) inhibitory peptides can be isolated from microalgae and seaweed sources that exhibit anti-hypertensive activities. Several dipeptides were isolated using hot water extraction from Undaria pinnatifida that reduced blood pressure in spontaneously hypertensive rats (SHRs) (Suetsuna and Nakano 2000). From the peptic digest of Undaria pinnatifida, four tetrapeptides were isolated that exhibited anti-hypertensive and ACE-I inhibitory bioactivity. Several peptides were identified from A. Platensis and C. vulgaris that displayed anti-hypertensive and ACI-I inhibitory activity against SHRs (Suetsuna and Chen 2001). ACE-I inhibitory peptides have also been isolated from *P. Palmate, P. columbina, H. fusiformis, Bangia fusco-purpurea,* and *P. Yezoensis* (Cian et al. 2015). For the generation of ACE-I inhibitory hydrolysates, N.oculata was digested with different proteases namely trypsin, pepsin, Neutrase, Alcalase, papain, and α-chymotrypsin, out of which the highest ACE-I inhibitory bioactivity was exhibited by the two peptide sequence: Leu-Glu-Gln and Gly-Met-Asn-Asn-Leu-Thr-Pro of pepsin hydrolysates (Samarakoon et al. 2013). Also, Val-Glu-Gly-Tyr peptide sequence exhibited maximum in vivo anti-hypertensive and in vitro ACE-I inhibitor, obtained by hydrolysis of C. Ellipsoidea using proteases Kojizyme, Protamax, Alcalase, papain, Neutrase, pepsin, trypsin, Flavourzyme, and chymotrypsin (Ko et al. 2012a, b).

15.4.8 Pigments

Pigments from microalgae are used widely for multiple commercial applications which includes pharmaceutical, food, aquaculture, cosmetic, and nutraceutical industry (Begum et al. 2016). There are three primary groups of pigments found in microalgae, namely: phycobilins (responsible for imparting blue or red color), carotenoids (among which xanthophylls impart yellow color and carotenes impart orange color), and chlorophylls (responsible for imparting green color). Different microalgae exhibit different colors that are favorable and beneficial over other commercial-based synthetic dyes due to their non-toxicity and for being non-carcinogenic in nature, which includes β-carotene (yellow pigment from Dunaliella), phycocyanin (blue pigment from Spirulina), and astaxanthin (yellow to red pigment from Haematococcus) (Dufoss et al. 2005). Pigment protects the microalgae from damage due to excess illumination and is responsible for carbon dioxide fixation and light harvest. The potential applications are centered on utilizing the complex biochemical pathways of the photosynthetic machinery of microalgae to produce a hub of by-products. Biotechnology provides modern cultivation techniques suitable for microalgae growth and cultivation (Chaumont 1993). Chlorophyll is green in color and is soluble in polar solvents, such as water. It is of three types: a, b, and c. Phorbine is the hydrocarbon skeleton of chlorophyll. It is formed by attaching one isocyclic ring to one pyrrole ring. Each pyrrole ring has one nitrogen atom and four carbon atoms (Humphrey 2004). A central hole contains nitrogen atoms that face inwards to which Mg^{2+} metal ion can bind easily. In chlorophyll b, the formyl group (CHO) in ring II is replaced by methyl group (CH_3) in chlorophyll (Scheer et al. 2004). This structural variability causes chlorophyll b to have green/yellow pigment at an absorbance of 642–652 nm and blue/

green pigment in chlorophyll a at an absorbance of 660–665 nm (Humphrey 1980). Chlorophyllin is derived from chlorophyll that exhibits anticarcinogenic and antimutagenic activity (Ferruzzi and Blakeslee 2007) and is also used as dietary supplements (Tumolo and Lanfer-Marquez 2012) and to control body odor of geriatric patients (Young and Beregi 1980). Spirulina encompasses 1:15 mg/g of chlorophyll that is utilized in cosmetic products, additive in pharmaceuticals, natural green coloring agent, and food (Gross 1991). Consumption of chlorophyll also reduces the risk of colorectal cancer (Balder et al. 2006). It is used as an additive in deodorants and prevents bad breath. Carotenoids are composed of terpenoid pigment obtained from 40-carbon polyene chain. Hydrocarbon carotenoids are termed as carotenes due to the presence of oxygen-containing functional groups. Oxygen-containing carotenoid pigments are termed as xanthophylls, which are hydrophobic in nature and are often confined in the thylakoid membrane. Examples are lutein, astaxanthin, and cantaxanthin (Cazzaniga et al. 2016). It absorbs light in wavelength ranging from 400 nm to 500 nm. The major carotenoids of microalgae are: β-carotene, lycopene, zeaxanthin, violaxanthin, and lutein. Of these, β-carotene, astaxanthin, lutein, and astaxanthin. β-carotene is an orange-yellowish pigment and human body converts β-carotene into vitamin A, which is helpful to prevent cataracts, skin disease, night blindness and builds up the immunity of the body. Dunaliella is used to isolate β-carotene and used as food colorant in various food products. β-carotene exhibits anti-cancer, immune modulator, and anti-aging properties. Dunaliella exhibits anti-cancerous activity due to the presence of oxygenated carotenoids (Roodenburg et al. 2000). Corymbia ellipsoidea and Chlorella vulgaris are used to extract β-carotene that can inhibit colon cancer. It is also useful to prevent heart disease, arthritis, pre-mature aging, and Alzheimer's disease. When β-carotene is subjected to stress, it gets converted to astaxanthin with the aid of β-carotene hydroxylase and β-caroteneoxygenase (Grunewald et al. 2001). It is insoluble in water and has a rosy appearance and acts as a super vitamin E. In comparison to other carotenoids, it has better antioxidant activity; hence, it is used for treatments such as diabetes, atherosclerosis, heart disease, anti-cancer, and other neural damages such as Parkinson's disease, Alzheimer's disease, spinal cord injuries and other central nervous system injuries (Tso and Lam 1996). The details of various rich-value bioproducts obtained from microalgae are shown in Table 15.2.

Based on absorption properties, phycobiliproteins or secondary light-harvesting pigments can be classified as: phycocyanins (blue brilliant), phycoerythrin (red), and allophycocyanins (green-blue). Phycobiliproteins are found in rhodophyta (red algae), cryptomonads, glaucophyta, and chloroplast stroma of cyanobacteria. Phycoerythrin pigment is present in red algae that imparts the red color while phycocyanin pigment is a blue colored pigment present in cyanobacteria (Parmar et al. 2011). Phycocyanin exhibits anti-inflammatory, antioxidant, hepatoprotective, and neuroprotective properties. Phycobilins find huge applications as chemical tags in research and as immunoassays due to its fluorescence activity at a certain wavelength. Phycocyanine isolated from Streptomyces platensis is applied in cosmetics and food industries such as eyeliners, lipsticks, soft drinks, jellies, candies, chewing gum, and dairy products (Santiago-Santos et al. 2004). Also, phycoerythrin extracted

Table 15.2 Rich-value bioproducts obtained from microalgae

Product	Uses	Examples	Producers
Polyunsaturated fatty acids (PUFAs)	Nutraceutics, food additives	Arachidonic acid, Eicosapentaenoic acid, Docosahexaenoic acid	*Parietochlorisincise,* *Chlorella minutissima,* *Schizochytrium sp.*
Phycobiliproteins carotenoids	Cosmetics, pigments, provitamins	β carotene, Phycocyanin, Astaxanthin, Leutin	*Dunaliella salina,* *Spirulina platensis,* *Haematococcus pluvialis*
Vitamin	Nutrition	α-Tocopherol, Biotin, Ascorbic acid	*Euglena gracilisa,* *Euglena gracilis,* *Prototheca moriformis, a* *Chlorella spp. a*

from Streptomyces platensis and Phorphyridium aerugineum is used in cake decoration, ice creams, cosmetics, color confectionery and desserts, beverages, transparent lollipops, and soft drinks. Phycoerythrin labeled with streptavidin can be utilized for the detection of protein probes and DNA (De Rosa et al. 2003). Benedetti et al. (2004) used Aphanizomenon flos-aquae (AFA) to extract phycocyanin and found that AFA extract exhibited antioxidant activity in human plasma against oxidative damage. Also, phycocyanin exhibited anti-inflammatory activity and can be a functional cofactor in the treatment of inflammation and clinical stress. Bei et al. (2002) found that R-phycoerythrin subunits in the form of photosensitizer are helpful for enhancing the selectivity of photodynamic therapy for the treatment of human liver carcinoma cells SMC 7721 both in vivo and in vitro. Liu et al. (2000) found that Phycocyanin obtained from Spirulina platensis hindered the growth and spread of human leukemia K562 cells. The different natural pigments derived from microalgae and their applications are shown in Fig. 15.3.

15.4.9 Biogas

Microalgae is a highly preferred potential aquatic energy crop for the production of liquid and gaseous biofuels in comparison to municipal solid waste or terrestrial biomass. Microalgae as a feedstock is more favorable for anaerobic digestion (AD) than other technologies such as pyrolysis, gasification, and direct burning because of its inherent high moisture content. AD involves the conversion of organic matter by different groups of bacteria into methane (60–70%), carbon dioxide (20–40%), hydrogen sulfide ($<3.5\%$), and trace amounts of N_2 and NH_3 and can operate suitably for biomass with high moisture content (Vanegas and Bartlett 2013). AD is an efficient technology that is used intensely for biofuel production and waste management and its advantages over bioethanol and biodiesel are that it eliminates the steps of oil extraction or drying, both of which require energy input. In

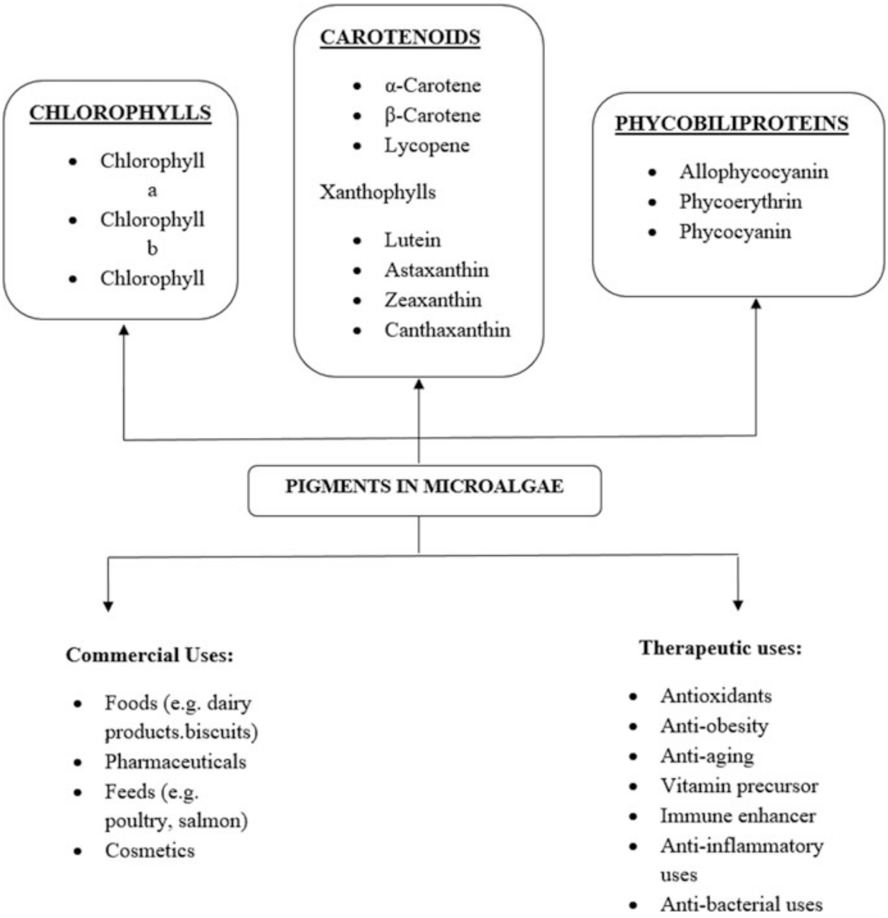

Fig. 15.3 Natural pigments derived from microalgae and their uses

AD the fuel is obtained in gaseous phase and the left-over biomass can be re-used as feedstock or fertilizer and the digestate can be reused as algae cultivation medium. Other advantages include higher growth rate, high amount of lipid and polysaccharide, absence of sparingly degradable lignocellulosic biomass, feasible for nutrient recycling, inexpensive and less energy intensive (Harun et al. 2010a, b). Seaweed species also possess the advantages of high biodegradable sugars such as alginate, laminarin and mannitol, absence of lignin and low cellulose concentration which also makes it a valuable biomass resource for biogas production. The challenges faced during AD of microalgae are: influence of the nature and composition of the cell wall on biodegradability; unbeneficial C: N ratio; production of certain compounds by algal strains that are toxic to anaerobic bacteria (Gonzalez-Fernandez et al. 2015). AD consists of four stages, namely hydrolysis, acidification, acetogenesis, and methanogenesis. Important parameters that must be taken into consideration to obtain an economically feasible process include: type of substrate, type of inoculum, organic loading rate, operational pH, temperature, hydraulic retention time (HRT), and bioreactor type (Meegoda et al. 2018). The additional key parameters that must be considered while using microalgae as feedstock include the type of species, cultivation method, and pretreatment methods. The calorific value of methane produced from microalgae is 39.9 MJ m^{-3}. There are a number of evaluation techniques to assess the potential of methane production, namely macromolecular composition and biomass elemental composition (Buswell and Mueller 1952).

Golueke et al. (1957) conducted the first trials of biogas production from microalgae using a mixed culture of Scenedesmus sp. and Chlorella sp. The methane composition was between 61% and 63%. The effectiveness of microalgae biomass and sewage sludge was found to be quite comparable to each other, i.e., 986 dm^3/kg organic dry matter (ODM) and 1020 dm^3/kg ODM. Mussgnug et al. (2010) fermented Dunaliella salina, Chlamydomonas reinhardtii, Arthrospira platensis and Euglena gracilis and obtained biogas yield of 505 dm^3 CH_4/kg organic dry matter (ODM), 587 dm^3 CH_4/kg ODM, 481 dm^3 CH_4/kg ODM and 485 dm^3/kg ODM. As such Zamalloa et al. (2011) investigated the fermentation of Phaeodactylum tricornutum, Scenedesmus obliquus and Spirulina platensis and obtained 350 ± 3.0 dm^3 CH_4/kg ODM, 210 ± 3.0 dm^3 CH_4/kg ODM and 280 ± 0.8 dm^3 CH_4/ kg ODM. Along with the type of microalgal species, biogas production is also dependent on the structure of cell wall. The cell wall is mainly composed of polysaccharide which includes pectin, cellulose, hemicellulose, and glycoprotein. Presence of a polymer named algaenan in the cell wall of some microalgae species provides resistance during chemical or enzymatic hydrolysis. Microalgal species such as Chlamydomonas reinhardtii, Dunaliella salina, Arthrospira platensis, Euglena gracilis, Chlorella kessleri, and Scenedesmus obliquus yields biogas production of 587 dm^3 CH_4/ kg ODM, 505 dm^3 CH_4/ kg ODM, 481 dm^3 CH_4/ kg ODM, 485 dm^3 CH_4/ kg ODM, 335 dm^3 CH_4/ kg ODM, 287 dm^3 CH_4/kg ODM, respectively, attributing to the cell wall composition along with the taxonomic group of algae (Zamalloa et al. 2011). Inglesby and Fisher (2012) investigated the anaerobic digestibility of Arthrospira maxima in three distinct reactor configurations for the production of methane. Highest methane yield of 173 mLg^{-1}at loading rate of 500 mg/TS/L was obtained. To optimize the C/N ratio and balance the high nitrogen level, co-digestion of algal biomass with an appropriate substrates mixture may enhance the effectiveness and productivity of biogas yield. A synergistic effect on the fermentation of macroalgae biomass with maize silage and hay silage reached to 386.8 dm^3 CH_4/kg ODM during experiments in flow reactors and 373.1 m^3 CH_4/Mg ODM under static conditions (Debowski et al. 2012). Ehimen et al. (2009) studied methane yield via AD of lipid extracted Chlorella biomass and co-digestion with glycerol that enhanced the CH_4 yield from 4–7%. In a further study by Ehiman et al. (2011), methane was recovered from post-transesterified residue of microalgae (Chlorella sp.) codigested with glycerol via anaerobic digestion using semi-continuously fed reactors. C/N ratio was increased to 12.44 which enhanced the CH_4 production to greater than 50%. Co-digestion also ameliorates the biomass loading capacity, process stabilization, inhibitor capacity, nutrition balance, and buffering capacity of digestates (Saratale et al. 2018). In case of macroalgae, anaerobic digestion with low lipid content is appropriate for biogas production. Some bottlenecks of macroalgal biomass over other biomass include high saline content that may restrict the growth of anaerobic microbes inside the reactor or fermenter. Also, high sulfate concentration in macroalgae may lead to the production of hydrogen sulfide. The above issues may be mitigated by blending and diluting the algal mass with other biomass types and binding H_2S with iron-based chemicals, respectively (Murphy et al. 2013).

15.5 Life Cycle Analysis (LCA) and Techno-economic Analysis

15.5.1 Life Cycle Assessment (LCA)

Life cycle assessment (LCA) is one of the most important aspects of a research methodology. It is the study, assessment, and compilation of the potential impacts on the environment of a product or a product system throughout its life cycle (Ertem-Kappler 2019). Life cycle of a product includes all production stages from raw material extraction, processing, manufacturing to the product's end-of-life treatment. Hence, popularly or colloquially LCA is also called the cradle-to-grave analysis as it envelopes the full range of quantitative analysis of the environmental impacts of a product or a process (Ertem-Kappler 2019). When developing a new technology or a process, LCA has become an integral quantitative tool for environmentally friendly design and manufacturing. Even for a pre-existing product, LCA can assist manufacturers in re-evaluating its environmental impacts and identify the most environmentally influential unit processes. By replacing those processes which are at fault, manufacturers can not only protect the environment but also significantly decrease the cost of energy use and waste treatment (Brentner et al. 2011).

LCA evaluation of microalgae biomass feedstock has been carried out for more than 10 years now. Conducting LCA is a comprehensive and time-intensive process. It also usually has a high level of uncertainty. Thus, to standardize the process, the International Standards Organization (ISO) has issued a series of standards, i.e., the ISO 14,000 series (Batan et al. 2010). Although not mandatory, but current LCA practitioners generally follow the ISO standards to implement the assessment. This is to ensure the transparency and repeatability of all projects, while allowing flexibility of project execution.

LCA starts with the determination of the research goals and the scope for analysis. The scope of LCA for any product is identified by determining the goal for analysis. It is also essential to describe the functional units (FU) of the study (Quinn and Davis 2015). The FU can be described as the quantifiable performance of a product system that can be used as a reference unit (Ertem-Kappler 2019). It is usually the functional

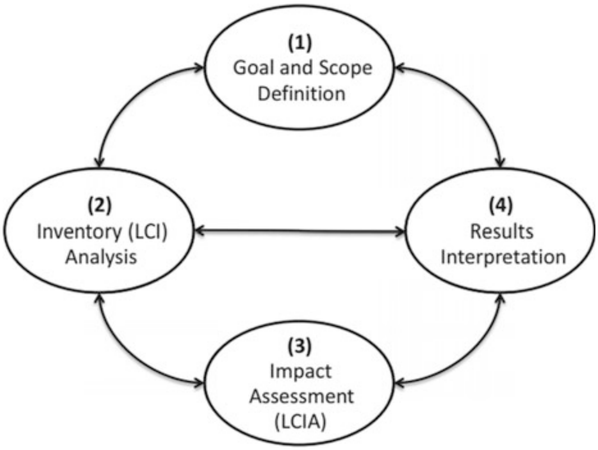

Fig. 15.4 Different phases of life cycle assessment

unit of the product and used in quantifying all environmental impacts. For biofuel production, the unit can be per liter (L) or per kilogram (kg) or per megajoule (MJ) of biofuel produced. After the determination of the FU, all the impacts will be related to FU in the impact analysis stage (stage 3 in Fig. 15.4).

It is also necessary to describe the system boundaries, data collection methods, and data quality requirements of the study in the first stage of LCA. These are critical in determining the efficacy of the LCA and also the time and labor required (Barlow et al. 2016). For microalgal biomass LCA, the research goal could be set as follows:

1. Analysis of environmental impacts of specific biofuels such as biodiesel, ethanol, crude oil, biogas.
2. Comparison of impacts of different biofuels in terms of production technologies and process integration pathways.
3. Comparing the impacts of biofuels to non-renewable fuels.

The life cycle of microalgal biomass production is generally divided into three major stages which are shown in Table 15.3.

15.5.2 Techno-economic Analysis (TEA)

Techno-economic assessment (TEA) is the method used for analyzing the economic aspect of an industrial process, product, or service. Generally, with the assistance of software-based model, it can estimate capital cost, operating cost, and revenue based on various input parameters. Development and commercialization of microalgae biofuels from bio-refineries depends on the social, environmental, and economic aspects (Clarens et al. 2011). TEA assesses the capital and operating costs and analyze relevant risks for various production processes and technologies, which are extremely important to evaluate the economic feasibility of microalgae-based

Table 15.3 Life cycle of microalgal biomass production

Stage	Details
Stage 1	Microalgae growth and collection which include microalgae farming, collection, separation, dewatering, and drying.
Stage 2	Conversion of microalgae to biofuels by various pathways such as pretreatment (e.g., hydrolysis/homogenization), production of crude oil (e.g., lipid extraction/pyrolysis/gasification/liquefaction), crude oil refining (e.g., cracking), and algae residue recycling (e.g., anaerobic digestion/combustion).
Stage 3	Biofuel distribution and combustion. It includes regular product transportation & distribution and engine burning of biofuel.

Table 15.4 Major steps of TEA

Step name	Step details
Study of the market	In this step, various factors that affect the commercialization of the product are investigated
Balance diagram for process flow, mass, and energy	In this step, excel-based spreadsheet model is constructed and applied in the entire TEA
Assessment of economic aspects	Here, various economic criteria such as net present value and internal rate of return are calculated and determined
Sensitivity assessment	In this step, the effects of variation in input parameters on the economic output parameters are examined

biofuels and co-products. Currently, a number of TEA studies have been undertaken to analyze the economic feasibility of various microalgae-based biofuels and the key factors that affect economic performance have been identified. Different solutions to reduce costs have been also evaluated by TEA. In general, the framework is comprised of four major steps as shown in Table 15.4 (Liu et al. 2013).

Apart from these, various modelings and calculations of cash flow which are based on various investigations such as algae strain, algae cultivation method and equipment, algae and water separation technique, and algae conversion method are also taken into consideration (Frank et al. 2012). The major contributing factors for algal cultivation and harvesting should also be mentioned. Other capital and operating cost may also be calculated while taking various assumptions into the consideration and it will affect the price of the main product (Davis et al. 2014).

15.6 Challenges and Future Prospects

Significant advances have been made in streamlining the microalgal biorefinery approach. Steadily, it is also being integrated into the circular bio-economy (Gouveia et al. 2006). This approach can solve many issues by efficiently exploiting most of the microalgal potential through recovering and separating the biomass components as well as by minimizing waste production. However, the current biorefinery approach is still streamlined and has its fair share of drawbacks. The main issue lies in downstream processes that account for almost 40% of the total cost (Wang et al. 2012). This is mainly because of the dilute nature of the autotrophic cultures from separately optimizing the operations involved in harvesting and fractionation. Challenges that hamper the microalgal bio-refineries are present in all the stages of its research and development. In laboratory-scale research, the main challenges lie in strain selection, strain engineering, and nutrient supply strategies. In the culture step, the main problem arises in the high cost of industrial photobioreactors and low biomass concentrations accumulation of different products that often require broad cultivation strategies (Glemser et al. 2016). Finally, downstream processes are designed for a single main product, and the remainder is frequently "waste" that must find a destination, with additional cost implications (Misra et al. 2016).

If we peep into the future, we can expect quite a few exciting developments within the microalgal biorefinery space. Bioactive components extracted from microalgae can be added to our everyday food products to enhance its nutritional benefits. Microalgae cells are already used as ingredients in various food products such as biscuits, cookies, and instant noodles (Beheshtipour et al. 2013). Microalgae such as Arthrospira spp. can also be incorporated with dairy products which stimulates probiotic growth in fermented milk and yogurt (Fradique et al. 2010). Microalgae have a lot of potential to be beneficial for humankind in the long run. It is useful in many ways from the production of biofuels, animal feed, human food products, cosmetics, and pharmaceuticals. However, for sustainability and profitability of microalgae cultivation, further research in an integrated biorefinery approach is required. Only then it will extract multiple products including biofuels, pigments, PUFAs, and antioxidants (Pan et al. 2010).

15.7 Conclusion

The scope and prospect of microalgae biomass for manufacturing high-value product is vast. To give a proper picture, the extracted lipids can be used as supplements for health and the production of biodiesel. Other fractions such as proteins and carbohydrates can be utilized in dietary supplements and related industries such as fermentation industry. Other factions such as pigments and vitamins are used in smaller industries such as cosmetic industry. Thus, the scope of producing value-added components from a single microalgal strain is huge and it will only increase with time. However, with the current state of technology and multiple product extraction is not financially lucrative and also produces a lot of emissions. Thus, more research and development is needed in this field to make the entire process streamlined and more financially viable for everyone involved.

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Chapter 16

Yeast Biomass: A By-Product for Application in the Food, Energy, Plastics, and Pharmaceutical Industries

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Abstract The production of beer and bread by using exogenous yeast of *Saccharomyces cerevisiae* became an usual practice at the end of the nineteenth century and its use by wineries in new wine regions of the USA, South Africa, Australia, and New Zealand occurred in the 50s decade and large quantities of dry yeasts started to be generated in European countries by yeast biomass producing industries in the 60s. As a result, there was a great demand for yeast biomass, mainly by the industries of alcoholic beverages fermented and distilled. Yeast biomass is an important raw material for the beverage industry and also an important by-product of that industry. Especially, the production of beer which initially started as a hand make activity has become an industrial power around the world and for this reason, yeast biomass is one of the by-products of the beer-brewing process. In addition to the industrial importance of yeast biomass reported before, the existence of a large number of academic researches enhances the importance of yeasts, especially *Saccharomyces cerevisiae* and related species that can be used to produce important compounds in the food, energy, and pharmaceutical fields. Finally, recent studies developed at the molecular level have achieved significant advances in the field of genetic engineering intending to convert raw materials into products of good quality and high value.

16.1 Introduction

Human foods have been prepared, over thousands of years, by using microorganisms naturally found and therefore growing spontaneously in these foods. From the year 1680, with the appearance of the microscope, scientists began to study these microorganisms. *Saccharomyces cerevisiae* is among the microorganisms widely reported in thousands of studies involving diverse biotechnological applications (Ali

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E. Jacob-Lopes et al. (eds.), *Handbook of Waste Biorefinery*,
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et al. 2017). Much of the initial studies involving *Saccharomyces cerevisiae* yeast were focused on the production of bread, wine, and beer (Pérez-Torrado et al. 2015).

Malt husks and spent grain are the first major by-products from brewing industry and *Saccharomyces* yeast biomass is the second major one (Olajire 2020).

Saccharomyces yeast biomass is still underutilized, mostly, for swine and ruminant feed, however it can be of value as a raw material with different uses. Brewer's yeast autolyzed and hydrolyzed have been applied as a source of nutrients in microbiological media, mainly because of the high level of protein, vitamin B complex, and minerals found on it. In this case, the yeast biomass is more expensive because it needs to be autolyzed and hydrolyzed and it presents higher grade of purity compared to yeast biomass for animal feed (Ferreira et al. 2010). Brewer's yeast autolysate have been used as a functional food additive based on beetroot juice fermented by *Lactobacillus plantarum*, *L. acidophilus* (Rakin et al. 2004). Brewer's yeast autolyzed and hydrolyzed have been characterized and its composition has high content of essential amino acids, which exceeds that of the reference protein developed by the FAO/WHO and high antioxidant activities comparable to those of tea, and a high content of polyphenols, which could be affected by the composition of wort used in the beer production (Podpora et al. 2016).

Several studies have evaluated the potential use of yeast-derived oil as an alternative to vegetable oil for biodiesel production. Yeast species like *Yarrowia lipolytica* (Do Yook et al. 2019), *Lipomyces starkeyi* (Calvey et al. 2016), *Cryptococcus curvatus* (Patel and Matsakas 2019), *Meyerozyma guilliermondii* (Ramírez-Castrillón et al. 2017), *Rhodotorula kratochvilovae* (Jiru et al. 2017), and *S. cerevisiae* (Watsuntorn et al. 2021) have been identified as oleaginous yeasts, whose lipid contents per dry biomass reported were 52.38%–56.58% (g/g dry biomass) and lipid yields were 1.31–12.90 g/L of culture medium. Consequently, oleaginous yeasts are expected to emerge as a promising alternative to vegetable oil for biodiesel production.

Baptista et al. (2021) have reviewed studies involving recombinant *S. cerevisiae* strains for the production of top value chemicals from biorefinery carbohydrates. Among these top value chemicals are reported organic acids (lactic, succinic, levulinic, and 3-hydroxypropionic acids) and sugar alcohols (sorbitol and xylitol).

In this chapter are described important developments concerning the production, characterization, and application of yeast biomass and studies involving recombinant *S. cerevisiae* strains as cell factory of compounds to be used in the food, energy, and pharmaceutical industries.

16.2 Yeast Biomass and Brewery

Beer is the most popular beverage all over the world and it is one of the oldest cultural achievements of mankind (Wunderlich and Back 2009). The traditional biotechnology can be exemplified by the conventional brewing process that has an extremely long history. Historical evidence for beer production dates back more than

8000 years, and since then, its pattern and consumption have changed considerably over the years (Ferreira et al. 2010). Brewers have produced beer at an advanced technological level while keeping in mind the importance of tradition. Water, malted barley, hops, and yeast are the basic ingredients to make beer in Germany, as it is fixed by the legislation governing commercial brewing, the *Reinheitsgebot* (Purity Law). Brewers in other countries have more flexibility, based on German recipe, whose part of barley malted is replaced by other starch supply. The source of starch commonly used is barley but it has to be malted to dissolve starch in the grains prior to brewing (Wunderlich and Back 2009). Grain contents are digested by enzymes during these processes and starch is prepared for further processes. Starch from milled malt is converted by further enzymes to fermentable sugars during mashing. Wort that is resulted from this procedure is boiled. Hops are added in this stage of boiling to provide bitterness and protect against bacterial spoilage; additionally, they are fundamental for good foam formation. Fermentable sugars produced during mashing are converted to alcohol by yeast during fermentation of cooled wort (Wunderlich and Back 2009; Ferreira et al. 2010).

The yeasts most used in the brewing industry are *Saccharomyces mikatae*, *Saccharomyces paradoxus*, *Saccharomyces kudriavzevii*, *Saccharomyces bayanus*, *Saccharomyces cariocanus*, and *Saccharomyces cerevisiae* (Ferreira et al. 2010).

Pilsners and lagers (“bottom fermenting”) to weissbiers and ales (“top fermenting”) are some variations of beer. Lager and ale are two very broad categories of beer according to which yeast is used. *Saccharomyces pastorianus* or *Saccharomyces carlsbergensis* are yeasts used to produce lager beer at cool temperatures of fermentation (8-15 °C), and the yeasts on the bottom of the vessel forms a cloudy mass (Pavsler and Buiatti 2008, 2009). Traditionally, to produce ale beer (“top fermenting”), strains of *Saccharomyces cerevisiae* are commonly used and the yeasts which rise to the top of the beer in the head of foam at temperatures between 16 °C and 24 °C (Pavsler and Buiatti 2009).

Various residues and by-products are inevitably generated during the manufacture of beer. Spent grains, spent hops, and surplus yeast are the most common by-products which are generated from the main raw materials used for beer production, the barley malt, hop, and yeast, respectively (Mussatto 2009).

The yeast is taken from one fermentation to start the next and it can be usually recycled 4 to 6 times (Ferreira et al. 2010). The surplus yeast is the second largest by-product from breweries which merits considerable attention, due to the large quantity produced and rich chemical composition (Mussatto 2009). Biomass of *Saccharomyces* yeast is still underutilized, mostly, for animal feed.

Yeast biomass from different species has received little attention as a by-product, and its disposal is often an environmental problem. Different uses of yeast biomass are reported; as a raw material rich in amino acids, protein, minerals, and other compounds of interest, several attempts have been done aiming to reuse the surplus yeast in biotechnological processes. Therefore, it can be source or can be used for production of top value compounds with different uses as bioactive compounds in functional food, source of oil for energy, and recombinant *S. cerevisiae* strains for the production of organic acids, sugar alcohols, and others compounds.

16.3 Yeast Biomass Production

Beet or cane molasses are the main substrates used for yeast production. These raw materials are mostly used because they are cheap as they are a waste product from sugar refineries and yeasts can hydrolyze sucrose, the main sugar in molasses, and the resulting monosaccharides, fructose and glucose can be transported through the yeast cells and metabolized by them. Although high sugar concentrations (65–75%) can be founded in molasses, weather conditions during crop growing and sucrose-refining procedures influence their composition. Different fungicides, insecticides, herbicides, heavy metals, and fertilizers can be used in the crops, which can inhibit yeast growth. Dilution of potential toxins is a common practice to attenuate toxic effects in the case of mixing different stocks (Pérez-Torrado et al. 2015).

The determination of the transcriptome of yeast growing in sugar beet molasses has been evaluated as a function of the effects of molasses composition on yeast gene expression during biomass production. Strong induction of the genes involved in biotin uptake and metabolism has been reported in studies that have not employed supplemented molasses, which reinforces that molasses supplementation with this vitamin is needed. Industrial or complete synthetic media used for yeasts growing can influence gene expression profiles. Formate detoxification causes the induction of genes FDH1 and FDH2 and low sulfate levels cause activation of gene SUL1. The improvement of yeast biomass production depends on molecular studies that provide knowledge about growth requirements in a suboptimal substrate (Shima et al. 2005).

The industrial production of yeast biomass is quite similar to the baker's yeast production; however, different yeasts may require slight variations in the process. The commercial production process of baker's yeast is designed as a sequence of fermentations with the transfer of the grown yeast from the smallest vessel to successively larger vessels, which are often as many as six stages. The trade fermentation is the last stage that produces the yeast for sale to bakeries. The first two or three stages (S1, S2, and S3) are always pure culture stages carried out batchwise in small fermenters with a set medium sterilized (Fig. 16.1). The following stages (S4, S5, and S6) are carried out in larger, "open" fermenters, that is, in fermenters in which complete sterility cannot be maintained and in which the level of contaminants (generally lactic acid bacteria) increases (Reed and Nagodawithana 1991). The stock cultures maintained under more stringent control procedures in a central quality control laboratory are used for production of cultures that are periodically renewed. Then, the first fermenter is inoculated with an initial culture and cells grow in various transient stages during the batch (S2-S4) and fed-batch (S5-S6) stages of the process. The yeast biomass grown in small fermenters is used to inoculate in larger tanks in a sequence of consecutive fermentations (Pérez-Torrado et al. 2015).

The yeast biomass from one stage is transferred to the next by pumping the contents into the next larger vessel or by centrifuging the fermenter contents to obtain a concentrated yeast slurry (called yeast cream). The yeast cells are washed with water or acidified water during the centrifuging operation that reduces the level

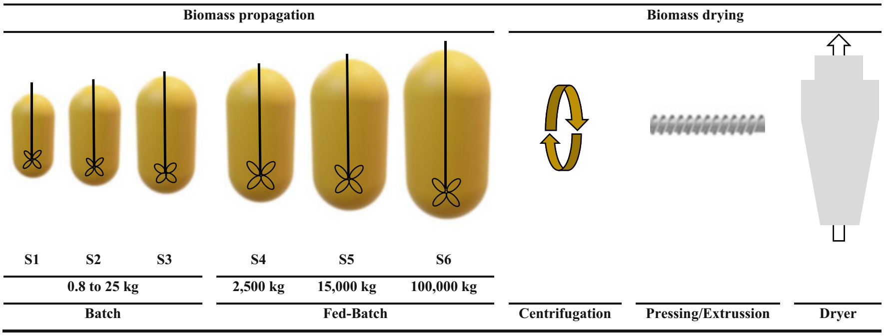

Fig. 16.1 Stages of the yeast biomass propagation and production of active dry yeast (ADY) in kg grown in succeeding stages. Pure culture batch fermentations are carried out in bioreactors (S1, S2, and S3) and fed-batch fermentations are carried out in bioreactors (S4, S5, and S6)

of contaminants appreciably. The optimization of yeast biomass yield is promoted by industrial fed-batch process (Reed and Nagodawithana 1991).

16.3.1 Active Dry Yeast and Application

The generation of stable active dry yeast (ADY) is required in the food industry, such as seasonal wine production. Viable yeast cells are recovered at the end of biomass propagation (stage S6) (Fig. 16.1) and are dehydrated to obtain ADY (Pérez-Torrado et al. 2015). Substrate composition, growth phase, and ion availability, as well as drying temperature and drying rate are important factors that must be taken into account to produce an ADY product with acceptable fermentative activity, storage stability, and yeast resistance to dehydration and rehydration (Trofimova et al. 2010; Laroche and Gervais 2003).

16.3.2 Yeast Starters in Wine, Beer, and Baker Industries

The production of alcoholic beverages from different substrates is one of the most important uses of yeast biomass, as well as its use as baker yeasts.

In modern wineries, using a selected starter *S. cerevisiae* strain is a common practice and it offers many advantages, such as the sugar consumption is ensured; the risk of sluggish and stuck fermentations and microbial contaminations are lowers; reproducibility in subsequent campaigns is enhanced; higher standards in quality and organoleptic parameters are achieved (Borneman et al. 2013; Fleet 2008). *S. cerevisiae* strains that adapt to specific oenological regions have been identified and isolated to be used as a regional starters (Guillamón et al. 1996). On the other hand, the absence of complex microbiota that would be present in the natural must cause the loss of the nuances and organoleptic diversity provided by the complex microbiota (Varela et al. 2009). Mixed inoculum of *S. cerevisiae* and other species has been evaluated to perform wine fermentations, where the fermentative efficiency is totally dependent on the complexity of spontaneous fermentations (Ciani et al. 2010).

In the brewer process the term pitching is the act to inoculate the brewer wort and the pitching rates depend on the fermentation temperature. The pitching rates from 15 to 25 million cells/mL are the most often used on the breweries (Wunderlich and Back 2009).

Industrial breweries have implemented a standard "in-house" biomass production process to avoid transport and handling and most brewers inoculate newly propagated yeast into each fermentation batch from master cultures (Quain 2006). The biomass newly propagated during initial wort fermentation has a poor fermentative efficiency, which is probably caused by the different growth rate in the cell population (Miller et al. 2018).

A common practice in wineries is the use of dried yeast, which has evaluated as an alternative for brewing yeast (Powell and Fischborn 2018). On the other hand, the use of dried yeast as starters in brewery can reduce viability, impair flocculation which changes foam and clarity in beer, and increase production of undesired compounds (Finn and Stewart 2018; Cyr et al. 2018). These negative characteristics caused by dry brewing yeast need to be further studied.

The production of bread and other bakery products uses baker's yeast, which can be commercialized as dry powder, cream, or compressed cakes for dough leavening. CO_2 and ethanol are produced from yeast fermentative metabolism of maltose, that modify the unfermented dough composition and they are determinant to generate the typical flavor and bread crumb structure formation (Cho and Peterson 2010). In general, bread flavor has been influenced by choice of ingredients, thermal reactions induced during baking, and enzymatic reactions occurring during dough fermentation by yeasts and/or lactic acid bacteria (Kirchhoff and Schieberle 2001). The fermentation of bread doughs are very short periods of time with a range of 30 min to 4 h. The doughs are inoculated with 300 to 10^6 cells per gram and during the fermentation there is little or no yeast growth. In contrast, beer and wine fermentations are longer, whose periods ranging from several days to several weeks (Reed and Nagodawithana 1991). Legras et al. (2007) suggested that origin of baker's yeast have a genetic character that contains alleles from different wine and beer yeasts subpopulations. Albertin et al. (2009) reported that baker's yeast strains are heterothallic and tetraploid, and suggested that they might emerge from tetraploidization between wine strains and ale beer.

16.4 Yeasts as a Source of Lipid for Biodiesel Production

Microorganisms oleaginous are those that can produce lipid in amounts exceeding 20% (w/w) of their cell dry weight (Huang et al. 2019). Lipids can be produced by yeasts, bacteria, fungi, and microalgae. Only 4% of yeast species have been

Table 16.1 Microbial oil production by yeasts

Yeast species	Substrate	Results	Reference
Trichosporon cutaneum	Corncob acid hydrolysate (glucose, xylose, and arabinose)	41.70% lipid/g dry cell weight	Chen et al. (2013)
Debaryomyces etchellsii	Deproteinized cheese whey	5.9% lipid/g dry cell weight and 0.40 g lipid/L fermentation broth	Arous et al. (2016)
Wickerhamomyces anomalus		24.0% lipid/g dry cell weight and 0.65 g lipid/L fermentation broth	Arous et al. (2017)
Cystobasidium oligophagum	Untreated cheese whey	21.79% lipid/g dry cell weight and 4.57 (g lipid/L fermentation broth	Vyas and Chhabra (2019)
Meyerozyma guilliermondii	Pure glycerol	34.97% lipid/g dry cell weight and 0.11 g lipid/L fermentation broth	Ramírez-Castrillón et al. (2017)
Lipomyces starkeyi	Glucose	54.85% lipid/g dry cell weight and 10.03 g lipid/L fermentation broth	Calvey et al. (2016)
Lipomyces starkeyi	Glucose and xylose	41.80% lipid/g dry cell weight and 6.80 g lipid/L fermentation broth	Probst and Vadlani (2017)
Cryptococcus curvatus	Glucose and sonicated waste cooking oil	52.66% lipid/g dry cell weight and lipid yield of 5.23 g lipid/L fermentation broth	Patel and Matsakas (2019)
Rhodotorula kratochvilovae	Glucose	56.06% lipid/g dry cell weight and lipid yield of 8.60 g lipid/L fermentation broth	Jiru et al. (2017)
Yarrowia lipolytica	Glucose	56.58% lipid/g dry cell weight and 12.90 g lipid/L fermentation broth	Yook et al. (2019)
Rhodotorula mucilaginosa	Glucose	21.63% lipid/g dry cell weight) and 0.58 g lipid/L fermentation broth	Bardhan et al. (2020)
Saccharomyces cerevisiae	Glucose	52.96% lipid/g dry cell weight) and 1.78 g lipid/L fermentation broth	Watsuntorn et al. (2021)

identified as oleaginous, among the 1600 reported in the literature and the potential use of yeast-derived oil is an important alternative to vegetable oil for biodiesel production (Bardhan et al. 2020). These yeasts are considered as cell factories for the commercial production of exotic fats like cocoa butter, polyunsaturated fatty acids, and biodiesel (Bellou et al. 2016; Papanikolaou and Aggelis 2019). The most of yeasts of genera *Yarrowia*, *Rhodosporidium*, *Cryptococcus*, *Rhodotorula*, *Trichosporon*, and *Lipomyces* are predominantly composed by oleaginous yeasts (Zhu et al. 2008; Abghari and Chen 2014; Zhang et al. 2016; Deeba et al. 2017; Khot and Ghosh 2017; Blomqvist et al. 2018). In Table 16.1 are listed some studies of microbial oil production by yeasts.

Chen et al. (2013) evaluated the microbial oil production by *Trichosporon cutaneum* on corncob acid hydrolysate (glucose, xylose, and arabinose) as a source of carbon. The maximum lipid content found was 41.70% lipid/g dry cell weight. Deproteinized cheese whey has been evaluated as agro-industrial wastewaters for lipid production by the oleaginous yeasts *Debaryomyces etchellsii* (Arous et al. 2016) and *Wickerhamomyces anomalus* strain EC28 (Arous et al. 2017), achieving maximum lipid contents of 15.9% and 24.0% (lipid/g dry cell weight) and highest lipid concentrations of 0.40 and 0.65 (g lipid/L fermentation broth). Untreated cheese whey has been evaluated as a feedstock for lipid production by the oleaginous yeast *Cystobasidium oligophagum* JRC1 isolated and characterized as a cellulase and lipase producing (Vyas and Chhabra 2019). In this study, it was found lipid content of 21.79% (lipid/g dry cell weight) and lipid concentration of 4.57 (g lipid/L fermentation broth).

Pure glycerol has also been used as a source of carbon for lipid production by the oleaginous yeast *Meyerozyma guilliermondii* BI281A, whose lipid content was 34.97% (lipid/g dry cell weight) and lipid concentration was ca. 0.11 (g lipid/L fermentation broth) (Ramírez-Castrillón et al. 2017).

The most of studies devoted to evaluate the microbial oil production by oleaginous yeast have used glucose as a source of carbon. Lipogenesis induction has been reported due to nutrient limitation, particularly, high C/N ratio in the growth medium causes accumulation of high amounts of triacylglycerol in the form of intracellular lipid bodies in the oleaginous yeasts (Poontawee et al. 2018; Bardhan et al. 2019).

Calvey et al. (2016) reported lipid accumulation in NRRL Y-1155 *Lipomyces starkeyi* strain by nitrogen and oxygen limitations, achieving lipid content of 54.85% (lipid/g dry cell weight) and lipid concentration of 10.03 (g lipid/L fermentation broth). Fed-batch fermentation strategy with glucose for growth and xylose for oil production by *Lipomyces starkeyi* ATCC 56304 yielded 41.80% lipid/g dry cell weight and 6.80 g lipid/L fermentation broth (Probst and Vadlani 2017). Patel and Matsakas (2019) reported lipid fermentation by oleaginous yeast *Cryptococcus curvatus* using glucose and sonicated waste cooking oil as substrates, achieving lipid content of 52.66% (lipid/g dry cell weight) and lipid yield of 5.23 (g lipid/L fermentation broth). Jiru et al. (2017) optimized cultivation conditions for lipid production by *Rhodotorula kratochvilovae* SY89 and they found lipid content of 56.06% (lipid/g dry cell weight) and lipid yield of 8.60 (g lipid/L fermentation broth). Lipid extraction optimization from the oleaginous yeast *Yarrowia lipolytica* was reported by Do Yook et al. (2019) that found lipid content of 56.58% (lipid/g dry cell weight) and lipid yield of 12.90 (g lipid/L fermentation broth).

Bardhan et al. (2020) identified fourteen yeast isolates belonged to seven different genera of oleaginous yeasts from traditional fermented foods and beverages to evaluate their ability to produce lipids for biodiesel production. *Rhodotorula, Pichia, Candida, Saturnispora, Wickerhamomyces, Zygoascus,* and *Saccharomyces* were the genera of identified yeast isolates. Among fourteen yeast isolates, the maximum lipid content and the highest lipid concentration were found in yeast *Rhodotorula mucilaginosa* R2 (21.63% lipid/g dry cell weight) and (0.58 g lipid/L fermentation broth), respectively. Watsuntorn et al. (2021) reported that a novel *Saccharomyces* *cerevisiae* CU-TPD4, isolated from coconut waste residues as an oleaginous yeast with high lipid content (52.96% lipid/g dry cell weight) and lipid yield (1.78 g lipid/L fermentation broth) under optimized growth conditions. The authors suggested that this *S. cerevisiae* CU-TPD4 is expected to emerge as a promising alternative for biodiesel production (Table 16.1).

16.5 *S. cerevisiae* as an Attractive Cell Factory for Novel Applications

The yeast *S. cerevisiae* is an attractive cell factory, generally regarded as safe (GRAS status), used in several microbiological industrial processes, such as the production of bread, bioethanol, beer, wine, nutraceuticals, pharmaceuticals, and chemicals. Genetic tools have been used to engineer this yeast to be able to grow with harsh fermentation conditions like the presence of inhibitory compounds, low pH, and high temperature (Nielsen and Jewett 2008; Hong and Nielsen 2012; Borodina and Nielsen 2014) In Table 16.2 are listed some studies of microbial production of several compounds by recombinant *Saccharomyces cerevisiae*.

16.5.1 *Production of Organic Acids: 3-Hydroxypropionic, Succinic, Levulinic, and Lactic Acids*

The production of organic acid is mainly petroleum-based and they are important building block chemicals with massive market potential. They present one or more

Table 16.2 Microbial production of compounds by recombinant *Saccharomyces cerevisiae*

Compound	Substrate	Results	Reference
3-hydroxypropionic acid	Glucose	13.7 g/L in fed-batch conditions at pH 5	Borodina et al. (2015)
Succinic acid	Glycerol and carbon dioxide as a source of carbon	10.7 g/L and yield 0.22 g/g of glycerol in shake batch culture	Xiberras et al. (2020)
5-aminolevulinic acid	Glycine	1.36 mg/L	Hara et al. (2019)
Lactic acid	Glucose, xylose and cellobiose	83 g/L and yield 0.60 g/g of sugar in a 1 L bioreactor fermentation	Turner et al. (2016)
Sorbitol	Glucose and fructose	1.17 g/L and 4.39 g/L	Jain et al. (2011)
Xylitol	Xylose and glucose (co-substrate)	196.2 g/L and yield 1g/g of xylose	Jo et al. (2015)

acidic groups (such as alcohol, phenol, sulfonic, carboxyl, among others) and low molecular weight (Yin et al. 2015).

16.5.1.1 3-Hydroxypropionic Acid

Acrylic acid, acrylamide, malonic acid, propiolactone, 1,3-propanediol are some compounds that can be produced from 3-hydroxypropionic acid (3HP) that comprises the functional groups (carboxyl and β-hydroxyl). 3HP shows a great potential to produce a vast number of high value-added compounds (Matsakas et al. 2018), including its use as a precursor for acrylic acid production (Becker et al. 2015).

Baptista et al. (2021) have reviewed the metabolic engineering of *Saccharomyces cerevisiae* for the production of several compounds including 3HP. They reported that there are several different pathways described in the literature to produce 3HP from glucose by *S. cerevisiae* focusing mainly on β-alanine and malonyl-CoA pathways. The production of 463 mg/L of 3HP from glucose as a substrate by *S. cerevisiae* was reported by Chen et al. (2014) which blocked the consumption of acetyl-CoA, therefore there was an accumulation of it and increased NADPH formation by MLS1 deletion and multiple gene overexpression, simultaneously with the overexpression of ACC1 catalyzing acetyl-CoA to malonyl-CoA, which led to the production of 3HP. Chen et al. (2017) reported the production of 477 mg/L of 3HP by *Corynebacterium glutamicum* that focused on the study of inositol and choline effect combined with downregulation of lipid synthesis. Kildegaard et al. (2016) have evaluated the engineering and systems-level analysis of *S. cerevisiae* for production of 3HP via malonyl-CoA reductase-dependent pathway. The resultant strain was able to produce 9.8 g/L of 3HP in fed-batch cultivation at pH 5, after optimization of acetyl-CoA supply and NADPH formation. Maury et al. (2018) evaluated the glucose-dependent promoters for dynamic regulation of metabolic pathways, through analysis of mRNA data of *S. cerevisiae* grown in chemostats under glucose excess or limitation and it was identified 34 candidate promoters that strongly responded to glucose presence or absence. The titer of 3HP by 70% was improved by promoter ILC1 in comparison to PGK1 promoter. Borodina et al. (2015) studied a synthetic pathway for high-level production of 3HP in *S. cerevisiae* via β-alanine pathway. It was observed production of a novel β-alanine-pyruvate aminotransferase coupled with overexpression of several native and heterologous genes discovered in *Bacillus cereus*, resulted in 13.7 g/L of 3HP in fed-batch conditions at pH 5. The same strain of *S. cerevisiae* was later used in a different study focusing on small-scale chemostats to scale up microbial processes of 3HP production, using glucose as substrate and yielding 15.9% C-mol and 0.45 g/g of cell dry weight under C-limiting conditions (Lis et al. 2019).

Kildegaard et al. (2015) evaluated the production of 3HP from glucose and xylose by metabolically engineered *S. cerevisiae*. They reported 3HP production from xylose, either through malonyl-CoA or β-alanine pathways by using two different approaches (NADH and NADPH-dependent route). The malonyl-CoA pathway was the better choice, when using glucose as a substrate. However, when using xylose as a sole carbon source, the NADPH-dependent β-alanine pathway yielded highest 3HP production, resulting in 7.37 g/L of 3HP in 120 h under fed-batch cultivation.

Ferreira et al. (2019) reported an improvement of endogenous metabolic fluxes toward increasing levels of malonyl-CoA and acetyl-CoA, as a consequence of fine-tuning of central carbon metabolism in yeast through dCas9-based regulation. This improvement resulted in the largest increase of 3HP production (36%) was achieved by targeting the gene encoding adenylate kinase 1 (ADK1), which reversibly converts two ADPs to AMP and ATP, when compared to the control strain of *S. cerevisiae* where no guide RNA was added.

16.5.1.2 Succinic Acid

Biotechnological or chemical synthesis can be used to produce succinic acid (SA). Paraffin oxidation and catalytic hydrogenation or electrolytic reduction of maleic acid or maleic anhydride are some chemical processes developed in the past to produce SA (Muzumdar et al. 2004; Cok et al. 2014). Biotechnological production of SA compared to its petrochemical synthesis is considered to be economically feasible and competitive due to its high conversion yield and efficiency (Hermann et al. 2007). The annual production in Europe and North America of SA microbial-based represents almost half of worldwide production (Kumar et al. 2020b). The most used microorganisms as recombinant hosts for SA production are *E. coli* (Wang et al. 2011) and *Corynebacterium glutamicum* (Okino et al. 2008; Litsanov et al. 2012), yielding concentrations of SA from glucose above 100 g/L. Li et al. (2017) evaluated the production of SA from glycerol by yeast engineered *Yarrowia lipolytica* in situ fibrous bed bioreactor, whose yielding was 51.9 g/L of SA that raised up to 198.2 g/L by fed-batch strategy. Mancini et al. (2019) reviewed second-generation feedstocks, innovative fermentation and downstream techniques used for succinic acid production. They reported that recombinant *S. cerevisiae* and *E. coli* are model engineered microorganisms both used for several companies, such as Biosuccinium that produce microbial-based SA by *S. cerevisiae* strains from starch/sugar as a substrate. Xiberras et al. (2020) reported the maximum SA titer of 10.7 g/L from glycerol and carbon dioxide as a source of carbon by engineered *S. cerevisiae* and a yield of 0.22 g/g of glycerol in shake batch culture. Kumar et al. (2020b) reviewed the sustainable production and purification of SA and reported that the process optimization and use of low-cost raw materials such as lignocellulosic biomass (lignin, cellulose, and hemicellulose) or waste glycerol left after biodiesel recovery have been used as feedstock microbial-based converted to SA by *S. cerevisiae* that can indeed play an important role in this field.

16.5.1.3 Levulinic Acid

Levulinic acid (LA) is a short chain fatty acid with molecular formula $C_5H_8O_3$. It is a linear C5-alkyl carbon chain that is known as 4-oxopentanoic acid or gamma ketovaleric acid and also 3-acetylpropionic acid (Signoretto et al. 2019). GF Biochemicals Ltd. is the main worldwide producer of levulinic acid, which developed a novel technology for production, recovery, and purification of this acid. LA can be produced through various routes; synthesis, bio, and extraction routes (Kumar et al. 2020a). Dehydration of biomass or carbohydrates through an acid treatment is the most common route to produce LA (Cha and Um 2020). No studies have reported biological production of LA; however, the production of its derivative 5-aminolevulinic acid (5-ALA) has been reported in *Chlorella* sp., *Rhodobacter sphaeroides*, or recombinant *E. coli*, among others (Baptista et al. 2021). The production of 5-ALA using an engineered *S. cerevisiae* strain was reported by Hara et al. (2019)), resulting in the production of 1.36 mg/L of 5-ALA.

16.5.1.4 Lactic Acid

Lactic acid (LA) can be produced by many organisms by fermentation of various feedstocks and the utilization of low-cost, non-food substrates, together with lignocellulosic biomass, food waste, or microalgae, has been strongly proposed for its economic production (Borodina and Nielsen 2014; Ahmad et al. 2020).

LA is an important chemical applied in cosmetics, foods, pharmaceuticals, textiles, and other industries (Sauer et al. 2008). Several studies have evaluated the metabolic engineering of *S. cerevisiae* to produce LA (Baek et al. 2015; Yamada et al. 2017; Novy et al. 2017, 2018; Lee et al. 2015, 2016; Stovicek et al. 2015; Turner et al. 2016; Turner et al. 2017; Sugiyama et al. 2016; Lian et al. 2018; Novy et al. 2018; Ryu et al. 2018; Kim et al. 2019). Baek et al. (2015) developed *S. cerevisiae* strains for production of D-LA that was achieved by expressing highly stereospecific D-lactate dehydrogenase gene from *Leuconostoc mesenteroides* in *S. cerevisiae* lacking natural LA production activity. They reported production of LA by engineered *S. cerevisiae* strains of 48.9 g/L, yield of 0.79 g/g glucose without pH control and 112.0 g/L, yield of 0.80 g/g glucose at fed-batch fermentation with neutralizing conditions. LA production from glucose by recombinant *S. cerevisiae* was evaluated by Yamada et al. (2017) that reported average LA production and yield with 10 repeated batch fermentations were 60.3 g/L and 0.646 g/g of glucose, respectively. Novy et al. (2017) evaluated the metabolic engineering strategy applied in *S. cerevisiae* strains to produce LA by homolactic fermentation from glucose and xylose. The anaerobic shaken bottle fermentations at pH ≥ 5 resulted in L-lactic yields of 0.67 g/g glucose and 0.80 g/g xylose for strain IBB14LA1_5. In aerobic conditions and pH stabilized, the same strain IBB14LA1_5 converted glucose in L-lactic with productivity of 1.8 g/L/h and yield of 0.69 g/g glucose.

Novy et al. (2018) using the same *S. cerevisiae* strains as Novy et al. (2017) observed that IBB14LA1 strain in anaerobic fermentation showed a higher yield of LA on xylose (0.27 g/g) than on glucose (0.18 g/g). In IBB14LA1_5 strain, the yields of LA were 0.80 g/g xylose and 0.67 g/g glucose. In aerobic conditions the LA yielding were IBB14LA1 0.18 g/g glucose; IBB14LA1_5 0.68 g/g glucose and LA production from xylose ceased completely in IBB14LA1 and decreased drastically in IBB14LA1_5 (yield aerobic ≤ 0.25 g/g xylose and yield anaerobic 0.80 g/g xylose). Lee et al. (2015) have engineered cellular redox balance in 8 *S. cerevisiae* strains for improvement production of L-LA. The final *S. cerevisiae* strain (SP7) produced 117 g/L of L-LA and an approximately 58% yield in a 2-L fed-batch bioreactor under pH 3.5. The improvement of LA production in *S. cerevisiae* by a deletion of SSB1 gene was reported by Lee et al. (2016) that found resulting strain demonstrated up to 33% increased cell growth, 58% increased glucose consumption, and 60% increased L-LA production. This genetic modification resulted in the production of 50 g/L of LA in shake batch culture with glucose as a source of carbon.

Stovicek et al. (2015) applied a CRISPR–Cas9 system for genome editing of different industrial strains of *S. cerevisiae* and the final titer of LA was 2.74 g/L in CEN.PK strain and 2.52 g/L in Ethanol Red strain resulting in yield of 0.61 g and 0.35 g LA/g of consumed glucose, respectively. LA production by engineered *S. cerevisiae* from glucose, xylose, cellobiose, galactose, mannose, and sucrose as a source of carbon was studied by Turner et al. (2016). In this study, they showed that an engineered *S. cerevisiae* strain, EJ4L, possessing the ability to ferment cellobiose and xylose into LA. The EJ4L strain in a 1 L bioreactor fermentation, converted 10 g/L of glucose, 40 g/L of xylose, and 80 g/L of cellobiose into 83 g/L of LA, yielding 0.60 g/g of sugar. Turner et al. (2017) reported LA production by EJ4L *S. cerevisiae* strain (obtained with the introduction of the ldhA gene into EJ4 yeast strain) from purified lactose (23.77 g/L of LA; yield of 0.58 g/g of lactose) or derived from dairy milk (10.3 g/L of LA; yield of 24.4 g/g of lactose) or cheese whey (15.6 g/L of LA; yield of 0.356 g/g of lactose). Sugiyama et al. (2016) studied the overexpression of ESBP6 *S. cerevisiae* strain carrying the ldh gene and they showed that LA production from glucose by this strain was 5.5 g/L and 4.6 g/L was the LA production by wild-type strain. Lian et al. (2018) have developed an efficient CRISPR/Cas9 system for industrial *S. cerevisiae* strain engineering and simultaneous gene deletion was achieved with a titer of 2 g/L of LA by using xylose as a source of carbon.

Engineering of *S. cerevisiae* for enhanced production of L-LA by co-expression of acid-stable glycolytic enzymes from acidophilic archaea *Picrophilus torridus* was studied by Ryu et al. (2018). They observed increasing of LA production of 17.4 g/L by SPP *S. cerevisiae* strain compared to production of 14.4 g/L by parental strain SPS. Kim et al. (2019) have used whole slurry of acid-pretreated spent coffee grounds as a substrate to produce LA by engineered *S. cerevisiae* strain expressing heterologous lactate dehydrogenase (ldh) gene on a xylose-consuming. The recombinant strain produced 11.15 g/L of LA and 0.24 g/L of ethanol from the whole slurry of pretreated, corresponding to 0.11 g LA and 0.10 g ethanol/g whole slurry before pretreatment.

16.5.2 Sugar Alcohol

Sugar alcohols (polyols or polyhydric alcohols) are carbohydrates that can found naturally in small amounts in vegetables, plants, and cereals. Sugar alcohols include hydrogenated monosaccharides, such as sorbitol and xylitol (Hernández-Pérez et al. 2020).

16.5.2.1 Sorbitol

The growing utilization of natural and sugar alcohols sweeteners, including sorbitol and xylitol, in the diet beverages segment is expected to drive the sweeteners demand in the next decade. Glucose syrup or glucose and fructose mixtures are the feedstocks used to produce sorbitol industrially, by catalytic hydrogenation using Raney nickel as catalyst, under high temperatures (120–150 °C) and pressure of 70 bar (Silveira and Jonas 2002). Biotechnological production of sorbitol has been studied by using *Zymomonas mobilis* and *Lactobacillus plantarum* from fructose and glucose, respectively (Silveira and Jonas 2002; Ladero et al. 2007). In *S. cerevisiae*, sorbitol production was achieved by overexpressing the native SOR1 gene encoding for NADH-dependent sorbitol dehydrogenase responsible for the conversion of sorbitol to fructose or fructose to sorbitol by using NAD+ as cofactor (Jain et al. 2011). The production of sorbitol by DM(SOR1) and DM(srlD) *S. cerevisiae* strains was 1.17 g/L and 4.39 g/L, respectively. A mutant of *S. cerevisiae* (ATCC 36859) lacking hexokinase activity was reported by Duvnjak et al. (1991) to produce sorbitol and ethanol from Jerusalem artichokes as a substrate and source that contain a large amount of fructose. The fermentation of Jerusalem artichokes juice supplemented with glucose and 3% yeast extract resulted in 2.23 g/L of sorbitol and 6.18 g/L of ethanol.

Wei et al. (2001) reported an intergeneric protoplast fusion method between *Kluyveromyces* and *S. cerevisiae* to produce sorbitol directly from Jerusalem artichokes. The fusant F27 achieved by intergeneric protoplast fusion between *Kluyveromyces* sp. Y-85 and *S. cerevisiae* E-15 is genetically stable and it had the highest inulinase activity and sorbitol productivity (48.7 g/L) reported in the literature.

16.5.2.2 Xylitol

A chemical route based on the catalyzed hydrogenation of purified xylose using nickel as catalyst is the current commercial production of xylitol at high temperatures and pressures. Xylan in biomass is converted into xylitol by chemical process with conversion of 50%–60% and the conversion of xylitol from pure xylose can reach up to 98%. Due to the high cost of the catalyst, the need for high pressure and temperature and the complexity of the xylose purification step, the chemical process used to produce xylitol is considered non-eco-friendly, energy-consuming, and costly (Hernández-Pérez et al. 2020). As an alternative to the chemical process, biotechnological process has advantages such as mild requirement of temperature and pressure, not requiring the successive steps of xylose purification and it is a selective biological process (Hou-Rui 2012; Canilha et al. 2013). Metabolic engineering strategies for xylitol production in *S. cerevisiae* have been reported in several studies (Hallborn et al. 1991; Lee et al. 2000; Govinden et al. 2001; Chung et al. 2002; Bae et al. 2004; Kim et al. 2017; Oh et al. 2013; Lane et al. 2018; Baptista et al. 2018; Romaní et al. 2020; Kogje and Ghosalkar 2016, 2017; Jo et al. 2015; Guirimand et al. 2015, 2019). Initial attempts for xylitol production by recombinant *S. cerevisiae* relied on the expression of XYL1 gene from the xylose-fermenting *Scheffersomyces stipitis* (*Pichia stipitis*). The batch fermentations of GPY55-15Bα and pMA91 *S. cerevisiae* strains converted xylose as a substrate and glucose as a co-substrate into 19 g/L of xylose, yielding 1 g of xylitol/g of xylose (Hallborn et al. 1991). Govinden et al. (2001) also reported xylitol production by recombinant *S. cerevisiae* expressing the XYL1 genes from *Pichia stipitis* and *Candida shehatae*. The highest production and yield of xylitol was 15 g/L and 0.86 g/g xylose in batch fermentations using glucose as co-substrate. Some studies have used strategy of two-substrate using a high molar ratio of xylose to glucose fermentation processes for xylitol production during the bioconversion phase using recombinant *S. cerevisiae*. High productions (105 g/L, 78 g/L, and 116 g/L) and high yields of xylitol (>0.95 g/g, 0.9 g/g, and 0.9 g/g of xylose) using glucose-limited fed-batch fermentation strategy have been reported by Lee et al. (2000), Chung et al. (2002), and Bae et al. (2004), respectively. Kim et al. (2017) reported high production (178 g/L) and high yield of xylitol ($\approx$ 1 g/g of xylose). In this study, they evaluated the production improvement of xylitol from xylose by expression of araE (arabinose: H+ symporter) from *Bacillus subtilis* together with the expression of XYL1 gene from *Scheffersomyces stipitis* xylose reductase in recombinant *S. cerevisiae* using xylose and glucose-limited fed-batch fermentation strategy. Oh et al. (2013) employed another strategy to improve xylitol production through simultaneous co-utilization of cellobiose (a dimer of glucose) and xylose by engineered *S. cerevisiae* strain expressing a xylose reductase (XYL1) from *S. stipitis* that was engineered for cellobiose utilization by the expression of the CDT-1 (cellodextrin transporter) and GH1-1 (β-glucosidase) genes from the filamentous fungus *Neurospora crassa*. The resulting D-10-BT XYL1 strain showed cellobiose and xylose co-consumption and high xylitol production (93 g/L) and high yield of xylitol ($\approx$ 1 g/g of xylose). Baptista et al. (2018) evaluated a simultaneous saccharification and fermentation process of lignocellulosic whole slurry corn cob obtained from the corn cob autohydrolysis pretreatment by engineered industrial PE-2-GRE3 *S. cerevisiae* strain and this approach resulted in 29.6 g/L of xylitol production and yield of xylitol 0.95 g/g of substrate. Romaní et al. (2020) have used the same PE-2-GRE3 *S. cerevisiae* strain for simultaneous saccharification and fermentation of hardwood xylan into xylitol using aqueous solutions of deep eutectic systems as reaction media, reaching 23.7 g/L of xylitol production and yield $\approx$ 1.0 g/g of substrate. Jo et al. (2015) reported the xylitol production in engineered *S. cerevisiae* by dual utilization of NADPH and NADH cofactors. The fed-batch fermentations of DWM-ZWF1-ACS1 *S. cerevisiae* strain converted xylose as a substrate and glucose as a co-substrate into 196.2 g/L of xylose, yielding 1 g of xylitol/g of xylose. Kogje and Ghosalkar (2017) expressed GRE3 and SUT1 genes in an industrial strain of *S. cerevisiae* using glycerol as a co-substrate to produce xylitol from a detoxified corn cob hydrolysate. The fed-batch fermentation of XP-RTK *S. cerevisiae* strain converted corn cob hydrolysate as a substrate and glycerol as a co-substrate into 47 g/L of xylose, yielding 1 g of xylitol/g of substrate.

Guirimand et al. (2015) reported cell surface engineering of *S. cerevisiae* strain to express XYL1 (xylose reductase) from *S. stipitis* and co-display three different hydrolases on its cell surface: BGL (β-glucosidase) from *Aspergillus aculeatus*, XylA (β-xylosidase) from *Aspergillus oryzae* and XYN (endoxylanase II) from *Trichoderma reesei*. This recombinant strain was used for xylitol production from rice straw with and without filtration (nanofiltration) by a membrane separation step. The xylitol production by recombinant strain from rice straw hydrolysate without nanofiltration was 5.8 g/L and from rice straw hydrolysate with nanofiltration resulted in the production of 37.9 g/L of xylitol, yielding 1 g of xylitol/g of substrate in both cases. Guirimand et al. (2019) modified the recombinant strain used by Guirimand et al. (2015) in terms of promoters, secretion signal, and anchoring domain sequences, finding maximal xylitol production from rice straw hydrolysate of 6.97 g/L and from Kraft pulp residue of 4.2 g/L.

16.6 Concluding Remarks

Saccharomyces cerevisiae yeast biomass is an important feedstock for alcoholic beverages fermented and distilled, bioethanol and baker industries. In addition to the importance of *Saccharomyces cerevisiae* yeast biomass for traditional industries, like active dry yeast starters in wine, beer, and baker industries, a large number of academic papers have been published involving yeasts, especially *Saccharomyces cerevisiae* and related species in different applications. Most of these applications are in academic level and their implementation as a sustainable biobased economy relies on the substitution of single product biorefineries for integrated versions producing bioethanol, for example, combined with biobased products, such as oleaginous yeasts as a source of lipid for biodiesel production or production of organic acids (3-hydroxypropionic, succinic, levulinic, and lactic acids) or production of sugar alcohols (sorbitol and xylitol), etc. Yeasts are an attractive cell factory for novel applications and metabolic engineering is an important tool to manipulate these microorganisms intending to convert feedstocks into products of good quality and high value.

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Chapter 17
Enzymes Applied to Lignocellulosic Biorefinery

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Abstract Recent approaches emphasize the importance of biorefineries that carries out the conversion of residual biomass into biofuels and chemical products in processes of high productivity and specificity and low environmental impact. In this scenario, the lignocellulosic biomass conversion is highlighted, mainly because it is a renewable and abundant resource and the primary structural composition of cellulose, hemicellulose, and lignin. The valorization of lignocellulosic biomass is a complex multiphase process that depends on efficient fractionation that allows the recovery of the structures that make up the biomass to convert into biofuels and chemicals. The approach based on biocatalysis by applying enzymes in biorefineries is of interest to industrial biotechnology, mainly in systems using residual raw material, associating means of production that result in a high yield system with products with high value-added and low environmental impact. Enzymatic and fermentation technologies allow the conversion of complex structures into economically valuable compounds, and different enzymes can be used to develop these systems. This chapter reviews the potential of residual lignocellulosic biomass for conversion into a multi-product scale and the critical role of enzymatic technologies for converting structures into high value-added products in environmentally sustainable processes.

17.1 Overview

The social and international agencies pressure due to the overexploitation of natural resources and dependence on fossil fuels has stimulated several countries to achieve sustainable development through the advancement of the bioeconomy (Aghbashlo

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et al. 2019; Usmani et al. 2021). The economic adaptations to systems focused on residual biomass use in closed cycles have promoted the development of strategies to merge waste management with industrial processes. Thus, stimulating the by-products reuse, aiming to efficiency increase and environmental damage reduce, integrating waste management and the biomaterials and energy production in biorefineries (Aghbashlo et al. 2019; Ubando et al. 2020; Usmani et al. 2021).

The residual biomass processing in biorefineries has been highlighted in recent years, as it presents an attractive strategy to improve industrial efficiency and promote the bioeconomy. In biorefineries, biomass is used to maximize its applications, converting it to different products with added economic value (Banu et al. 2021). In this scenario, lignocellulosic biomass is being widely studied. It is a renewable and abundant resource, generated in large volumes in agricultural and industrial processes. It is one of the most exciting bioresources for biorefineries.

The majority composition of cellulose, hemicellulose, and lignin has essentially made lignocellulosic biomasses of interest as a raw material since these structures can be fractionated and converted into various ‘green’ chemicals, biomaterials, and biofuels and can supply market demand for products that are currently mainly obtained from petrochemical sources (Alonso et al. 2017; Pellegrini et al. 2020). In contrast, as well as the structure is critical for the importance of lignocellulosic biomass in biorefineries, it is also a significant challenge. The biomasses recalcitrance challenges biochemical routes for valuing systems, which interact with each other through chemical bonds that vary in each biomass by type, origin, composition, degree of crystallinity, and polymerization (Pellegrini et al. 2020).

The lignocellulosic biomass valorization is only achieved through integrated biorefinery. It is environmentally friendly and has less generation of compounds that can result in microbiological inhibition. A holistic view of processes ensures the better exploitation of the structures through conversion into different products, such as biopolymers and organic acids, pigments, and biofuels (Ruiz et al. 2020; Banu et al. 2021). Among the various routes for obtaining products in biorefineries, enzymatic catalysis is widely explored.

Enzymes are amino acid polymer macromolecules that can vary in molecular weight and have catalytic sites buried in hydrophobic pockets in their structure, which determines the specificity of the substrate to which the enzyme has an affinity (Singh et al. 2016). The hydrolysis of lignocellulosic biomass structures is performed by different enzymes, which can be subdivided into three large groups: (1) enzymes capable of degrading lignin, which includes laccases and peroxidases; (2) cellulolytic enzymes, which are the cellulase group capable of converting cellulose to glucose; (3) hemicellulases enzymes, which correspond to an enzymatic cocktail capable of cleaving hemicellulose bonds; this group is heterogeneous and usually has as primary representative the xylanases (Scapini et al. 2020; Saldarriaga-Hernández et al. 2020). In addition, enzymes are responsible for the hydrolysis of other structures such as amylases, proteases, pectinases, and lipases.

The expansion in the commercial applications of enzymes and the advancement of technologies for second-generation ethanol production have resulted in a growth in the enzyme production market. Currently, almost 75% of the enzymes produced on an industrial scale are hydrolytic, with a vast industrial application in sectors such as pharmaceuticals, textiles, biofuels, and food (Fasim et al. 2021). Until 2026, the enzyme market is projected to reach USD 1.5 billion, stimulate mainly by second-generation biofuels (Research and Markets 2020). This scenario highlights the biocatalysis importance in the biorefineries context strengthening the bioeconomy since enzymatic processes are generally conducted under ambient temperature and pressure conditions and are mainly relatively easy to integrate into cascade processes. Furthermore, biocatalysis complies with the green chemistry principles, raising as an innovative and sustainable technology, and due to advances in biotechnology, it has become a process with economic viability (Sheldon and Woodley 2018).

In this perspective, this chapter will present the significant advances in enzymes application in the lignocellulosic biomass biorefineries context. The relevance of biomass as a raw material with high aggregate potential will be addressed, and how the biomass structures can be converted to products in integrated processes using enzymes. Perspectives and challenges of the biocatalysis scenario in biorefineries will be discussed.

17.2 Lignocellulosic Biomasses as a Raw Material with High Value-Added

Several raw materials can be proposed for a waste biorefinery; some will stand out due to their chemical, physical, and constituent properties. Lignocellulosic biomass can be subdivided into municipal solid waste (organic waste components), agricultural waste (corn straw, sugarcane bagasse, rice husk, straw cereals), forest residues, and residues derived from the pulp and paper industries (chips and wood shavings) (Yao et al. 2018; Sahoo et al. 2019; Lin and Zheng 2021). The composition based on cellulose, hemicellulose, and lignin makes these different biomasses have a high potential for conversion into high value-added products.

The chemical formation of the biomass is an important parameter that determines the potential as a biorefinery feedstock. Residual biomass is composed of cellulose (35–50%), hemicellulose (20–35%), and lignin (15–30%), which may vary according to the conditions and geographic location of the crops. Cellulose is a linear polymer organized into microfibrils through cross-linking between various hydroxyl groups, providing a rigid structure and hydrogen bonds and Van der Waals forces. Hemicellulose is a heteropolysaccharide, highly branched with an acetyl group composed of C5 and C6 sugars, pentoses, and hexoses. Lignin is a heteropolymer, amorphous, and branched. Due to this, biomass with lower lignin content is more easily disintegrated since lignin provides structural resistance to the biomass (Islam et al. 2020; Vu et al. 2020; Clauser et al. 2021; Duque et al. 2021).

Emerging technologies for lignocellulosic biomass valorization must integrate two main steps: (i) the structure fractionation that aims to separate the fractions of

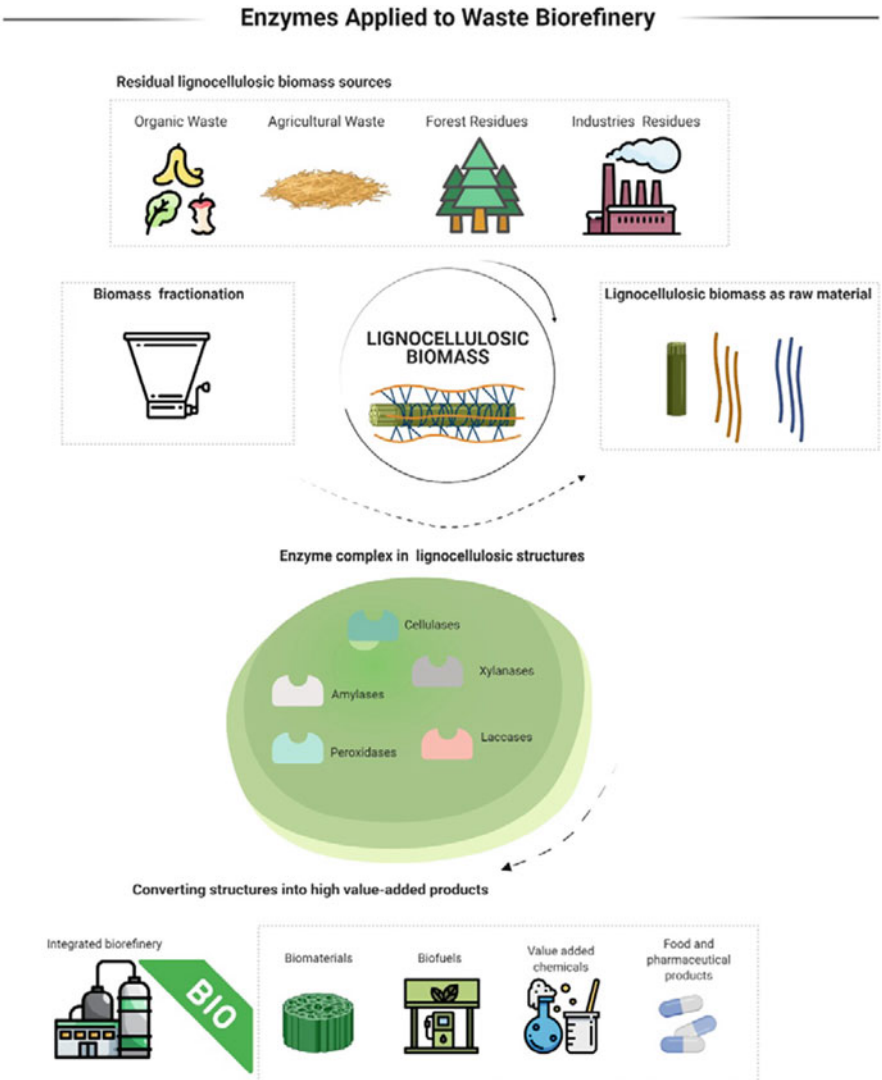

Fig. 17.1 Illustrative scheme of the use of biocatalysis in the valorization of lignocellulosic biomass. (Created by BioRender)

lignin, hemicellulose, and cellulose; (ii) the processing of individual fractions into high value-added products, which can be carried out through enzymes (Banu et al. 2021). Figure 17.1 illustrates the steps of converting lignocellulosic biomass into high value-added products.

To improve the accessibility of lignocellulosic biomass, the structure fractionation by pretreatment step is essential. This step makes it possible to increase the accessibility to the primary residual raw material (*e.g.* lignin, cellulose, hemicellulose, pectin, among others). Pretreatment influences directly process based on biocatalysis since it will facilitate the access of the enzyme in the affinity structure.

Different pretreatments can be used to biomass fractionate, and the action mechanisms can separate into physical, chemical, biological, and combinations methods. Anyway, the pretreatments aim for significant changes in residual biomass, like particles size, structure, and composition. Concerning biocatalysis, which is expected after pretreatment to achieve biomass hydrolysis efficiency, making the biomass accessible and reactive in places that make the hydrolysis rate more flexible and possibility the obtention value products (Al-Battashi et al. 2019).

Although the pretreatment makes the residual biomass more homogeneous and facilitates its use, it should be considered that the process can cause inhibitory effects, interfering with the metabolism of microorganisms and enzyme mechanisms in the residual biomass bioconversion steps. Inhibitor compounds can be divided into process-derived inhibitors (furan derivatives) and raw material-derived inhibitors (*e.g.* acids and phenolics). But not all inhibitors formed during pretreatment are inconvenient, depending on the products intended to be obtained in the biorefinery, since some of these compounds have value-added and can be applied in other processes. For example, furfural and its derivatives can replace chemical products, offering possible recovery and efficient use of these compounds (Treichel et al. 2020; Patel and Shah 2021).

After pretreatment, ideally, biomass fractions that can be converted into different products are obtained. And in this scenario, biocatalysis stands out since enzymes can intermediate these conversion processes with high efficiency and affinity in environmentally safe operations with low energy expenditure.

17.3 Biocatalysis of Lignocellulosic Structures

The lignocellulosic biomass fractionation structures allow three different streams to be valued: cellulose, hemicellulose, lignin. Each structure has conversion characteristics, is dependent on different enzymes, and can be converted to a range of building blocks, which can be used as raw material to generate other products. In this section, the structures of lignocellulosic biomass are treated separately with the potential of biocatalysis of the structures for valorization in biorefineries.

17.3.1 Cellulose

Cellulose is a homogeneous, linear polysaccharide formed by glucose monomers linked by hydrogen bonds between and within chains, which is why its recalcitrant nature. This structure is composed of the plant's cell wall and is the most abundant and significant polymer globally (Champreda et al. 2019).

The cellulose depolymerization via enzymatic hydrolysis requires a cellulases enzymatic cocktail with synergistic action that allows the cleavage of the structural bonds until obtaining glucose. Three enzymes represent the major cellulases, named: exo-glucanases (cellobiohydrolases: CBH), endoglucanases (EG), and β-glucosidases (β-GLU). This classification is based on the depolymerization stage that the enzymes attack, that is, on the structural enzyme–substrate affinity (Saini et al. 2015; Scapini et al. 2020; Barbosa et al. 2020; Patel and Shah 2021).

EGs act in the amorphous region of the cellulose structure and promote random attacks on internal and amorphous β-glycosidic bonds. This cleavage causes the loosening of the structure. It reduces the length of the cellulose chain, promoting the opening of new ends and the oligomer's release of different lengths being the main hydrolysis products. Other enzymes easily attack these new ends generated by the EG hydrolysis in the cellulose structure. Synergistically, CBH is enzymes with an affinity for the crystalline region of cellulose and can act on the reducing ends of the structure by the action of CBH I (exo-1,4-β-cellobiosidase) and at the non-reducing ends by the action of CBH II (exo-1,4-β-D-glucanase) generating cellobiose. And β-GLU is capable of cellobiose hydrolysis structures, and its main product is glucose formation from non-reducing ends. CHB and β-GLU are mainly differentiated by the former having catalytic preference in longer forms and by the slower rate of hydrolysis of β-GLU due to the degree of polymerization of the substrate (Saini et al. 2015; Liao et al. 2016; Jayasekara and Ratnayake 2019; Adsul et al. 2020; Barbosa et al. 2020).

In industrial cellulases production, fungi are preferred over bacteria, and within fungi, the *Trichoderma reesei* strain is the most used, mainly for application in biofuels. Other fungi of the *Penicillium* sp. and *Aspergillus* sp. are also industrially exploited to produce cellulases. However, no strain efficiently produces all cellulase enzymes for the development of a cocktail that has high performance in lignocellulosic biomass, because in nature, substrate deconstruction rarely occurs in isolation by a single microorganism, requiring a collective effort to produce enzymes with different affinities (Bischof et al. 2016; Adsul et al. 2020).

In second-generation ethanol production, discussions on the cellulase application are already well known, which has advanced in the last decade and has been crucial to improving the economic viability of the application of the enzyme in large-scale processes. The global enzyme market is dominated by companies like Novozymes (Denmark), Genencor/DuPont (Holland), Solvay Enzyme (Germany), DSM (Holland), and Diádico (USA) (Champreda et al. 2019). Due to the cellulosic ethanol demand, the cost of producing cellulases has declined over the last decade. Initially, obtaining enzymes for biomass hydrolysis cost almost half the amount invested in biofuel production. The expansion of biofuel production and advances in research have reduced the cost of the enzyme from nearly USD 2 per gallon of ethanol in 2010 to approximately USD 0.30 in less than five years (Biofuels Internacional 2014).

The great challenge in biocatalysis in lignocellulosic biomass biorefineries involves developing enzyme cocktails that are efficient for biomass with different characteristics and is possible to obtain the complete hydrolysis of the biomass polysaccharides. Thus, the industrial development of enzymatic cocktails is relevant, but it should not be the only strategy. Therefore, studies that aim to address the bioeconomy by cellulosic ethanol conversion and high value-added products through biocatalysis have focused on processes that allow cost reduction and improvement in reactor operation. Increased solids loading, reduced enzymatic load, operating parameters, biomass characteristics, and applied pretreatment are essential factors to be considered for cellulosic ethanol biorefineries (Patel and Shah 2021). In addition to prospecting for microorganisms strains and genetic engineering to increase the genes expression responsible for the cellulase production (Adsul et al. 2020). Microorganisms capable of expressing enzymes with the potential to act at room temperature (25–30 °C) with high conversion efficiency are desired for the biofuel industry, considering the possibility of carrying out fermentation and hydrolysis processes in the same reactor to obtain ethanol (Scapini et al. 2020).

In recent decades, studies have focused on enzymatic hydrolysis with increased substrate loading to increase ethanol production's sugar concentration. However, growing solids loading can be challenging by reducing free water content at concentrations greater than 20% (w v^{-1}) due to reduced mass transfer which can result in lower efficiencies, and generally the need to increase the enzyme load, which can increase process costs (Ying et al. 2021). Enzymatic immobilization has also been widely evaluated and is a promising technology and has emerged again with studies focused on nanotechnology (Qamar et al. 2021). However, the cellulosic ethanol production in biorefineries can be a challenge, considering more unit operations, but it presents itself as a promising technology with potential for integrated processes. Recently, cellulase enzyme recycling has been explored by the reinserting technique of the non-hydrolyzed solid into the reactor, considering that up to 50% of cellulases can be adsorbed on the biomass surface (Xin et al. 2020; Ying et al. 2021). These enzymes can be recovered by desorption processes and reinserted into the system or reused by inserting the unhydrolyzed solid. In this scenario, two effects need to be considered; the positive impact of enzyme reuse that can reduce the cost associated with biocatalysis; and the negative impact due to cellulase inhibition processes by the presence of non-hydrolyzed solids charge (Xin et al. 2020). Promising results have been observed, such as a 50% reduction in the enzymatic load of cellulases in poplar biomass and corn stover (Xin et al. 2020; Ying et al. 2021).

In addition to its use in cellulosic ethanol, the cellulose conversion into monosaccharides catalyzed by cellulases is of interest for obtaining other products and biofuels in biorefineries. 2,3-Butanediol was obtained by fermentation with *Enterobacter ludwigii* mutant strain from brewery residual lignocellulosic biomass through cellulase enzymes after physicochemical pretreatment (Amraoui et al. 2022). The cellulases cocktail improved biohydrogen production by agave bagasse in a continuous system, demonstrating a better reaction balance and competitiveness in costs and productivity (Valencia-Ojeda et al. 2021). In lactic acid production by co-fermentation of food waste and mushrooms, the cellulases of *A. niger* increased the reaction yield by 22.97% compared to the control group with commercial enzymes, demonstrating the potential of prospecting strategies for non-commercial enzymes for biorefinery processes (Ma et al. 2021). In the pulp and paper industry, cellulases enzymes may be required in the processing or the recovery of waste from this sector (Subhedar et al. 2015; Arthur et al. 2021).

Cellulosic ethanol production biorefineries are still a promising scenario for cellulases application, but not the only one to be intended. In the biorefinery context, cellulases have been increasingly explored for strategies beyond ethanol production, which has expanded the biocatalysis scenario, expanded the enzyme market, reduced process costs, and made more accessible the cellulases' uses and other enzymes for different purposes. Expanded by the search for a more sustainable economy, cellulases application routes in product development with wide applicability have been explored. It is a potential strategy for future perspectives in biotechnology.

17.3.2 Hemicellulose

Hemicellulose is a heteropolysaccharide with an amorphous structure, branched with short side chains, easy to degrade and that makes up approximately 20-35% of the lignocellulosic biomass. This structure is present on the plant's cell walls, being composed of pentoses (D-xylose and L-arabinose) with a minor part of hexoses (D-mannose, D-glucose, and D-galactose) containing sugar acids, and inter-linked to an intricate three-dimensional network of lignin and cellulose (Champreda et al. 2019; Hazeena et al. 2020; Clauser et al. 2021). Based on structural composition, hemicelluloses are divided into four main classes: xylans, mannans, xyloglucans, and mixed-link β-glucans (Qaseem et al. 2021). Due to its diversity of structural components, hemicellulose requires a cocktail of enzymes with various specificities so that complete conversion of monomeric units is possible (Limayem and Ricke 2012).

The hemicellulose structure is degraded by enzymes, which compound the large group of hydrolytic and non-hydrolytic enzymes (Moreira and Filho 2016). This hydrolytic enzymes group is formed by two different types corresponding to substrate specificity: endo-1,4-β-xylanases and β-D-xylosidases (Polizeli et al. 2005). Among the hydrolytic enzymes capable of cleaving hemicellulose, xylanases are generally highlighted for their ability to cleave xylan bonds and convert xylose. Other enzymes with endo and exo mechanism action were reported, which increases the hemicellulose hydrolysis, *e.g.*, α-arabinofuranosidase, ferulic acid esterase, acetyl xylan esterase, and α-glucuronidase (Champreda et al. 2019; Adsul et al. 2020). Industrially, xylanase enzymes began to be produced in the 1980s for animal feed preparation and later expanded to be used in the food, textile, and paper industries. And as well as in cellulases production, fungi are predominantly used, mainly from the *Trichoderma* and *Aspergillus* genera (Polizeli et al. 2005).

The hemicellulosic structure was not explored in scientific studies a few years ago, is considered a by-product of second-generation ethanol production. However, with the advances in the bioeconomy and biorefineries concepts, it was realized that neglecting the co-products that can be obtained in parallel with the primary processes results in economic unfeasibility, and the techniques become non-competitive when compared to oil refineries (Abejón 2018; Ubando et al. 2020; Scopel and Rezende 2021). This scenario was explored by the academic community and resulted in unquestionable advances in techniques for studying the hemicellulose structure. In a bibliometric analysis developed by Abejón (2018), after 2012, the exponential growth of scientific production was found regarding hemicellulose derivatives valorization. After 2016, the development of scientific articles was even more significant. Using the *Web Of Science* platform (keywords 'valorization' and 'hemicellulose') can be observed 34 scientific papers were published in 2016 and 179 in 2020.

In a lignocellulosic biorefinery context, sugars derived from the enzymatic hydrolysis of hemicellulose can be applied in various industrial sectors. These compounds play an essential role in the context of biorefineries, being considered building blocks for the range of possible applications. Hemicellulose compounds can be converted into biofuels, organic acids, sugar alcohols, or furans (Ajao et al. 2018).

Xylooligosaccharides (XOS) are one of the leading products derived from hemicellulose commercially exploited, mainly due to their application in the food industry as a prebiotic (Lian et al. 2020; Valladares-Diestra et al. 2021). For prebiotics, the DP of XOS is relevant and is indicated to be between 2 and 6 (Samanta et al. 2015). Therefore, in the preparation of xylanase cocktails, the β-xylosidase activity must be low, considering that this enzyme acts on oligomers for xylose production, not being desired when the objective is the XOS production (Cho et al. 2020; Lian et al. 2020).

The enzymatic hydrolysis of the xylan structure to obtain XOS is an interesting biotechnological route as it does not produce by-products and because of its high specificity, in addition to not relying on robust equipment as it acts at ambient temperature and pressure (Lian et al. 2020; Valladares-Diestra et al. 2021). The enzymatic hydrolysis of wheat straw for the XOS production in DP 2–6 demonstrated results superior to 90% of conversion with 5 h of hydrolysis due to the combination of endo-1,4-β-xylanases and β-glucosidase enzymes (Álvarez et al. 2017). A strategy of autohydrolysis, nanofiltration, and enzymatic hydrolysis from alkaline xylan extracted from corn straw demonstrated high hydrolysis efficiency (96–98%) for XOS production by adding the enzyme xylanase and high conversion yield (41.22% in 100 g of xylan) (Lian et al. 2020). Recently, studies have demonstrated the potential for the xylanases production using lignocellulosic biomass and applying it to the XOS production, presenting as a strategy enzymes production in biorefineries aiming at compounds production with high value-added and as a possible commercialization product (Pereira et al. 2018; Valladares-Diestra et al. 2021).

Hemicellulose monomers are also products of interest in biorefineries. The hemicellulolytic enzyme cocktails can generate products such as xylose, which is generally exploited for biofuels production (mainly ethanol) and xylitol production. In the scenario of converting xylose to ethanol, different strategies are still being explored and expanded in recent years to improve the efficiency and yield of the process. The xylose production by a hydrolysate rich in hemicellulose-derived oligomers by enzymatic routes is an area that advances scientific knowledge.

Although it still faces some gaps, the biggest challenge of ethanol production from xylose is concentrated in the fermentation process of this pentose, which prospecting yeasts have explored, such as *Scheffersomyces shehatae* and *Scheffersomyces stipitis* (Hickert et al. 2014; Cadete et al. 2017), and genetic engineering as an alternative to improve the efficiency and yield of these processes (Chandel et al. 2018; Lee et al. 2021). The advancement of scientific research on ethanol from pentoses is an area that tends to have significant biotechnological development over the next few years, to improve the yield of ethanol biorefineries.

Another product derived from hemicellulose monosaccharides obtained from enzymatic routes is the xylitol ($C_5H_{12}O_5$). This product is a sugar-alcohol with lower caloric content that made this product of great importance for the pharmaceutical and food markets (Dasgupta et al. 2017). The xylitol production in biorefineries is of great interest, mainly because it is among the 12 main building blocks cited by the United States Department of Energy (Werpy and Petersen 2004), enhancing economic gain in integrated processes. In 2015, the global xylitol market was valued at $737.2 million, and there are projections to grow 6.6% from 2016 to 2025. Most interesting are the prospects that the largest xylitol manufacturers are focusing their research on reducing production costs and environmental footprint by introducing innovative technologies, such as biotechnological routes (Grand View Research 2017).

The xylitol production from lignocellulosic biomass generally occurs after fractionation processes that solubilize the compounds of the hemicellulose structure and result in hydrolysates rich in XOS (low DP) xylose. These hydrolysates can be used in biotechnological routes that apply microorganisms for xylitol conversion. The biotechnology route produced xylitol from D-xylose (present in the hemicellulose hydrolyzate) is carried out by fermentation, usually conducted by yeasts dependent on a metabolism leading to metabolic pathways that producing two enzymes; xylitol dehydrogenase and xylose reductase; resulting in xylitol (Xu et al. 2019). Among the microorganisms used, yeasts of the *Candida* genus stand out for their ability to produce xylitol from xylose (Mohamad et al. 2009; López-Linares et al. 2018). Other yeasts of the genera *Scheffersomyces* and *Spathaspora* have also shown high potential for this process (Dall Cortivo et al. 2020).

Obtaining hemicellulose monomers for conversion into products demonstrates outstanding potential for biorefineries advancement. And along with these advances, enzymatic approaches have also been highlighted for making the process more sustainable and highly specific. It is important to emphasize that studies that performed an economic analysis of biomass biorefineries demonstrate that it is essential for processes viability that all lignocellulosic fractions are used to develop a range of products for different industrial sectors (Medina et al. 2018).

17.3.3 Lignin

Lignin is a major natural aromatic heteropolymer present in nature and represents 15–30% of the dry weight biomass of the plant's cell wall (Ragauskas et al. 2014). Although the structure and composition of lignin vary in each biomass, the primary lignin structure is compound by three alcohols molecules or monolignols: ρ-coumaryl, coniferyl, and sinapy; these structures can result in three phenylpropanoid monomeric units: ρ-hydroxyphenyl (H), guaiacyl (G), and syringyl (S); and can be classified according to origin (Davis et al. 2016; Pang et al. 2021). The radicals coupling between monomers results in forming a wide variety of possible bonds between the units, including ether and C–C bonds (Pang et al. 2021). The main challenge of lignin valorization in biorefineries lies in the structure: it is heterogeneous, recalcitrant and the variations concerning the origin biomass; *e.g.* lignins obtained from softwood are mainly composed of G, with low levels of S, and absence of H. Lignins got from grass possess G and H equally with more molecules of H than softwood and hardwood. Hardwood lignin contains a mix of G and H with few traces of H. Hardwood lignin has both G and S, including two or three methoxy groups included per aromatic ring. In addition, the methoxy groups inhibit the aromatic rings from forming specific linkages, resulting in a linear and resistant structure compared to softwood (Fisher and Fong 2014).

Lignin is used in biorefineries mainly for energy production by combustion, and the exploration of lignin as co-products with high added value has recently emerged with more prominence. This scenario is visualized in the economic market when only 2% of lignin waste is used commercially (Schoenherr et al. 2018; Nguyen et al. 2021a). It is estimated that most lignin is used as a form of lignosulfonates, applied to building materials, low-grade fuel, or discarded as residue, ignoring the capacity and usability of lignin applied to products with high value-added (Cao et al. 2018). The market involved in the large-scale production of lignin was estimated at USD 954.5 million in 2019 (Grand View Research 2020). Economic valorization of lignin for biofuels and bioproducts can significantly promote lignocellulosic biomass biorefineries (Ragauskas et al. 2014). Many strategies tend to explore new applications in these scenarios, and biotechnologies will be developed, with an even more significant growth expected in the coming years.

Biological degradation of lignin, mainly using fungi (*e.g.* white-rot fungi) and some bacteria, is accomplished through the intermediary of ligninolytic enzymes. This enzyme group capable of degrading lignin is divided into lignin-modifying enzymes and auxiliary enzymes, which most commonly include peroxidases and laccases, with different substrate affinities (Shin et al. 2019; Scapini et al. 2020). Different peroxidase types as lignin peroxidases (LiP), manganese peroxidases (MnP), versatile peroxidases (VP), and dye-decolorizing peroxidases (DyP) are lignin-modifying enzymes (Lambertz et al. 2016). These enzymes can act as auxiliaries in the depolymerization of lignocellulosic biomass to obtain products from lignin monomers and can be combined with thermochemical pretreatment processes (Nguyen et al. 2021a).

After depolymerization, lignin monomers can be converted to industrially relevant chemicals by biological processing. These processes are carried out by microorganisms and mediated by intracellular enzymes in different degradation pathways (Davis et al. 2016). Due to the complexity and diversity of the structure, hydrolysates of lignin derivatives after fractionation are a mixture of different compounds, such as guaiacol, ferulic acid, vanillin, vanillic acid, coumaric acid, syringic acid, and other products (Nguyen et al. 2021a). They can be commercialized building blocks for other industrial processes or as a source of nutrients to develop integrated systems.

These degraded lignin monomers can be intermediates in the conversion of compounds such as vanillin, which is currently one of the main compounds obtained from lignin (Ragauskas et al. 2014; Davis et al. 2016; Harshvardhan et al. 2017; Nguyen et al. 2021a). Other products that biological conversion processes can obtain from lignin monomers is muconic acid (Sonoki et al. 2018), polyhydroxyalkanoates (Li et al. 2019), lipids that the accumulation of phenolic compounds can acquire (He et al. 2017), coumaric acid (Jung et al. 2016), and others (Nguyen et al. 2021b).

Of all the fractions that make up lignocellulosic biomass, the development of biological processes for lignin conversion is the most limited; however, it has been explored by several research indicating important advances for the monomer's valorization. In the biorefinery context, the lignin valorization is highlighted by the economic relevance of the compounds obtained from this structure and the importance of advances in genetic engineering of microorganisms that have high efficiency for application on an industrial scale.

17.4 Perspectives and Insights

The scenario proposed by a biorefinery based on lignocellulosic biomass is mainly to reduce costs, focusing on value-added multi-products production with environmental and investment security. One of the obstacles in biorefineries is overcome by using lignocellulosic biomass, which is the cost of the raw material associated with the opportunity to minimize environmental damage through integrated waste management (Patel and Shah 2021).

The use of residual biomass offers numerous possibilities for obtaining value-added products capable of stimulating the market in commodities. For this, biomass conversion technologies must be interconnected and with a common goal: transforming biomass into valuable products for society and minimizing the need to use raw materials derived from energy crops that compete with food (Champreda et al. 2019).

The enzymes used for the products derived from cellulose, hemicellulose, and lignin fractions are promising and are already a reality in some industrial processes. Biocatalysis methods are considered environmentally safe, generally do not require chemical addition, and act under mild conditions. In addition, the high specificity of lignocellulosic enzymes allows for a vast catalogue of building blocks, which can be converted into a range of high value-added products and biofuels in biorefineries.

Bottlenecks for increased efficiency, on-site enzyme production, and reduced process costs by consolidated systems are the main challenges of biocatalysis. Also associated with the need to design efficient centralized enzyme cocktails for the target biomass.

The strengthening of lignocellulosic biorefineries is an emerging and necessary market. It is required to think of ways to value-added to waste, transforming them into rich biomass through biocatalytic processes. Contemplating economic development with promising materials and high value-added will make biorefinery platforms more functional, multidisciplinary, and technological. For this, multidisciplinary work will be necessary, starting with public policies and cooperation between scientists, universities, investors, industries, and society (De Corato et al. 2018).

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Part III

Waste to Energy–Food–Feed–Chemical–Material Technologies (WtEFFCM-Tech)

Chapter 18
Waste to Chemicals

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Abstract Waste is generated globally in various sectors like forest, food, agriculture, wastewater treatment plants, and industrial left out. Globally, various research groups have explored these wastes as a sustainable resource for the production of energy (biofuels), feed, chemicals, and value-added materials. These wastes are primarily biodegradable and underutilized. Reduce, recycle, and reuse are the common terms that come in waste management, in the current scenario, "recover and reutilize" has also been added to it since it is a valuable resource. Aim and need for sustainable production and latest technologies pave way for the usage of waste biomass for synthesis of valuable materials. Platform chemicals (lignin, biofuels, bioactive compounds, Nano cellulose, 5-Hydroxymethyfurfural (5-HMF), etc.) were produced via fermentation, depolymerization, hydrothermal liquefaction, etc. from waste biomass. Value-added products recovery primarily depends upon the biochemical composition of waste. Processing of renewable and abundantly available waste helps in reduction of production costs and environmental concerns. This book chapter provides the routes for sustainable production of platform chemicals from waste with simultaneous solution of effective waste management.

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18.1 Introduction

Research is being undertaken on the use of waste with a great deal of interest in transforming waste into an alternative feedstock that may produce green energy and valuable items while leaving a low carbon footprint. Waste recovery has become a crucial need for treating biodegradable organic fractions of waste in certain operating circumstances using biocatalysts. As a result, a massive change from waste disposal to reuse has taken place recently. Waste-based combustion and bioproduct production have significant promise for climate change mitigation, energy independence promotion, and rural economic revitalization (Mohan et al. 2016; Sarkar et al. 2018).

Solid organic waste has received specific attention, which generally involves an organic biodegradable component of less than 85–90% moisture content. Sludge, municipal waste solid (MSW), animal waste, garden waste, food waste, agricultural waste, animal waste, etc. might be categorized as solid organic waste. Improper handling of the sector might result in subsequent social, economic, and environmental detrimental effects, so scientists and policy makers require more attention (Chen et al. 2020).

The world's focus is on regulating and controlling urban energy, water and land consumption for reduced utilization, and wastewater and solid waste management and recycling for the betterment of quality of life and public well-being. A developed country's average citizen produces a lot of debris. Hence, waste management is necessary. The previous system of management employed involves collecting and transporting waste to disposal facilities that have a major influence on society and the environment (Rana et al. 2020). The growing need for green energy, bioactive materials, and biochemicals in today's world has encouraged researchers to create green energy technologies in order to process food waste. Bio-rich food waste can thus be utilized as a possible feedstock to produce valuable goods (Sharmila et al. 2020).

Food waste is divided into two categories: preventable and inevitable. Preventable food waste may be reduced by taking necessary measures, but inevitable food waste should be managed properly. This problem will be solved more effectively by using the preventable and inevitable food and cooking waste as a source for the production of value-added substances such as fuels and chemicals. Three techniques, such as disposal, reduction, and reuse, can decrease the generation of unnecessary food waste (Trivedi et al. 2020). By adopting a waste to value-added approach, we reduce the negative consequences and also enhance the profit. Food waste are mainly generated during food products production, storage, transportation, and food consumption (Sindhu et al. 2020).

Due to the inherent chemical resources of food waste, it is possible to employ the chemicals with different methods such as extraction, hydrolysis, digestion, and fermentation (Matharu et al. 2016; Packiyadhas and Shanmuganantham Selvanantham 2020). Recent research indicated that the synthesis of fine chemicals from biomass waste is 3.5 times more profitable than biofuel production (Mohan et al. 2016). The unused food ingredients, including seeds, peelings, and decaying leftovers, provide a rich supply of bioactive substances and vital nutrients waste constitutes a rich supply of phytochemicals and vital minerals (Sharmila et al. 2020).

In India, proper waste management is still in its under developmental stage. Thermal conversion, biochemical conversion and chemical conversions are still adopted as common techniques. The processing, purification, and breakdown of rigid polymers into chemicals and fuels are all still extremely challenging. To solve these difficulties, there is a lot of ongoing research and development necessary (Sindhu et al. 2020).

18.2 Waste-Types and Source

Migration of people from rural to urban locations and the industrial revolution have been the major source and primary cause of increase in waste quantum (Amasuomo and Baird 2016), leading to excessive littering and huge landfills (Agarwal et al. 2015). Over a period of time waste started gaining attention requiring proper management rather than simply being disposed of as a nuisance-causing substance (Pradhan et al. 2012). To implement effective management, a detailed diagnosis to classify the waste has become essential. The economy of a region and the industries located characterize the quality and quantity of waste generated (Abdel-Shafy and Mansour 2018). Primarily based on the physical state, waste has been classified into liquid, solid, and gaseous waste (Demirbas 2011; Rajadurai et al. 2021). Waste is classified into two types such as solid and hazardous waste. However, some common characteristics used in the classification of waste include the physical states, physical properties, reusable potentials, biodegradable potentials, source of production and the degree of environmental impact (Dixon and Jones 2005). Management of solid waste is practised not only to have a cleaner environment but also to valorise waste for the recovery of value-added materials. Henceforth, food waste, agricultural waste, and algal rejects have been prioritized. In the present section, focus has been given to solid waste, as liquid and gaseous waste are more source specific, and several mechanisms have been devised to manage them effectively (Rajadurai et al. 2021). Large quantity of waste in solid is generated by Paper industry 27%, yard trimmings 14%, food 15%, plastic 13%, metal 9%, glass 4%, rubber, leather and textiles 9%, wood 6%, and others 3% (Christy et al. 2014; Abdel-Shafy and Mansour 2018). The composition of liquid waste depends on three main sources residential, commercial, and industrial areas (Syed 2006). Gaseous wastes are primarily generated by anthropogenic activities, internal combustion engines, incinerators, coal-fired electrical generating plants, and industrial processes. However, when compared to liquid and gaseous waste, solid waste does not flow like water or gas. Examples include paper, wood, metals, glass, plastic, and contaminated soil. Solid wastes can be hazardous or non-hazardous. Aesthetic problems (litter and odours), leachate from the infiltration of water through the waste, and off-gases resulting from biodegradation are the major problems associated with non-hazardous solid waste (Ahsan et al. 2014). An intense understanding of this category of waste before identifying its potentials in valorisation hence becomes important.

18.2.1 Food Waste

Among the most common sources of food waste in India are food production industries, commercial shops, hostels, restaurants, commercial shops, private residences, and airport cafeterias. Food waste occurs for a variety of complicated reasons throughout the food production chain. The farm produces waste from unharvested food. Trimming for end-product usage might be required during product production, resulting in edible sections being underutilized and causing waste. The need for variety and an abundance of food results in waste at residences. For example, a customer may prefer a different variety of food, but she or he may lack the necessary skills to reuse the food and properly preserve it. The majority of food prepared or purchased is unplanned, resulting in either over-purchasing or food deterioration. Many families are attracted to buying a large quantity of food at once in order to take advantage of the low-cost per unit offer. Perishable goods account for around 80% of food waste, including meat, milk products, seafood, fresh vegetables and fruits, and certain starchy foods. Non-perishable foods, such as pasta, tinned food, and processed foods, as well as shelf-stable items, are often wasted less since they do not degrade quickly. Because perishable food has a short shelf life and is affordable, it is frequently wasted. Vegetables and fruits are the cheapest and most quickly deteriorating foods. The minimal wasted and perhaps most costly food types are seafood and meat.

18.2.2 Agricultural Waste

The agricultural industry is one of the main sources of agricultural waste materials. These waste materials can either be left to build up and pose a threat to world health and food security, or they can be used as raw materials in the bioeconomy.

Agricultural waste is generated primarily through agricultural operations. But it is not confined to production but also encompasses other aspects of farms and the food supply. Each and every stage of the agro-based food chain has the capacity to produce a substantial amount of agricultural solid waste. The broad categorization of agriculture waste materials covers animal-producing solid waste produced from livestock production for any purpose. Wastes include bedding, broken feeders, and water troughs, to name a few examples. Agricultural solid wastes are generated during the preparation of food or livestock products for human use, such as in slaughterhouses. Bones, hoofs, banana peels, and feathers are all examples of agricultural solid wastes generated throughout the food and meat processing industries. Crop solid waste is related to agricultural solid wastes, which are often generated as a result of crop production operations. Crop leftovers, husks, and others are examples of this type of agricultural solid waste. On-farm medical wastes are wastes that come from things like drugs, insecticides, and vaccines that are used on or in animals. Vaccine envelopes or boxes, disposal needles and vials are all examples of such waste. Solid wastes from horticultural production refer to wastes created during the growth and upkeep of horticultural crops and landscaping for aesthetic purposes. Pruning and grass waste are examples of such waste. In addition to being grown and made for food, industrial agricultural waste is also used to make fertilizer and other products. They are put to other purposes, and it is not improbable that such operations generate agricultural solid waste. Wood processing and trimmings are obvious sources of agricultural waste materials. Paper manufacturing, which uses agricultural goods as raw ingredients, also generates some agricultural solid waste. Pesticides, herbicides, and insecticides, as well as pesticide containers and bottles, produce chemical waste on the farm or in the shop.

18.3 Waste to Value Added Products

Waste disposal reduction and management is the ultimate aim to achieve sustainable development. Waste is generated from local producer to international consumer. This waste can be processed via appropriate techniques for production of value-added compounds.

18.3.1 Waste to Energy

18.3.1.1 Hydro Thermal Liquefaction (HTL)

Hydrothermal liquefaction is ultimately aimed at turning the biomass into biocrude, which may be employed to substitute commercial fossil fuels (Gollakota et al. 2018). The HTL method may employ a variety of current biomasses such as wood, compost, plant material, manure, and sewage sludge as well as wastes from houses, dairy production, and similar fields. However, most biomasses treated in HTL are employed due to their hydrophilic characteristics and the relative ease of producing liquid slurries of biomass particles at pumpable concentrations, usually 5–35% dry solids (Sahu et al. 2020). At high temperatures of 250–500 °C and pressure of 5–35 MPa in pure water or water with co-solvents/alcohols and with or without the addition of catalyst (homogenous/heterogeneous). The biomass HTL treatment produces the following important products: water-soluble products (WSP), biocrude, gaseous products, and solid products (biochar) (Beims et al. 2020).

A broad variety of biomass was used for the use of hydrothermal liquefaction. The utilization of high-moisture biomass without prior drying is one of the advantages of hydrothermal treatment. Cellulose, hemicellulose, lignin, and aquatic biomass such as duckweed, microalgae, animal dung waste, and domestic wastewater can be used as feedstock (Wu et al. 2014). The inclusion of cellulose and hemicellulose in biomass generally yields more bio-oil. Biomass hydrothermal liquefaction necessitates careful consideration of time, temperature, pressure, catalyst, including the utilization of reductive gases (Gollakota et al. 2018).

It is beneficial to raise the temperature within a particular range. Temperature management is vital because, after the oil production reaches its optimum, increasing the temperature hinders biomass liquefaction owing to char formation, secondary decomposition and adnBourdard gas reactions. Temperature selection is also influenced by the biomass kind (Rogalinski et al. 2008). Pressure raises solvent density to enable solvent penetration into biomass molecules, resulting in increased degradation and evacuation. Temperature selection is also influenced by the type of biomass. Between 513 and 583 K, the rate of cellulose hydrolysis in water at 25 MPa increased ten-fold, and at 553 K, % conversion of cellulose was reached in 2 min (Wu et al. 2014). The catalyst greatly impacted the biomass hydrothermal liquefaction. Lignocellulosic biomass includes primarily polymers of cellulose and lignin. The first interacts easily with acid; the latter reacts easily with alkaline. The liquefaction of lignocellulosic biomass in the presence of alkaline catalysts leads to products similar to oil (Mészáros et al. 2004).

A highly complicated combination of liquid products generates catalytically hydrothermal liquefaction of lignocellulosic biomass such as 1,3dihydroxyacetone dimers, soluble polyols, anhydroglucose, 5-HMF, furfural, organic acid and phenolic hydrocarbons. Therefore, the new separation and extraction method for downstream products must be developed from hydrothermal lignocellulosic liquefaction (Wu et al. 2014).

18.3.1.2 Pyrolysis

Pyrolysis is widely recognized as the chemical decomposing of a material by thermo-heating above 250–300 °C. Pyrolysis may be used to break down any molecule, whether non-polymeric or polymeric, in a solid state, liquid state, or gaseous state, and on pure chemicals as well as complex materials (Uden 1993).

Pyrolysis products are divided into three classes: biochar, bio-oil, and gas. The pyrolysis process has an effect on several factors, such as particulate size, type of reactor and reaction conditions, temperature, heating rate, time, gas (nitrogen, carbon, and hydrogen), and feedstock type. The characteristics and yields of pyrolysis products are determined by the interaction of these factors. The solid product (biochar) has a similar composition to charcoal, consisting mostly of carbon and oxygen. The liquid product (bio-oil) has a black or dark-brown appearance and a strong odour, and it has a variety of uses, including transportation fuel alternatives and value-added chemical manufacturing. Hydrogen, carbon monoxide, carbon dioxide, methane, and other low molecular weight hydrocarbon gases make up the gaseous product (Adhikari et al. 2018). Depending on the reaction residence time, the pyrolysis of biomass can be classified as slow (hours to days), fast (10–30 s), or rapid (less than 1–2 s) (Bridgwater 2012). Fast pyrolysis creates a high quantity of bio-oil, whereas slow pyrolysis produces mostly charcoal with a lengthy residence period. Fast pyrolysis generates 75% of liquid, 12% of solid, and 13% of gas, whereas slow pyrolysis gives liquid (30%), solid (35%), and gas (%), respectively. In certain circumstances, the liquid product is split into two phases: dark bio-oil (organic phase) and transparent aqueous phase. A recent pyrolysis research employing rice straw revealed a similar pattern, with fluidized-bed rapid pyrolysis producing more liquid product and a fixed-bed slow pyrolysis reactor producing the more quantity of charcoal (Adhikari et al. 2018; Nam et al. 2015).

18.3.1.3 Anaerobic Digestion

Anaerobic digestion, in green technology, uses available biomass to manufacture biogas through a natural biological process (for instance, food waste, fumes, and bioenergy plants) (renewable methane). Biogas may be utilized for power and heat production or improved as fuel for vehicles or injected into the network of natural gas. Biogas comprises around 45–65% of methane and between 30% and 40% of carbon dioxide, together with minor gases and humidity (Kirk and Gould 2020).

Anaerobic digestion is a complicated metabolic reaction performed by numerous species of bacteria in a number of stages that do not require oxygen to exist. This process generates biogas mostly made from methane and carbon dioxide. Specialized micro-organisms in an anaerobic environment break up complex organic materials (carbohydrates, proteins, and lipids) into molecules with a lower atomic volume that are water soluble (sugars, amino acids, and fatty acids). The main end products of the anaerobic process, called biogas, are methane and carbon dioxide. There are four stages in the total conversion of complex organic matter to methane and carbon dioxide. They are hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Kirk and Gould 2020; Gould 2015).

18.3.2 Waste to Feed

Increased future consumption of animal products will result in a huge feed demand. Meeting the feed demand in a sustainable manner will be a challenge against the backdrop of climate change, food-fuel-feed competition, land degradation, water shortage and biodiversity loss, among others. Food security and wastage of food are interdependent. Food wastage has not only become a resource for valorisation, but has also become an issue of sustainability endangering biotic and biotic components of the ecosystem. Major sources of food waste identify landfills for disposal, especially in developing countries. More than 10,000 tonnes of municipal solid waste, of which one-third is food waste, is disposed to landfills. Decomposition of food waste in landfills produces substantial quantities of methane—a potent greenhouse gas with 20 times the global warming potential of carbon dioxide (Singh et al.

2018). This makes landfilling an unsuitable choice for disposal of food waste in China. Incineration is also not a suitable option because the high-moisture content of food waste results in low net caloric value (Longanesi et al. 2018). It has been predicted that the current landfill sites may be exhausted in the mid to late 2010s. Utilizing food waste as fodder instead of discarding has been witnessed in the past (Salemdeeb et al. 2017). Novel animal feeding operations, diversion food grains, including soyabean, maize, to witness increased breeding in animals have contributed to the fade away of the age-old practises (Banhazi et al. 2012).

18.3.2.1 Waste as Animal Feed

Owing to the lesser growth period and ability to grow in any part of the world, chicken is always in demand. To enhance the chicken productivity, many food waste products are diverted as chicken feed globally. The main concern with feeding food waste to broilers is high lignocellulosic content (Truong et al. 2019). The processing of food waste as poultry feed is also of important because of mould growth. Prevent mould growth by drying or fermenting the food waste is the conventionally followed technique to maintain the nutrient levels in the chicken feed prepared with the food waste. A well-formulated feed based on the requirements of the animal and the nutrient analyses of the feed ingredients is recommended. Among the many food-based industry wastes, bakery waste has been successfully used in broiler feed (Stefanello et al. 2016).

18.3.2.2 Waste as Fish Feed

Food waste can be used to make fish feed instead of going to the landfill, being burned, composted, or digested. Food waste conversion to fish feed on a wider scale has been promoted. However, there is very little information about how food waste can be used as fish feed. DDT and mercury levels were lower in fish fed food waste pellets than in fish fed commercially available feed pellets (Cheng et al. 2016). Mo et al. (2018) suggest that mixed food waste usually has about 20% protein content, which would still be less for lower trophic level fish. Another technique to increase the protein percentage of food waste and decrease the quantity of fibre in food waste for use as feed is the bioconversion of food waste through microbes. Food waste that has a good amount of carbohydrates could be very beneficial for growth. It is still unclear how food waste is used as feed, and additional study is definitely needed.

18.3.3 Waste to Platform Chemicals: Types and Economics

Economic expansion, continued industrialisation, growing population, and technical advancements have sparked interest in finding alternate renewable energy and raw

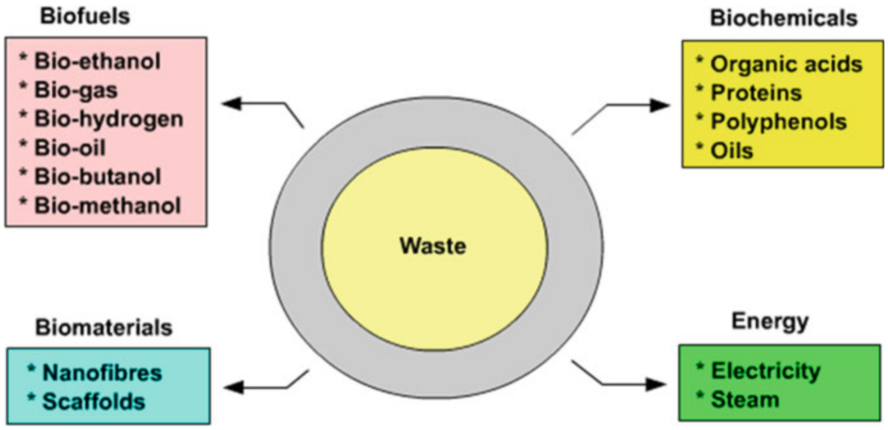

Fig. 18.1 Schematic representation of waste to value-added products

materials to complement the world's limited present resources (Aljammal et al. 2019). Figure 18.1 highlights the various products that can be recovered from waste materials. The following platform chemicals sources: Succinic acid, 2,5-furandicarboxylic acid, glycerol, isoprene, lactic acid, sorbitol, levulinic acid, hydroxymethylfurfural (HMF), xylitol, ethanol, 3-hydroxypropionic acid/aldehyde and furfural are all examples.

18.3.3.1 Hydroxymethylfurfural (HMF)

Hydroxymethylfurfural is a promising biomass-derived platform chemical that can be used to make alternative polymers or liquid biofuels (Su et al. 2009). Hydroxymethylfurfural is a flexible biomass-derived platform compound that may be utilized to make a variety of petroleum-derived compounds (Werpy et al. 2004). In addition, liquid fuels derived from HMF through chemical procedures could be a viable alternative to ethanol produced through fermentation (Román-Leshkov et al. 2007). It is a high-value-added chemical that can be made from biomass (Bozell and Petersen 2010), also has a higher commercial value due to its versatility as a precursor for pharmaceuticals, polymers, resins, solvents, and biofuels (Mukherjee et al. 2015). One of the most important building components for fuels, polymers, and fine chemicals is 5-(Hydroxymethyl)furfural (HMF or 5-HMF) (Rosatella et al. 2011). One of the most appealing platform chemicals is HMF, which is generated from hexose (glucose or fructose) and lignocellulosic biomass (Li et al. 2019).

18.3.3.2 Lactic Acid

Lactic acid (LA) is a biocompatible and biodegradable bio-plastic that can be utilized as a substitute for petrochemical-based plastic materials in the food, chemical, cosmetic, medical, and pharmaceutical industries. It can also be used as a precursor for polylactic acid manufacturing (Abdel-Rahman et al. 2013; Subramanian et al. 2015; Saini et al. 2016). Chemical synthesis and biological fermentative techniques can both be used to make LA. Because of its advantages like as high purity LA, the use of inexpensive renewable substrates, and gentle procedures, microbial fermentation is used to manufacture LA in a wide range of applications (Abdel-Rahman et al. 2011). In 2018, the annual demand for LA was reported to be 1947.2 million tonnes, with a 16.2% yearly increase expected from 2019 through 2025 (Abdel-Rahman et al. 2019a). Microbial fermentations of various renewable resources, which could act as carbon and/or nitrogen sources, can efficiently create LA (Abdel-Rahman et al. 2019b).

18.3.3.3 Sorbitol

Sorbitol, a hydrogenated version of glucose, was chosen as a model system for studying both hydrolysis and hydrogenation in this study (Han and Lee 2012). Sorbitol is widely used as a sweetener, in cosmetics as a moisture controller, and in medical applications. It is also being looked into as a source of hydrogen, alkanes, and value-added compounds like ethylene glycol and propylene glycol (Cortright et al. 2011; Huber et al. 2005). Sorbitol is one of the most important sugar alcohols, and it may be used to make a variety of value-added products such glycerol, glycols, lactic acid, isosorbide, 1,4-sorbitan, and L-sorbose (Deng et al. 2015).

18.3.3.4 Succinic Acid

Succinic acid is a carbon intermediate chemical that is utilized in culinary and medicinal goods, as well as surfactants and detergents, green solvents, and plant and animal growth stimulant chemicals (Akhtar et al. 2014; Nghiem et al. 2017). Succinic acid, a dicarboxylic acid utilized as a precursor for a variety of compounds, is at the forefront of biotechnology research. *Actinobacillus succinogenes* is capable to produce a fairly massive quantity of succinic acid from a wide variety of decreasing sugars which include arabinose, fructose, glucose, lactose, xylose, and sucrose underneath CO_2 (Beauprez et al. 2010; Xi et al. 2013). Succinic acid, as a versatile constructing block that holds a large range of purposes in detergent/surfactant, food, and pharmaceutical industries (Yan et al. 2014), has drawn first-rate interest over the current years (Table 18.1).

Table 18.1 Feedstocks and processing methods and applications of various platform chemicals

Platform chemicals	Feedstock	Process	Yield	Applications
Hydroxymethylfurfural	Carbohydrates/ C_6 sugars	Hydrolysis, Isomerization by Lewis acid and Dehydration	60% over silica composite catalyst 52% from glucose	• For the production of polyesters. • As a potential biofuel. • Well-known component of baked foods. • Used as an indicator for excess heat treatment.
Lactic acid (LA)	Lactobacillus species for fermentation process	Pre-treatment enzyme hydrolysis, LA fermentation, Separation, Purification	0.99 g lactic acid/g lactose	• Used as a food preservative, curving agent and flavouring agent. • Used as a decontaminant during meat processing. • Can undergo self-esterification to form polylactic acid, which is an eco-friendly biopolymer. • Used for the production of yogurt and sauerkraut.
	Acetaldehyde for chemical synthesis	Addition of hydrogen cyanide (HCN) and catalyst, Hydrolysis by sulfuric acid (H_2SO_4)	Greater than 60%	
Succinic acid	Lignocellulosic biomass	Hydrolysis, Fermentation, Addition of water	0.4–0.8 g/g of biomass (72% by *cocos nucifera*)	• Used as an antibiotic and curative agent. • Used in manufacture of surfactants/detergents or foaming agents. • Used as an ion chelator in electroplating. • Used as flavouring agent and antimicrobial agent in food industry.

(continued)

Table 18.1 (continued)

Platform chemicals	Feedstock	Process	Yield	Applications
Sorbitol	Glucose	Addition of water and hydrogen	38.4% from glucose	• Used in modern cosmetics as a humectant and thickener. • Used in mouthwash and toothpaste. • Used as a cryoprotectant additive in the manufacture of surimi, a processed fish paste. • Used as a humectant in some cigarettes.

18.3.4 Waste to Biomaterials

18.3.4.1 Biopolymers

Waste Valorisation to recover value-added products is gaining significance owing to the health and the environmental concerns. Geographical location plays a vital role in the food consumption pattern and the food waste generated. Among many products generated from food wastes, biopolymers are gaining more interest owing to their biodegradability/compostability, biocompatibility, bio-based nature, adequate chemical and mechanical properties to facilitate wide range of applications (Ranganathan et al. 2020), including packaging medicine/food, biosensors, industrial plastics, clothing fabrics, water treatment chemicals, cosmetics, pharmaceuticals, and even as data storage elements (Sanchez-Vazquez et al. 2013). However, biopolymers have limited large-scale industrial applications because of their poor mechanical, thermal, and barrier properties (Wróblewska-Krepsztul et al. 2019). Even with the reported many applications, utilizing all waste materials as useful bioresources still remains a challenge. Reports published by (Nduko and Taguchi 2021) predict that in future Polylactic acid (PLA) and polyhydroxyalkanoates (PHA) will be the key biopolymers in the biodegradable plastic market. Apart from the food waste being explored as eminent substrates for biopolymer synthesis, the effluents from food oil and food waste industries are also being utilized as carbon-rich nutrient substrates for bacterial fermentation to produce PHA.

18.3.4.2 Waste Biomass as Lignocellulosic Feedstock

Biomass waste contains cellulose, hemicellulose, and lignin. Chemical composition of the same finds its application as a value-added compound in several industrial applications. With the increasing potentials of the biomass in waste processing industries, many alternate recovery methods are being investigated by researchers worldwide (Tripathi et al. 2019). The main purpose of pre-treatment is to remove as much hemicellulose and lignin as possible, while simultaneously keeping enough cellulose undamaged (Ballinas-Casarrubias et al. 2016) to produce biomass polymers. The higher yields of cellulose from the biomass are controlled by pre-treatment method that makes recycling of biomass to biopolymer expensive and time-consumptive. Furthermore, the wide variety of raw material composition makes it challenging to generalize process settings even for similar biomass types. Currently, cellulose is extracted from cellulosic biomass using inefficient methods, including sulphite, soda treatment, and kraft, resulting in harmful byproducts. In recent years, new rules have been put in place to deal with growing environmental concerns. They focus on how to turn biomass into useful products in a way that is both safe and environmentally friendly.

18.3.4.3 Agro-industrial and Forestry Wastes for Agglomerated Materials

There is also a lot of waste from farming and forestry that is harmful to the environment and the economy. This waste is made every year. Sawdust particles are suspended in the air, exposing hazardous leftovers to the environment. These residues are utilized to make pellets (Ballinas-Casarrubias et al. 2016); unfortunately, the level of bioaccumulation is quite high, therefore this technology cannot be employed. Usually, these products are used as fuel or to make agglomerated substances, but this is not enough to solve the problem of how to dispose of them (Bożym et al. 2021). The basic material for tequila production is *Agave tequilana*, of which the bagasse is the last residue generated after the plant's head is boiled and squeezed to recover the sugar liquor that will be fermented with *Saccharomyces cerevisiae* to make tequila (Iñiguez-Covarrubias et al. 2001). The National Tequila Consortium reports that 350, 000 tonnes of bagasse residue are generated annually on a dry basis, which is compared to 14.1 million litres of tequila manufactured in 2012. The agave bagasse used as just a feedstock aids in the reduction of environmental deterioration caused by tequila waste accumulation. These chemicals are gathered and disposed of in huge quantities, and they are persistent in the environment. They can be held for up to 6–8 years (Kiatkittipong et al. 2009). The global concern for the utilization of bagasse is commonly used in electricity generation, producer gas generation, charcoal briquettes, pulp, and paper, as well as fiberboard production (Xu et al. 2019; Quereshi et al. 2020).

18.4 Platform Chemicals Synthesis Process

18.4.1 HMF

HMF can be transformed into a platform chemical, 2,5-dihydroxymethyl-tetrahydrofuran, which is a treasured cloth with a broad variety of functions as a solvent and beginning fabric for the manufacturing of polyesters, polyurethanes, and fragrant resins (Lima et al. 2017; Zhang et al. 2018). The molecule HMF can be produced from carbohydrates (glucose, fructose, and cellulose) by means of a chemo-catalytic route significantly mentioned in literature over range of heterogeneous catalysts. Many articles discuss about the manufacturing of HMF from timber-derived cellulose which can be a smooth bulk supply of glucose carbohydrates (Menegazzo et al. 2018; Oozeerally et al. 2019). Such sources are of activity to produce bulk merchandise like plastics (e.g. polyethylenefuranoate, PEF). However, agriculture produces a massive extent of waste containing excessive volumes of carbohydrate feedstock in the shape of (hemi-)cellulose and free sugars (Sarwono et al. 2019; Ito et al. 2016). HMF can be produced through the easy technique of conversion as per Eq. (18.1).

$$\text{Glucan} \xrightarrow{\text{Hydrolysis}} \text{Glucose} \xrightarrow{\text{Isomerization}} \text{Fructose} \xrightarrow{\text{Degydration}} \text{HMF} \qquad (18.1)$$

18.4.2 Lactic Acid

Lactic acid (LA) is used in the culinary, chemical, cosmetic, medicinal, and pharmaceutical sectors for a variety of reasons (Subramanian et al. 2015). In 2018, the annual demand for LA was estimated to be 1947.2 ok piles, with an expected yearly increase of 16.2% from 2019 to 2025 (Abdel-Rahman et al. 2019a). Because of the high purity of the LA, the use of less expensive renewable substrates, and reasonable techniques, LA is generated in a wide variety of conditions by microbial fermentation (Abdel-Rahman et al. 2013). Microbial fermentation reaction process and chemical synthesis reactions are shown in Eqs. (18.2 and 18.3).

$$\begin{aligned} \text{Renewable source} &\rightarrow \text{Fermentable carbohydrates} \\ &\xrightarrow{\text{Micrbial fermentation}} \text{Fermented broth} \\ &\xrightarrow{\text{Recovery\&purification}} \text{Lactic acid} \end{aligned} \qquad (18.2)$$

$$\text{Petrochemical source} \rightarrow \text{Acetaldehyde} \xrightarrow{\text{Catalyst\&Hydrogen cyanide}} \text{Lactonitrile} \xrightarrow{\text{Hydrolysis with sulfuric acid}} \text{Recemic Lactic acid} \tag{18.3}$$

18.4.3 Succinic Acid

In the hydrolysis process, two commercial enzymes, cellulase and cellobiase, are utilized. Cellulase used to have a 75 FPU mL enzyme activity (filter paper activity, FPU). Cellobiase'sβ 1–4 glucosidase recreation used to be 132 CBU mL (Ghose 1987). revealed how to measure the enzyme reproduction of cellulase and cellobiase. EFB is pre-treated. The following are the approaches for a variety of pre-treatment strategies: (i) AA pre-treatment was performed in an autoclave under the following conditions: EFB (20 g) was soaked in 2.5 M NaOH (20% w/v) and heated at 121 °C for 2 h under 0.12 MPa pressure. (ii) Sequential DA-MWA pre-treatment was carried out under the following circumstances: Pre-treatment with diluted acid: 20 g of dry EFB were soaked in an 8% (v/v) H_2SO_4 solution and heated at 121 °C for 1 h in an autoclave. After that, the dilute acid-handled EPB (20 g) was soaked in 200 mL of 2.5 N NaOH and microwaved (model MAS-II microwave, SINEO) under the following conditions: 900 W, 90 °C, and 20 min. The conditions picked were entirely based on previous findings (Akhtar et al. 2015). Both pre-treatment techniques improve the enzymatic hydrolysis of EFB, using cellulase enzymes, as compared to control (untreated EFB), as seen by the increase in glucose content. The influence of different ratios of cellulase and cellobiase enzymes on the enzymatic hydrolysis of DA-MWA prepared EFB was reported, and it was shown that combining cellulase and cellobiase in a 7:1 ratio generated 34.43% more glucose than cellulase alone. As an agricultural waste, EFB might be an appealing substrate for the manufacture of SA since it is less costly and widely available (Akhtar and Idris 2017). Production of Succinic acid reaction from lignocellulosic biomass and petrochemical source was performed as per Eqs. (18.4 and 18.5).

$$\text{Lignocellulosic biomass} \xrightarrow{\text{Hydrolysis}} \text{Sugars} \xrightarrow{\text{Fermentation}} \text{Succinic acid} \tag{18.4}$$

$$\text{Petrochemical source} \rightarrow \text{Maleic anhydride} \rightarrow \text{Succinic anhydride} \xrightarrow{\text{Water}} \text{Succinic acid} \tag{18.5}$$

18.4.4 Sorbitol

A cotton fabric design that used to be provided with the following features: 100% cotton, arranged for dyeing, de-sized, and bleached until today. Lignocellulose is the most abundant and least luxurious type of biomass on the planet, making it a viable feedstock for renewable energy, particularly biofuels, and chemical compounds (Feng et al. 2016). Under the current conditions, the transformation of cellulose into sorbitol is possible (Ribeiro et al. 2017). Following impregnation, the resulting fabric was dried in an oven at 110 °C for a single day. Finally, the catalyst was heated for 3 h at 121 °C under nitrogen float and then reduced for 3 h at 121 °C under hydrogen float. The pattern was previously known as Ru/CNT. After 5 h of response in the conversion of ball-milled cellulose with 50 bar H_2 at 205 °C, a full yield of sorbitol of 51% was obtained. By combining milling cellulose with the catalyst, the yield of sorbitol was increased to 61% in just 1 h of reaction. Equation (18.6) describes the sorbitol synthesis process.

$$\text{Cellulose} \xrightarrow{\text{Water}} \text{Glucose} \xrightarrow{\text{Hydrogen}} \text{Sorbitol} \tag{18.6}$$

18.5 Conclusions

This chapter was devoted to focus completely on utilization of waste as source for recovery of value-added compounds like energy, biopolymers, and as feed material. Initially the possible route of food waste generation was explored, and it was found like marriage halls, educational institutions, and hotels are the leading waste generators. Agricultural wastes are available plenty in our world and its rich in lignocellulosic compounds. In turn all these waste materials are effective candidate for value-added compounds like biofuels, biomaterials, etc. In this chapter, we have identified that pyrolysis, hydrothermal liquefaction, and anaerobic digestion are the common methods that processes waste material for biofuel production. Biopolymers and biomaterials are preferred compounds that are produced from algae, food, and lignocellulosic waste biomasses. Waste utilization paves way and future directions for waste-based circular economy.

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Conflict of Interest
None.

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Chapter 19

Fundamentals for Waste-to-Energy from Anaerobic Digestion Technologies: An Overview

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Abstract Anaerobic digestion (AD) is a mature technology adopted extensively for the microbial conversion of organic substrates into value-added products. This chapter presents an overview of AD, emphasising the process mechanism and current challenges associated with its utilisation in the industry. Moreover, the chapter examines three promising methods to remedy the deficiencies of AD, thereby optimising resource recovery. The techniques discussed are pre-treatment, co-digestion and the use of additives. A comparative economic assessment of the aforementioned options is also provided. The findings reveal that pre-treatment technologies increase the bioavailability of organic matter to microbes for AD, thus enhancing product recovery. However, these processes are costly and energy-intensive, varying linearly in effect with the chemical composition of the substrate used. Consequently, these technologies should be employed selectively. Alternatively, multiple organic substrates may be co-digested. This approach amends the substrate C/N ratio to the suggested optimum range of AD and improves digestion stability by raising the digester tolerance to potential inhibitory compounds. Notwithstanding, the efficiency of this process is highly dependent on feedstock availability and sustainable waste management systems. The role of additives on improving biogas generation efficiency is undeniable. Additives are accessible and more importantly, adaptable for most AD systems. In this chapter, the recent advances in applying different types of additives that can be implemented on a large scale have been discussed.

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19.1 Introduction

Anaerobic digestion (AD) is a naturally occurring biological process through which bacteria degrade organic substrates in anoxic environments into two value products: biogas and a digestate (solid–liquid slurry remaining after the AD process). This technology is well-established and currently utilised for the bioconversion of various feedstock types, including wastewater, sewage sludge, farm animal manure, food processing waste, plant residues, and food waste (Nizami et al. 2017). Figure 19.1 presents an AD flow diagram from feedstock to product (biogas and digestate) and highlights potential applications of these derivatives.

Biogas, the primary product of AD, is composed of 50–70% methane (CH_4), 30–50% carbon dioxide (CO_2) and trace amounts of other gases such as hydrogen sulphide (H_2S), hydrogen gas (H_2) and water vapour (Deepanraj et al. 2014). This energy-dense fuel can be captured and utilised in heating, electricity generation and cooling systems. Biogas may also be purified and upgraded to natural gas for injection into pipelines or utilisation as a sustainable alternative to petroleum-based transport fuels (Mao et al. 2015). Another added value from AD is solid–liquid digestate. The digestate from AD is nutrient-rich, presenting agronomic potential. The solid phase of the slurry contains a high concentration of digested solids which improves its nutritional properties. Nevertheless, remediation is

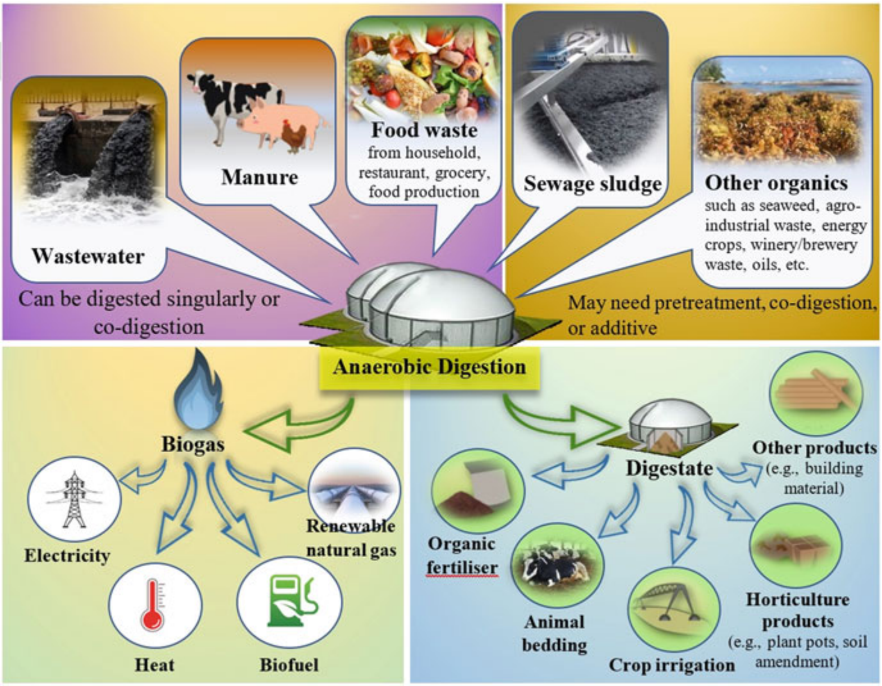

Fig. 19.1 Anaerobic digestion system

warranted before utilisation due to high pathogenic and weed seeds composition. On the other hand, the liquid phase of the slurry can be applied directly to soils as an agricultural fertiliser due to a reasonable nutrient level, in addition to lower pathogen and weed seeds content (Deepanraj et al. 2014).

Anaerobic digestion is an inexpensive and eco-friendly process that mitigates atmospheric greenhouse gas (GHG) emissions. This technology is a viable waste management option as it facilitates solid waste reduction, landfill odour control and groundwater pollution prevention (Bhatt and Tao 2020). From literature, AD technology has been shown to enhance energy production from various biomass. However, the process efficiency is substrate-specific, varying linearly with the feedstock structural and chemical composition (Bougrier et al. 2007; Ngo et al. 2021), in addition to the production of recalcitrant compounds such as H_2S, volatile fatty acids (VFAs) and ammonia (NH_3) during digestion (Montingelli et al. 2016). To remedy the above challenges for enhanced AD performance, several methods, including pre-treatment (Solé-Bundó et al. 2020), co-digestion (Gu et al. 2020) and chemical additives (Cheema et al. 2018) have been investigated.

This chapter provides a comprehensive understanding of the AD mechanism and outlines limitations to the process. Three technologies (pre-treatment, co-digestion and chemical additives) to remedy the deficiencies of AD and optimise resource recovery are discussed. A comparative economic assessment of the aforementioned processes is also given.

19.2 Biochemical Mechanism of AD

The AD process can be sub-divided into four phases: (1) hydrolysis, (2) acidogenesis, (3) acetogenesis and (4) methanogenesis (Bhatt and Tao 2020; Van et al. 2020) as shown in Fig. 19.2.

19.2.1 Hydrolysis

Hydrolysis is the first step of the AD process. It involves the extracellular enzyme breakdown and solubilisation of large complex polymeric compounds such as polysaccharides, proteins and lipids into their soluble monomeric units (sugars, amino acids and long-chain fatty acids). This biotransformation enhances the availability of organic matter for transport across the cell membrane of fermentative bacteria in the subsequent step (Fig. 19.2) (Karuppiah and Azariah 2019; Van et al. 2020). Hydrolytic microorganisms are unique in operation given their low sensitivity to environmental fluctuations and feedstock toxicity in comparison with other classifications of microbes/enzymes (Böske et al. 2014). This specialisation facilitates function across a broad pH spectrum of 4.0–11.0.

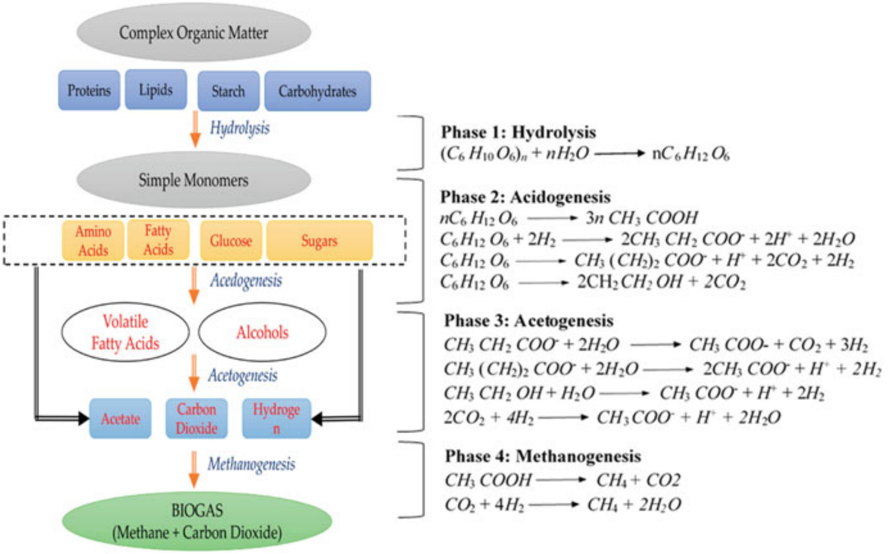

Fig. 19.2 Biochemical pathway of organic matter anaerobic degradation (Bhatt and Tao 2020; Van et al. 2020)

Notwithstanding, the literature suggests the optimum pH working condition for hydrolysis as pH 6.0–8.0 (Zhang et al. 2005). Hydrolytic bacteria are also nutrient specific and can be categorised accordingly as cellulolytic, amylolytic, proteolytic or lipolytic (Karuppiah and Azariah 2019; Pavlostathis 2011). In the AD of lignocellulosic biomass, hydrolysis is the process rate-limiting step. Industrial operations have incorporated biomass pre-treatment technologies prior to AD to overcome this challenge and optimise hydrolytic cleavage (Rodriguez et al. 2017a, b; Thompson et al. 2019). Section 19.4 discusses various pre-treatment techniques which can be applied to biomass for biogas production enhancement.

19.2.2 Acidogenesis

Acidogenesis is the second and fastest phase of complex organic matter anaerobic conversion due to the rapid proliferation rate of acidogens (30 min). During acidogenesis, the monomeric products of hydrolysis are either fermented or anaerobically oxidised (β-oxidation) by acidogens (Sikora et al. 2017). Sugars and amino acids are fermented to H_2, CO_2, alcohols and a mixture of short-chain or VFAs, primarily acetic, propionic and butyric acids (Fig. 19.2). In this process, organic compounds serve as both electron donors and acceptors acids (Karuppiah and Azariah 2019). Alternatively, long-chained fatty acids and alcohols are anaerobically oxidised to H_2, CO_2 and VFAs. Noteworthy, H_2 production via β-oxidation requires the transfer of reducing equivalents directly to hydrogen ions (H^+) (Karuppiah and Azariah 2019; Mao et al. 2015). However, this reaction can trigger H_2 partial pressure build-up in the digester, promoting system acidification and inhibiting the AD process. It is therefore necessary to regulate the H_2 concentration for process stability and thermodynamic viability. Ammonia (NH_3) and H_2S are also generated by amino acid fermentation and must be closely monitored to prevent AD inhibition and system failure. The optimum pH range of acidogenesis is 5.5–6.5, with inhibition triggered at $pH < 4.0$ (Mao et al. 2015; Van et al. 2020).

19.2.3 Acetogenesis

Acetogenesis is the process through which acetate is synthesised by VFA and CO_2 reduction (Fig. 19.2). This step facilitates the conversion of complex intermediates generated from acidogenesis to acetate, thus improving metabolism to CH_4 and CO_2 in the subsequent step, methanogenesis (Sikora et al. 2017; Van et al. 2020). In this oxidative reaction, termed the Wood-Ljungdahl pathway or acetyl-CoA pathway, H_2-producing acetogens oxidise VFAs and alcohols formed by fermentation to acetate. The oxidation of VFAs produces electrons that are transferred to H^+ for H_2 or formate production (Sikora et al. 2017). However, acetogens obligately utilise H^+ and CO_2 as the electron donor and electron acceptor for acetate production autotrophically. Noteworthy, the efficiency of acetogenesis necessitates a low H_2 partial pressure ($<10^{-4}$ atm) (Van Lier et al. 2008). Replication of acetogens is slower than acidogens, occurring every 1.5–4 d (Ramos-Suárez et al. 2015; Van et al. 2020). The optimum working pH range of acetogens is 6.0–6.2 (Kothari et al. 2014).

19.2.4 Methanogenesis

Methanogenesis is the final metabolic phase of AD and involves the conversion of products from the previous stages to CH_4 and CO_2 (see Fig. 19.2) (Van et al. 2020; Van Lier et al. 2008). Methane (CH_4) generation in fermentation occurs via two main mechanisms, with the utilisation of varied substrates and bacteria:

1. Acetotrophs cleave acetate into CH_4 and CO_2 by electron transport-linked phosphorylation. Methane (CH_4) generation from this mechanism accounts for approximately 60–70% of the total methane yield. Noteworthy, acetotrophic bacteria are the most active methanogens, doubling in volume every 2–3 d (Ramos-Suárez et al. 2015; Van Lier et al. 2008).
2. Hydrogenotrophs transform CO_2 (electron acceptor) reduced by H_2 (electron donor) as the substrate for methane production. This reaction process contributes

to 30–40% of methane production. The growth rate of hydrogenotrophic bacteria is 4–12 d (Ramos-Suárez et al. 2015; Van Lier et al. 2008).

Overall, methanogens operate best in a neutral pH environment (6.8–7.2) and are highly sensitive to fluctuations in the digester pH conditions as affected the production of VFAs, free ammonia-nitrogen (FAN) and H_2S during AD (Karuppiah and Azariah 2019; Van et al. 2020).

19.3 Classifications of AD

AD systems may be categorised accordingly: (1) batch, semi-continuous and continuous depended on the substrate feeding mode (2) wet and dry based on the total solid (TS) content and (3) single-stage and multi-stage based on metabolic phase sequencing.

19.3.1 Digester Feeding Type

Anaerobic digestion reactors can be categorised into a batch, semi-continuous or continuous process based on the feeding method. Batch AD refers to a digester fed at only one time with organic material and inoculum. The reactor subsequently closed for a certain period to create an anaerobic environment for degrading substrate. Due to the high volume of input feedstock required for bioprocessing, batch AD is typically applied on a small scale. The anaerobic sequencing batch (ASB) reactor (Table 19.1) is an example of batch AD widely applied for high contaminated wastewater. Other notable benefits of the batch process include low implementation and maintenance cost, flexibility of use, simple operation and minimal energy loss (Chen et al. 2015; Kothari et al. 2014).

In continuous AD systems, feeding material is continuously loaded into the digester at OLR equal to the amount of solid removed, thereby maintaining the system thermodynamic and energy balance. In these systems, biogas recirculation or mechanical agitators can be employed for continuous mixing of the feed and inoculum (Kothari et al. 2014). Biogas production from continuous AD is steady-state and volumetrically higher than that yielded by batch AD (Park et al. 2018). However, drawbacks to continuous operation mode which could inhibit methanogenic activity in AD include limited microbial population acclimatisation to the input feed and VFA accumulation due to constant mixing (Park et al. 2018; Pramanik et al. 2019). Continuous AD systems are also challenged by feedstock seasonality, while the immediate supply for large volumes of material at the start of AD may be problematic in the batch process. Of equal importance, organic materials usually should not be stored for a longer time due to spoilage. Therefore, the concept of a semi-continuous reactor for bioprocessing has received a wide commendation.

Table 19.1 Types of AD reactors. Data adopted from Böske et al. (2014), Kim et al. (2013), Kothari et al. (2014), Mao et al. (2015), Stabnikova et al. (2008)

	AD categorisation							
Reactor type	Batch	Semi-continuous	Continuous	Wet	Dry	Single stage	Multi-stage	Application
Anaerobic baffled (AB)			✓	✓		✓		Very high-strength wastewaters
Anaerobic contact (AC)			✓	✓		✓		High concentrations of suspended solids such as food industry wastewater, pulp, and paper mills
Anaerobic filter reactor (AF)			✓	✓		✓		Wastewater with a high concentration of suspended biomass
Anaerobic fluidised bed (AFB)			✓	✓		✓		Domestic wastewater
Anaerobic plug-flow (APF)		✓		✓			✓	Semi-solid waste; thick manure (11–14% TS)
Anaerobic sequencing batch (ASB)	✓			✓		✓		Wastewater
Continuous stirred tank (CST)			✓	✓		✓		Wastewater containing high levels of suspended solids
Dry anaerobic composting (DRANCO)			✓		✓	✓		Organic waste
Expanded granular sludge blanket (EGSB)			✓	✓		✓		Low-strength wastewater
Internal circulation (IC)			✓	✓			✓	Low-strength wastewater
Modified upflow anaerobic sludge bed (MUASB)			✓	✓			✓	Wastewater
Hybrid anaerobic solid–liquid (HASL)	✓				✓	✓		Food waste
Upflow anaerobic solid-state (UASS)			✓	✓	✓		✓	Solid organic waste; lignocellulosic biomass

(continued)

Table 19.1 (continued)

Reactor type	AD categorisation							Application
	Batch	Semi-continuous	Continuous	Wet	Dry	Single stage	Multi-stage	
Upflow anaerobic sludge bed (UASB)			✓	✓		✓		Wastewater
VALORGA			✓		✓	✓		Solid organic waste

In semi-continuous AD systems, the input feed is added to the digester from one to several times per day rather than continuously supplied as in the continuous AD process (Lim et al. 2008).

19.3.2 Wet or Dry Digestion

The AD process can occur as either wet (TS $<$ 15% w/w) or dry (TS $>$ 15% w/w) based on the feedstock water content (Karthikeyan and Visvanathan 2013; Le Hyaric et al. 2011). Generally, dry AD operates at a solid concentration and organic loading rate (OLR) of 12–15 kg VS/m^3/d. This reactor configuration is approximately three-fold greater than that for wet AD ($<$5 kg VS/m^3/day) and overall achieves higher methane production due to increased VFA formation and volatile solid (VS) content (Kothari et al. 2014; Yi et al. 2014). Notwithstanding, no direct correlation exists between energy production and VS removal as wet AD exhibits a higher solid VS removal rate (40–75%) than dry AD (40–70%). The above-listed result may be attributed to the incomplete mixing of feedstock and microorganisms in dry AD, affecting process stability and bioconversion.

Additionally, high TS content ($>$30%) promotes VFA accumulation and the growth of *Clostridium* spp., which can reduce methane production (Li et al. 2013). The biomass retention time of dry AD and wet AD ranges from 14–60 d and 25–60 d, respectively, depending on the feedstock composition. Dry AD utilisation is more cost-effective than wet AD due to the omission of a digestate post-treatment and dewatering phase, coupled with lower energy consumption due to smaller reactor size (Abbassi-Guendouz et al. 2012).

19.3.3 Single- or Multiple-Stage AD

Single-stage digestion employs one reactor for all four metabolic phases (Pramanik et al. 2019). This reactor configuration is common across Europe, utilised in approximately 95% of full-scale plants for organic waste treatment (Nagao et al. 2012). Two main advantages of the process are low investment and maintenance cost when compared to other digestion types. However, the system is challenged by long retention and a low methane production rate (Xu et al. 2018). This result is due to the absence of reactor pH fluctuations that impair different microorganisms' function and reduce the bioconversion efficiency (Mao et al. 2015). For example, hydrolysis and acidogenesis of organic material result in rapid acidification in the reactor, distorting methanogenic bacterial groups' operation. Nevertheless, this problem can be rectified through feeding rate adjustment or buffer addition. Alkaline sources such as sodium bicarbonate ($NaHCO_3$), lime, waste eggshell have been used to amend and stabilise the digester pH for shorter biodegradation time and methane production enhancement (Chen et al. 2015; Nagao et al. 2012).

Alternatively, the physical separation of metabolic phases may be used for higher bioconversion efficiency. Presently, multi-stage AD is either two-stage or three-stage. In two-stage AD, methanogenesis occurs in a single digester, while hydrolysis, acidogenesis and acetogenesis are grouped in a secondary digester. However, three-stage AD, hydrolysis, acidogenesis/acetogenesis and methanogenesis are performed separately in various reactors. Multi-stage AD improves process stability, shorten the process retention time, optimise AD performance and increase methane production (Hagos et al. 2017; Micolucci et al. 2018). Nevertheless, phase separation of AD increases the process capital, operation and maintenance cost (Xiao et al. 2018).

19.4 Parameters Affecting AD Performance

As discussed in Sect. 19.3, AD involves the operation of different bacteria at varied reaction conditions. However, process stability and efficiency may be impaired by parameters such as feedstock composition and digester operational configuration (Rodriguez et al. 2017a, b). This section discusses the effect of multiple variables on AD process optimisation and biogas productivity.

19.4.1 Biomass Characterisation

19.4.1.1 Nutrient Composition

The potential of biogas generation in AD depends primarily on the chemical composition of the feedstock. Biomass sources comprise varied concentrations of three main organic components: carbohydrates, proteins and lipids, each with a different energy potential (Bhatt and Tao 2020; Hagos et al. 2017). Notably, due to the chemical content of the aforementioned organic components, biogas generation from a single classification is challenging. Thus, energy optimisation techniques such as pre-treatment, co-digestion and enzyme additives need to be employed (see Sect. 19.5). Notwithstanding the organic components listed above, lipids exhibit the highest potential (1014 m^3/kg) to generate biogas (Harris et al. 2018). Apart from composition, the AD process requires microelements at a relatively lower concentration. Iron (Fe), nickel (Ni), cobalt (Co), molybdenum (Mo), zinc (Zn), manganese (Mn), copper (Cu), selenium (Se) and tungsten (W) are the preliminary metal microelements with a recommended concentration between 1×10^{-6} and 1×10^{-15} M (Rasapoor et al. 2020). In the aforementioned range, trace elements can boost the efficiency of biogas generation in AD. Some researchers have also reported that the micronutrients (Fe, Co and Ni) can improve the AD process by increasing COD solubilisation and organic acids formation in the hydrolysis and acidogenesis stages (Thompson et al. 2021; González-González et al. 2013).

19.4.1.2 pH and VFA

As stated in Sect. 19.2, microorganisms' proliferation and metabolic activity in AD is pH specific (Zhang et al. 2005). At the individual optimum pH condition, anaerobic digester stability and performance are achieved, resulting in higher bioconversion efficiency and biogas production. In literature, pH values ranging from 5.0 to 7.5 are required for the growth and performance of microorganisms in AD (Appels et al. 2008; Leung and Wang 2016). Interestingly, the microbial conversion of biomass may result in the formation of concentrated bicarbonate (HCO_3), VFAs and CO_2, which alter the system pH value, subsequently inhibiting microbe metabolic activity. The VFA concentration of 5800–6900 mg/L negatively influences methanogenesis (Appels et al. 2008). Therefore, VFA/ HCO_3 molar ratio $>$ 1:1.4 is recommended for optimum biogas production (Shi et al. 2018; Xu et al. 2014).

19.4.1.3 Carbon to Nitrogen (C/N) Ratio

The biomass carbon to nitrogen (C/N) ratio of biomass is an important parameter that can influence AD process stability. Nitrogen is an essential element produced from protein degradation and necessary for enzyme function in metabolic pathways (Hanrahan and Chan 2005). However, high nitrogen content in the feedstock is a potent inhibitor to methanogens as it promotes ammonia formation, which can lead to digester failure. On the other hand, low nitrogen levels restrict bacteria proliferation and extend the digestion time (Pramanik et al. 2019). Therefore, the correct balance between C/N is necessary for a higher methane generation and stable AD. The optimum C/N ratio reported in the literature for effective AD is approximately 20–30:1 (Kondusamy and Kalamdhad 2014; Leung and Wang 2016.

19.4.1.4 Free Ammonia-Nitrogen (FAN) Content

The decomposition of nitrogenous materials in the feedstock (mainly proteinaceous content) resulted in the formation of ammoniacal contents known as total ammonia-nitrogen (TAN), FAN and the ammonium ion (NH_4^+) (Rajagopal et al. 2013). While ammonia is an essential element for protein synthesis and neutralisation of the acidic condition derived from the metabolic activity of acidifying bacteria, its high concentration limits the productivity of AD by poisoning methanogenic bacteria (Astals et al. 2018). The optimum concentration of ammonia for better microbial growth and efficient AD with a higher methane production ranges from 50 to 200 mg/L (McCarty 1964). Previous studies also reveal a reduction in AD process performance and productivity at TAN and FAN concentrations above 3 g/L and 0.2 g/L, respectively (Duan et al. 2012; Lauterböck et al. 2012). As stated in Sect. 19.2.4, a pH range of 6.8–7.2 is necessary for effective methanogenic growth and activity (Karuppiah and Azariah 2019; Van et al. 2020).

19.4.2 *Digester Operational Configuration*

19.4.2.1 Temperature

AD can be conducted at a wide range of temperatures, sub-divided into the following three groups: psychrophilic (<25 °C), mesophilic (25–45 °C) and thermophilic (>45 °C) (El-Mashad et al. 2004; Zhang et al. 2009). Thermophilic temperatures offer a higher AD metabolic rate and biogas productivity, coupled with the elimination of potential inhibitors such as pathogenic bacteria. Notwithstanding, achievement and maintenance of operating temperatures in thermophilic digestion requires high energy input which negatively impact economic viability in industrial application. Additional disadvantages of thermophilic conditions include increased digester instability and system failure as thermophilic bacteria are more sensitive to temperature changes than the other temperature conditions (Jiang et al. 2020; Pramanik et al. 2019). Mesophilic conditions are generally most stable and endure stress factors, including elevated ammonia levels, high amount of VFAs, alkaline and temperature fluctuations (Eskicioglu et al. 2011). While mesophilic reactors exhibit higher process reliability and operation, biogas production may be lower than that derived from thermophilic AD (Trisakti et al. 2017). Psychrophilic conditions are least effective for biogas production as at temperatures <20 °C, bioconversion and methanation stop completely. Vanegas and Bartlett (2013) reported optimum biogas production of 336 mL/g VS enriched with 55% methane from *L. digitata* incubated at 35 °C for 54 d. However, when the reaction temperature condition was increased to 45 °C, biogas production and its methane content decreased by 30 and 23%, respectively, due to inhibited methanogen growth and adaptation to the temperature condition. These above results corroborate work by Jiang et al. (2020) and Pramanik et al. (2019).

19.4.2.2 Retention Time

Retention time is an operational parameter that must be addressed for AD process efficiency. The retention time is defined as the time taken for organic matter to degrade in the digester completely. In AD, two types of retention time must be considered: hydraulic retention time (HRT) and solid retention time (SRT). The HRT denotes the average time the feedstock/sludge spends in the digester, whereas the SRT refers to the stay of the inoculum in the digester. The HRT employed fluctuates with process parameters such as substrate composition and temperature. Generally, HRTs vary from 30 to 50 d (Yadvika et al. 2004). Notably, HRTs <30 d offer insufficient time to optimise substrate digestion and thus result in decreased biogas productivity. On the contrary, HRTs exceeding 50 d promote bacterial culture mortality, system instability and failure (Shi et al. 2017; Yadvika et al. 2004). Dareioti and Kornaros (2014) investigated the effect of HRT on the two-staged co-digestion of agro-industrial waste. The authors measured maximum methanation of 0.33 L CH_4/L Rd. after 25 d. At this HRT, VFA accumulation was minimised, and reactor stability was established. An HRT of 20 d is necessary for optimum biogas production from municipal solid waste materials and fruit and waste given their low solid content (Bouallagui et al. 2003). Lignocellulose and fibre-rich biomass such as brown macroalgae and wheat straw require longer microbial exposure of 40 and 60 d, respectively, to achieve higher chemical oxygen demand (COD) destruction and better AD performance (Shi et al. 2017). Increasing the digester temperature condition from mesophilic to thermophilic can reduce the HRT (Kothari et al. 2014; Pramanik et al. 2019). The SRT is important for microbial community acclimatisation and adaptation to the digester conditions. However, long SRTs promote the accumulation of AD recalcitrant compounds, which negatively influence biogas production. Research indicates that SRTs <4 d are insufficient for biomass conversion in AD (Pramanik et al. 2019).

19.4.2.3 Organic Loading Rate (OLR)

The OLR is a measure of the VS input to the digester per unit volume. This variable impairs AD performance, efficiency and stability by altering the digester's operational conditions and microbial communities. Low OLRs limit substrate bioavailability to microorganisms for conversion and reduce the digester buffering capacity, reducing methanation. Alternatively, overfeeding the digester (high OLR) may promote recalcitrant compound accumulation such as VFAs, which negatively influences biogas production and triggers system failure (Kothari et al. 2014; Pramanik et al. 2019). In a study on the macroalgal species *Macrocystis pyrifera*, increasing the OLR from 1.37 to 4.12 kg VS/m^3 d enhanced biogas production from 438.9 to a maximum yield of 480.1 mL/g VS d. However, at OLR of 6.85 kg VS/m^3 d, VFA accumulation to 26.28 g/L and a rise in the pH and salinity to 7.5 and 63%, respectively, altered the microbial community structure and behaviour, which resulted in digester instability and lower biogas production (Sun et al. 2017). Importantly, the optimum OLR for methane production is substrate-specific (Pramanik et al. 2019). For example, the optimal OLR for the single-stage AD of two-phase solid oil mill residue is 9.20 kg VS/m^3 d (Rincón et al. 2008), whereas that for food waste was 1.5 and 2.5 g VS/L d under mesophilic and thermophilic conditions, respectively (Liu et al. 2017). Cattle and pig manure mono-digestion can be optimised under mesophilic conditions at OLR range of 2.5–3.5 kg VS/m^3 d (Fernández et al. 2008).

19.5 Opportunities to Improve AD Process

19.5.1 Pre-treatment Technologies

As previously mentioned in Sect. 19.2.1, pre-treatment technologies may be applied to biomass to increase hydrolytic cleavage, thereby shortening the HRT and optimising biogas production (Thompson et al. 2019). Pre-treatment methods such as physical (mechanical; ultrasonication; microwave irradiation), thermal (heating; freeze-thawing), chemical (alkali; acid; oxidation; ozonation), biological and several combinations thereof (steam explosion; hydrothermal; ammonia fibre expansion) have been evaluated with varying success. This section presents the different pre-treatment technologies studied and challenges of process up-scale to industry-level.

19.5.1.1 Physical Pre-treatment

19.5.1.1.1 Mechanical Pre-treatment

Mechanical pre-treatment involves the use of blades and knives to grind, mill and shred biomass into smaller particles before AD. This technology accelerates cell wall breakdown, thus optimising the surface to volume ratio and availability of fermentable sugars to anaerobic microorganisms for better enzymatic hydrolysis and AD performance (Rodriguez et al. 2017a, b; Tedesco et al. 2014). Rodriguez et al. (2018) reported peak methanation of 283 mL/g VS from the brown algae, *P. canaliculata* after pre-treatment in a Hollander beater for 50 min. Relative to the untreated substrate, this yield represented a 45% increase in energy production (see Table 19.1). Szlachta et al. (2018) also achieved higher digestibility and biogas production in AD from nine different agricultural substrates following processing in a grinder to particle lengths 1.5–10 mm.

Notwithstanding, mechanical pre-treatment methods' industrial application has been limited due to high energy consumption and operational costs (Thompson et al. 2019). This technology is also substrate specific with process efficiency directly proportional to the feedstock moisture content (Annoussamy et al. 2000). Therefore, researchers contend the mechanical pre-treatment application is most suitable for dry feedstock as water-logged biomass would require dewatering before processing and incur additional operational costs (Rodriguez et al. 2017a, b).

19.5.1.1.2 Ultrasonication

Ultrasound pre-treatment (UP) is an emerging technology that applies high-intensity ultrasonic wave to biomass to increase cell wall lysis by forming air cavities or micro-bubbles that rupture the cell envelope. This change to the physical structure facilitates the exposure of fermentable sugars to microorganisms for degradation and bioconversion to biogas (Lee et al. 2014; Park et al. 2013). Ultrasonication may be classed accordingly depending on the frequency employed: power (20–100 kHz), high frequency (100 kHz–1 MHz) and diagnostic (1–500 MHz) (Pilli et al. 2011). However, optimum cell lysis and disintegration efficiency are achieved at high energy intensities and low ultrasound frequencies due to larger micro-bubble formation and increased cell wall collapse (Alzate et al. 2012). Tiehm et al. (2001) studied the effect of UP at 0.41 to 3.22 kHz on activated sludge disintegration, in addition to AD performance and stability. The authors reported the lowest UP frequency (0.41 MHz) as the most effective condition for VS reduction, sludge turbidity increase and maximum biogas productivity. Several researchers have achieved a higher disintegration rate at the lower UP frequency of 0.02 MHz (González-Fernández et al. 2012; Passos et al. 2014; Rasapoor et al. 2016). Process efficiency is also dependent on the sonication exposure times. Long reaction times (>150 min) support VS degradation and COD solubilisation (Cho et al. 2013). Ultrasonic pre-treatment is energy-intensive technology (205–900 kJ/L) and demands substrate dewatering prior to application for economic viability (Passos et al. 2015). Presently, UP industrial utilisation in AD includes Sonix, Biosonator and Hielscher (Panigrahi and Dubey 2019; Pramanik et al. 2019).

19.5.1.1.3 Microwave Irradiation

Microwave pre-treatment utilises short electromagnetic waves (0.3–300 GHz) to disintegrate and solubilise biomass. This technology heats water in biomass to a boiling state, accelerating cell wall expansion and subsequent rupture. This structural change to the substrate improves the efficiency of organic matter enzymatic hydrolysis in AD (Rodriguez et al. 2015; Thompson et al. 2019; Uma Rani et al. 2013). Several studies have explored microwave irradiation as a replacement for conventional heating owing to lower energy consumption and shorter reaction time (Hosseini Koupaie and Eskicioglu 2016). Nevertheless, lab-scale application of MP to feedstock, including agricultural and energy crop residues, woody biomass, sewage sludge and macroalgae, has achieved varied success (Hosseini Koupaie and Eskicioglu 2016; Montingelli et al. 2016; Sapci 2013; Uma Rani et al. 2013). Uma Rani et al. (2013) investigated the impacts of MW on the semi-continuous AD of dairy waste-activated sludge. Increasing the intensity of MW irradiation from 50–90% linearly influenced COD solubilisation and sewage sludge degradation. While optimum biogas production was achieved post exposure to 90% MW intensity for 12 min, the energy-intensive nature of these pre-treatment conditions resulted in a negative energy balance. On the contrary, Sapci (2013) and Pellera and Gidarakos (2017) both reported no correlation between the MW induced solubilisation of lignocellulosic agro-industrial waste and biogas production performance. This result may be attributed to the increased formation of recalcitrant compounds which hindered methanogenic activity (Hosseini Koupaie and Eskicioglu 2016). Overall, the contradictory results indicate that MW pre-treatment may be substrate-specific technology (Sapci 2013; Thompson et al. 2019).

19.5.1.2 Thermal Pre-treatment

19.5.1.2.1 Heating Pre-treatment

Thermal pre-treatment uses heat exchange to apply temperatures ranging from 50 to 250 °C directly to the surface of biomass, thereby breaking the H-bonds that retain structural integrity and causing cell wall breakdown. The enzymatic hydrolysis of organic matter is improved by this process and results in higher biogas productivity (Rodriguez et al. 2015; Solé-Bundó et al. 2020; Thompson et al. 2019). Low temperature (<110 °C) and high temperature (>110 °C) reactions are two types of thermal pre-treatment. High temperatures are preferred because they improve lignocellulose solubilisation and optimise energy extraction. However, temperatures exceeding 160 °C may negatively influence microbial bioconversion by forming AD inhibitory phenolic compounds (Cho et al. 2013). These extreme conditions also promote Maillard reaction between amino acids and carbohydrates, reducing volatile organics content and lower biogas production (Liu et al. 2012a, b). Exposure of four agricultural by-products (wheat, barley, rice and maize stalk) to conventional heating at 120 °C for 30 min before AD increased the energy yield by 64.2, 40.8, 32.4, 7.1%, respectively (Menardo et al. 2012). Application of thermal pre-treatment (120 °C for 30 min) to urban and industrial waste-activated sludge altered the microbial community structure by increasing hydrogenotroph proliferation. At the end of the AD process, biogas production was increased by 27% for urban sludge, and 37% industrial waste-activated sludge (Ennouri et al. 2016). Liu et al. (2012a, b) applied thermal pre-treatment at 170 °C to three different municipal biomass waste samples for 60 min. Compared to the control samples, methanation of waste-activated sludge increased by 34.8%. However, melanoidin formation decreased biomethanation from kitchen waste and vegetable residue by 7.9 and 11.7%, respectively.

19.5.1.2.2 Freeze-Thawing Pre-treatment

Freeze-thawing pre-treatment improves the natural dewaterability of food waste and sludge for enhanced digestibility and AD performance. During freezing, intracellular water solidifies and ice crystals develop in the floc matrix (Montusiewicz et al. 2010; Thomashow 1998). More water molecules are constantly being incorporated into the lattice as the ice grows, thus creating a force that compresses the biomass's unfrozen parts, causing cell rupture (Meyer et al. 2017). Subsequent thawing exposes the frozen intercellular cells to further structural changes and cell breakdown. The Resulting is the release of various intracellular organics into the liquid phase and the enhanced accessibility of sugars for enzymatic hydrolysis (Hu et al. 2011; Wang et al. 2001; Zhang et al. 2021). Freeze-thawing pre-treatment demands zero energy input or chemical additives which renders it an eco-friendly and cost-effective pre-treatment option. Additionally, freeze-thawing pre-treatment positively influences microbial community growth (Kothari et al. 2014). Li et al. (2019) reported higher methanogenic bacteria growth and 41% increase in methanation from corn stalk pre-treated for 21 d at 1:6 solid-to-liquid ratio. Noteworthy, this technology is most suitable in territories with natural seasonal changes and fluctuations in atmospheric temperature. Nonetheless, the process efficiency varies with the temperature and exposure time (Hu et al. 2011; Wang et al. 2001). Freeze-thawing pre-treatment of wheat straw at −20 °C for 96 h shortened the microbial growth lag phase by 21.39% but exhibited negligible influence on methane production in fermentation. In this study, peak methane recovery of 189.20 mL/g VS was obtained from wheat straw pre-treated at −40 °C for 24 h (Zhang et al. 2021). Alternatively, the specific biogas yield from pulp and paper mill biosludge increased by approximately three-fold following freeze-thawing pre-treatment for 10 d at −10 and − 18 °C, respectively (Meyer et al. 2017).

19.5.1.3 Chemical Pre-treatment

Chemical pre-treatment relies on chemical agents of varying strengths to cleave and solubilise complex macromolecular components such as lignin and cellulose in biomass cell walls. This technology facilitates the microbial attack of fermentable sugars, which improves AD performance downstream (Montingelli et al. 2016; Rodriguez et al. 2015, 2017a, b; Thompson et al. 2019; Zhang et al. 2020). Chemical pre-treatment can be classified based on the reagent/chemical utilised: alkaline pre-treatment, acid pre-treatment and oxidative pre-treatment.

19.5.1.3.1 Alkaline Pre-treatment

Alkaline pre-treatment triggers biomass swelling, disrupting the cell wall structure by breaking bonds between lignin and other carbohydrates. This pre-treatment condition is commonly achieved with salts or hydroxides such as sodium hydroxide (NaOH), potassium hydroxide (KOH), aqueous ammonia ($NH_3 \cdot H_2O$) and calcium hydroxide or lime ($Ca(OH)_2$) (Ma et al. 2018; Rodriguez et al. 2017a, b). Noteworthy, the metal ion concentration of the alkaline reagent must be monitored to prevent methanogenesis inhibition and digester failure (Montingelli et al. 2016). For example, the concentrations of calcium and magnesium should not exceed 0.2 g/L and 0.72 g/L, respectively. On the contrary, the maximum tolerable limit of potassium and sodium are significantly higher at 8 g/L and 5 g/L, respectively (Thompson et al. 2020).

19.5.1.3.2 Acid Pre-treatment

Acid pre-treatment is more effective than alkaline pre-treatment at hastening lignocellulose degradation and hydrolysis. The chemical reagents in acid pre-treatment may be concentrated or diluted organic and inorganic acids such as hydrochloric acid (HCl), sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4), acetic acid (CH_3COOH), nitric acid (HNO_3) and hydrogen peroxide (H_2O_2) (Ma et al. 2018; Zhang et al. 2020). Concentrated acid pre-treatment is typically performed at low temperatures, whereas diluted acid pre-treatment is conducted at high temperatures. Pre-treatment with strong acids is expensive and generally avoided due to numerous human health and environmental concerns. Additionally, strong acids promote the formation of AD inhibitory products such as aliphatic carboxylic acids, furans and phenols, which alter the digester pH, consequently suppressing methanogenic activity and biogas production (Jönsson and Martín 2016; Vanegas et al. 2015). Dilute acids are less corrosive, toxic and costly than concentrated acids. Moreover, these weak acidic reagents warrant less neutralisation before disposal than strong acidic reagents, thus reducing their environmental impact and the overall digester operation cost (Pramanik et al. 2019; Zhang et al. 2020).

19.5.1.3.3 Oxidative Pre-treatment

Wet air oxidation increases interactions between molecular oxygen and organic materials, allowing for a complete breakdown of organic molecules into CO_2 and water. This processing method is energy-intensive, requiring high temperature and pressure operation conditions (Karuppiah and Azariah 2019; Pan et al. 2010). Noteworthy, high pressure aids the maintenance of the high pre-treatment temperature condition and increases the process oxidation rate by accelerating the formation of dissolved oxygen. Chandra et al. (2014) investigated the effect of wet air oxidation on the biodegradability of biomethanated distillery effluent. They reported methane enhancement of approximately three-fold from processed sewage when compared to untreated wastewater.

19.5.1.3.4 Ozonation

Ozone is a strong oxidising agent which accelerates cell wall rupture and delignification, in a way similar to that outlined for alkaline pre-treatment (Sect. 19.5.1.3.1). This oxidant reacts with nutrient constituents such as polysaccharides, proteins and lipids, accelerating their solubilisation for microbial attack and subsequent bioconversion. In literature, ozonation has been proven effective at improving AD process performance (Karuppiah and Azariah 2019). Goel et al. (2003) applied ozone pre-treatment to sludge particles and observed enhanced solid solubilisation. However, the extent of the solubilisation achieved varied in direct proportion to the ozone dosage used. At the ozone dose of 0.05 g O3/g TS, the AD process efficiency increased by 59% as compared to the control (31%). Similarly, Cardeña et al. (2017) reported 66% increase in methane production from three mixed microalgae sources post ozone pre-treatment at 382 mg O_3/g $VS_{algal.}$

19.5.1.4 Biological Pre-treatment

Biological pre-treatment (BP) is characterised by the utilisation of natural microorganisms, mainly white, brown and soft-rot fungi, to biomass to accelerate lignin, hemicellulose and cellulose degradation prior to AD (refer to Table 19.2) (Wagner et al. 2018). Fungi and bacteria produce different enzyme systems with varied pre-treatment effects. Brown-rot fungi secrete enzymes that target cellulose breakdown. However, white- and soft-rot fungi produce ligninolytic enzymes, catalysing the hydrolysis of lignin and cellulose to CO_2 and water (Ghasemzadeh et al. 2017; Zabed et al. 2019; Zhang et al. 2020). From literature, white-rot fungi are the most commonly used and efficient microorganisms for BP. Major advantages of BP over the other pre-treatment methods discussed in this section (physical, thermal and chemical methods) include low energy input and capital cost, minimal chemical requirements, reduced recalcitrant compound formation due to milder operation conditions and negligible environmental emissions (Ortíz and Quintero 2014; Saritha and Arora 2012; Zhang et al. 2020). However, bottlenecks to the process are the slow microbial growth and hydrolysis rate, long pre-treatment time (7–60 d) and high cost of commercial enzymes (Wagner et al. 2018). Additionally, BP demands vast operational space, which increases the process cost and renders the technology less attractive at an industrial scale (Ortíz and Quintero 2014; Saritha and Arora 2012; Zabed et al. 2019).

19.5.1.5 Physicochemical Pre-treatment Methods

To improve efficiency of AD process and the resulting methane potential, integration of physical and chemical pre-treatment processes may be utilised. This section reviews several combined pre-treatment methods reported in the literature (see Table 19.2).

19.5.1.5.1 Steam Explosion

In steam explosion, biomass is exposed to high pressure (5–50 bar) saturated steam at temperatures ranging from 160 to 260 °C for varied intervals, causing a rise in pressure and the expansion of the fibrous cell walls. After 1–5 min incubation time, rapid depressurisation to ambient conditions leads to an explosion that causes the structural breakdown and deconstruction of biomass and particle size reduction (Karuppiah and Azariah 2019; Paudel et al. 2017). Notwithstanding, the temperature and time required for steam explosion pre-treatment vary with biomass

Table 19.2 Effect of various pre-treatment technologies on methane/biogas production enhancement

Pre-treatment	Substrate	Pre-treatment condition	Energy yield	Increase in production rate (%)	References
Physical					
Mechanical	*P. canaliculata*	Hollander beater; 50 min	283 mL CH_4/g VS	+ 45	Rodriguez et al. (2018)
	Waste paper	Hollander beater; 55 min	253.62 mL/g VS	+ 21	Rodriguez et al. (2017a, b)
	Giant reed stems	Milling; 20 mm particle size	212 $Nm^3{}_{biogas}$/t VS	+ 137	Dell'Omo and Spena (2020)
	Wheat straw		250.3 $Nm^3{}_{biogas}$/t VS	+ 49	
Ultrasonication	Mixed microalgae	10 MJ kg/TS	314 mL CH_4/g VS	+ 24	Cardeña et al. (2017)
	Scenedesmus biomass	128.9 MJ kg/TS; 20 Hz; 15 min	153.5 mL CH_4/g COD_{in}	+ 88	González-Fernández et al. (2012)
	Anaerobic sludge	41 kHz; 150 min	436 L_{biogas}/kg VS	−11	Tiehm et al. (2001)
	Food waste	360 kJ/L; 30 min	206.4 mL CH_4/g $VSS_{removed}$	+ 56	Naran et al. (2016)
Microwave	Mixed microalgae	65.4 MJ kg/TS	307.1 mL CH_4/g VS	+ 78	Passos et al. (2013)
	Dairy waste-activated sludge	1814 kJ/L; 20 min	453 mL_{biogas}/g VS	+ 35	Uma Rani et al. (2013)
Thermal					
Heating	Mixed microalgae	170 °C, 15 min	398 mL CH_4/g VS	+ 46	Alzate et al. (2012)
	Scenedesmus biomass	80 °C; 15 min	128.7 mL CH_4/g COD_{in}	+ 57	González-Fernández et al. (2012)
	Food waste	120 °C; 30 min	176.6 mL CH_4/g $VSS_{removed}$	+ 77	Naran et al. (2016)
	Raw mixed kitchen waste	120 °C; 1 bar; 30 min	0.36 L_{biogas}/g $COD_{removed}$	+ 3	Ma et al. (2011)

(continued)

Table 19.2 (continued)

Pre-treatment	Substrate	Pre-treatment condition	Energy yield	Increase in production rate (%)	References
Freeze-thawing	Corn stalk	21 d; solid–liquid ratio (1:6)	253 mL_{biogas}/g VS	+ 41	Li et al. (2019)
	Pulp and paper biosludge	−10 °C; 10 d	310 mL_{biogas}/g COD_{added}	+ 279	Meyer et al. (2017)
		−18 °C; 10 d	323 mL_{biogas}/g COD_{added}	+ 291	
	Wheat straw	−40 °C; 1 d	189.20 mL CH_4/g VS	+ 11	Zhang et al. (2021)
	Raw mixed kitchen waste	−18 °C; 6 h	0.38 L_{biogas}/g $COD_{removed}$	+ 9	Ma et al. (2011)
Chemical					
Alkali	Food waste	NaOH (0.4 N); pH 12.7; 60 min	158.7 mL CH_4/g $VSS_{removed}$	+ 25	Naran et al. (2016)
Acid	Mixed fruit waste	Acetic acid (0.2 M); 62.5 °C; 30 min	53.58 mL CH_4/g VS	+10	Saha et al. (2018)
	Raw mixed kitchen waste	HCl (10 N); pH 2; 24 h	0.16 L_{biogas}/g $COD_{removed}$	−54	Ma et al. (2011)
Oxidative	Biomethanated distillery effluent	150–200 °C; 6–12 bar; 15–120 min	79.31 mL CH_4/g $COD_{reduced}$	+ 283	Chandra et al. (2014)
Ozonation	Mixed microalgae	382 mg O_3/g VS	432.7 mL CH_4/g VS	+ 66	Cardeña et al. (2017)
Biological					
Enzymes	Mixed food waste	10 U/g dry FW for glucoamylase; 60 °C; 100 rpm; 24 h	457.3 mL CH_4/g VS	+ 230	Uçkun Kiran et al. (2015)
Fungal mash			468.2 mL CH_4/g VS	+ 350	
Physicochemical					
Steam explosion	Rice straw	205 ° C; 15 bar; 15 min	486 NmL CH_4/g VS	+ 147	Aski et al. (2019)
	Birch wood	210 °C; 10 min	179 mL CH_4/g VS	+ 118	Mulat et al. (2018)

(continued)

Table 19.2 (continued)

Pre-treatment	Substrate	Pre-treatment condition	Energy yield	Increase in production rate (%)	References
	Reed biomass	200 °C; 15 min; 298 K	335 L CH_4/kg VS	+ 89	Lizasoain et al. (2016)
	Rice straw	200 °C; 2 min	328.7 mL_{biogas}/g TS	+ 51	Zhou et al. (2016)
Hydrothermal	Pelagic *Sargassum*	140 °C; 30 N_2 bar; 30 min	116.72 mL CH_4/g VS	+ 265	Thompson et al. (2020)
	Wheat straw	180 °C; 60 min	615 NmL_{biogas}/g VS	+ 53	Rajput et al. (2018)
Alkali + thermal	Food waste	NaOH (0.4 N); pH 12.7; 120 °C; 30 min	195.8 mL CH_4/g $VSS_{removed}$	+ 33	Naran et al. (2016)
Acid + thermal	Raw mixed kitchen waste	HCl (10 N); pH 2; 24 h; 120 °C	0.30 L_{biogas}/g $COD_{removed}$	−14	Ma et al. (2011)

characteristics (Paudel et al. 2017). Steam explosion of reed biomass at the pre-treatment condition of 200 °C for 15 min enhanced the specific methane yield by approximately 89% (355 L/kg VS) (Lizasoain et al. 2016). Biogas production rice straw increased by 51% after pre-treatment at 200 °C for 2 min (Zhou et al. 2016). Noteworthy, at pre-treatment temperature conditions >200 °C, the formation of degradation compounds such as furan derivative compounds may inhibit methanogenesis (Lizasoain et al. 2016; Zhou et al. 2016). The feedstock moisture content also influences the efficiency of steam explosion on biogas production. Aski et al. (2019) examined the effect of steam explosion pre-treatment at three different moisture levels (0, 35 and 70%) on structural modification and biodegradability of rice straw. The authors noted that while feedstock of 0% moisture content achieved complete lignin removal, the formation of AD inhibitory compounds impaired methanogenesis. In this study, rice straw of 70% moisture content exhibited the highest biodegradability and methane production (Table 19.2).

19.5.1.5.2 Hydrothermal Pre-treatment

Hydrothermal pre-treatment (HTP) is eco-friendly technology which involves the utilisation of compressed liquid hot-water at moderate temperature (120–200 °C) and pressure (up to 150 bar) in a non-oxidative atmosphere to accelerate cellulose and hemicellulose hydrolysis, thus enhancing microbial exposure to digestible constituents for bioconversion (Munir et al. 2018; Yousefifar et al. 2017). Phuttaro et al. (2019) reported 35% increase in the methane output from Napier grass after HTP at 175 °C for 15 min. Rajput et al. (2018) obtained 615 NmL/g VS of biogas from wheat straw hydrothermally pre-treated at 180 °C for 60 min. Similarly, hydrothermal pre-treatment of pelagic *Sargassum* (Thompson et al. 2020) and *Saccharina latissima* (Lin et al. 2019) at 140 °C for 30 min increased methane production by 265 and 22.6%, respectively, relative to the untreated samples. Noteworthy, pre-treatment temperatures $\geq$160 °C promote Maillard reactions between solubilised sugars and proteins and the formation of AD inhibitory compounds such as NH_3-N, VFAs and phenolics, which reduce microbial degradation of organic matter in AD (Hauser et al. 2014; Lin et al. 2019).

19.5.1.5.3 Ammonia Fibre Expansion Pre-treatment

Ammonia fibre expansion (AFEX) pre-treatment is a thermochemical pre-treatment technology used to enhance the conversion of lignocellulosic biomass into biofuels. Ammonia presents high selectivity for biomass delignification and crystalline cellulose reduction, facilitating microbial access to fermentable carbohydrates for digestion downstream (Antonopoulou et al. 2015; Chundawat et al. 2020). The mechanism of AFEX involves the application of liquid ammonia treatment to lignocellulosic biomass at low temperatures (70–200 °C) and pressure (6–30 bar) for a specific time interval. This pre-treatment condition affects biomass swelling and subsequent explosion, altering the feedstock structural properties (Karuppiah and Azariah 2019). Aqueous ammonia soaking (AAS) of perennial energy crops and agricultural residues at 25 °C for 3 d enhanced methane production from wheat straw, miscanthus and willow by 37–41%, 25–27% and 94–162%, respectively, when compared to the control (Jurado et al. 2013). Similarly, poplar sawdust, sunflower straw and grass exposed to AAS treatment at 25 °C for 3 d revealed methane yield enhancements of 148.7%, 37.7% and 26.2%, respectively (Antonopoulou et al. 2015). Of importance, AAS treatment eliminated toxic compound formation, which contributed to improved AD performance (Antonopoulou et al. 2015; Jurado et al. 2013).

19.5.2 Co-digestion

Anaerobic co-digestion (AcoD) is the simultaneous digestion of two or more substrates in a single digester (Astals et al. 2014). This technique is predominantly used to increase methane generation from low biodegradable and energy-yielding feedstock by amending critical AD parameters such as the C/N ratio, pH value, TS content and organic loading rate (refer to Sect. 19.4). The mixing of different organic substrates in AcoD can provide the following benefits over mono-digestion: (1) improve process stability, (2) increase dilution of toxic chemicals, (3) amend

Table 19.3 Effect of substrate co-digestion on AD process performance

Substrate	Co-substrate	Ratio (v/v)	Effect on AD process performance	References
Co-digestion				
Pig slaughter-house residue	Tomato industry waste	4:1	• 80% reduction in COD and improvement in biogas generation	González-González et al. (2013)
Chicken manure mixing	Corn straw	1:3	• 600% improvement in CH_4 generation	Feng et al. (2017)
Dairy manure	Spent mushroom substrate	1:3	• 400% improvement in biogas yield	Luo et al. (2018)
Pig manure	Corn stover and cucumber residue	5:2:3	• 350% improvement in CH_4 generation	Wang et al. (2018a, b)
Organic cattle manure	Crop silage	1:1	• 20% improvement in biogas yield	Ahlberg-Eliasson et al. (2018)
Slaughterhouse wastewater	Olive mill	2:3	• 50% improvement in biogas yield; COD reduction	Gannoun et al. (2007)
Pre-treatment + co-digestion				
Cow manure	Thermally pre-treated food waste at 121 °C; 30 min; 30% TS	1:1	• 62–81% improvement in CH_4 production	Arelli et al. (2018)
Food waste	Waste-activated sludge	70:30	• Thermal pre-treatment—120 °C; 30 min: 38% increase in CH_4 yield	Naran et al. (2016)
			• Alkali pre-treatment—NaOH (0.4 N); pH 12.7; 60 min: 23% increase in CH_4 yield • Alkali-thermal pre-treatment—NaOH (0.4 N); pH 12.7; 120 °C; 30 min: 34% increase in CH_4 yield	
			• Ultrasonication—360 kJ/L; 30 min: 56% increase in CH_4 yield	

the micro- and macro-nutrient imbalance, (4) amend the TS and moisture content of the feed, (5) mitigate atmospheric GHG emissions, (6) accelerate microorganism growth and function and (7) optimise biogas production for higher economic viability in industry application (see Table 19.3) (Astals et al. 2014; Gu et al. 2020; Hagos et al. 2017; Mu et al. 2020). In literature, feedstock such as food waste (Mu et al. 2020; Thompson et al. 2021), energy crops and agricultural waste (Zhong et al. 2020), livestock effluents (Glanpracha and Annachhatre 2016; Zhang et al. 2016) and sewage sludge (Cabbai et al. 2013; Kim et al. 2003) are viable feedstock for AcoD.

Zhang et al. (2016) investigated the co-digestion of sorghum stem with cow manure on biogas production using high-solid AD. Cumulative biogas production from Sorghum stem mono-digestion was 328, 381, 413, 333 mL/g VS at C/N ratios 35, 30, 25 and 20, respectively. The addition of cow manure to the input feed eliminated digester acidification at the start of AcoD, thus stabilising the pH value and boosted the methanogenesis stage in AD. However, no correlation can be drawn between the system buffering capacity and the feedstock C/N ratio. In this study, a maximum biogas yield of 478 mL/g VS was achieved at a C/N ratio of 25. Glanpracha and Annachhatre (2016) reported that pig manure can increase the methanation of cyanide containing cassava pulp in laboratory-scale mesophilic AcoD operated in semi-continuous mode. At a C/N ratio of 35, optimum methane production from the mixed feedstock ratio of cassava pulp-to-pig manure (77:23) was 0.37 mL CH_4/kg VS_{added} at the OLR of 6 kg VS/m^3 d. Overall, pig manure promoted swift inoculum acclimatisation, which facilitated degradation of the cyanide present in cassava pulp for biogas optimisation. Previous studies have also demonstrated food waste and sewage sludge co-digestion as effective for methane yield enhancement (Gu et al. 2020; Mu et al. 2020). For example, Kim et al. (2003) achieved 215 mL CH_4/g VS from a mix of food waste and sewage sludge (50:50), representing an 85.3% increase in methanation compared to food waste mono-digestion.

Different pre-treatment technologies may also be combined with AcoD to optimise methane production (Table 19.3) (Naran et al. 2016; Thompson et al. 2021). Biological pre-treatment with lipases increased specific methane production from the batch AcoD of pig manure with vegetal oil residue by 29% (Sunada et al. 2014) and slaughterhouse wastewater and grease by 100% (Affes et al. 2017), in comparison to the control. Thermal pre-treatment of microalgae at 75 °C for 10 h followed by AcoD with primary sludge and fat from a sewage treatment plant accelerated the bioconversion process. It improved the AD first-order kinetics constant by up to 67% for methane production enhancement of 47% (Solé-Bundó et al. 2020). Ultrasound pre-treatment of a mixture of 87% chicken manure, 10% food waste and 3% glycerine at 520 kJ/kg TS in an Induced Bed Reactor also enhanced the specific methane yield by 120% (Ormaechea et al. 2017).

19.5.3 Conductive Materials

In some circumstances, it is necessary to adjust the micro- and micronutrient content of the feedstock to the optimum range for efficient bioconversion (Sect. 19.4.1.1). Blending biomass with additives such as activated carbon, biochar and neutral red can amend the nutrient composition for increased biogas production (Table 19.4). This section of the paper discusses the mechanism of conductive materials operation

Table 19.4 The role of conductive materials on biogas generation.

DIET promoting additives	Electron donor	Mode	Additives specifications	Effect on methane (CH_4) production rate (%)	References
AC	Food waste	Semi-continuous	15 g/L with 385 m^2/g surface area	+ 41	Zhang et al. (2018)
GAC	Waste-activated sludge	Semi-continuous	27 g/L with 8–12 mm diameter	+ 20	Peng et al. (2018)
GAC	Waste-activated sludge	Batch	33 g/L with <10 mm diameter	+ 17	Yang et al. (2017)
GAC	Food waste	Batch	10 g/L with 250–550 kg/m^3 density		Capson-Tojo et al. (2018)
GAC	Dog food	Batch	50 g/L with <20 mm diameter	+ 1650	Dang et al. (2017)
GAC	Glucose	Batch	10 g/L with 1.22–1.43 diameter and 600 m^2/g surface area	+ 168	Yan et al. (2017)
GAC	Ethanol	Batch	25 g/L with <20 mm diameter	+ 250	Liu et al. (2012a, b)
GAC	Corn straw	Batch	6 g/L coconut shell obtained at 600 °C	+ 38	Liu et al. (2021)
GAC	Sludge	Batch	9 g/L	+ 21	Kang et al. (2021)
Biochar	Complex biomass waste	Batch	15 g/L sawdust obtained at 500 °C for 1.5 h	+ 40	Wang et al. (2018a, b)
Biochar	Ethanol	Continuous	1.25 g/L	+ 30–45	Zhao et al. (2015)
Biochar	Ethanol	Semi-continuous	12 g/L woodchips originated at 900 °C	+ 47	Qi et al. (2021)
Biochar/Ce^{3+}	Organic waste	Batch	3.8 g/L cow dung derived at 400 °C	+ 22	Pan et al. (2021)
Carbon nanotubes	Butyrate	Batch	5 g/L with 10–20 nm in diameter and 10–30 μm in length	+ 50	Zhang and Lu (2016)
NR (phenazine)	Food waste	Continuous	7 mg/L	+ 100	Beckmann et al. (2016)

(Direct interspecies electron transfer) and highlights their utilisation on AD process performance and biogas productivity.

19.5.3.1 Mechanism of Conductive Materials: Direct Interspecies Electron Transfer (DIET)

The direct interspecies electron transfer (DIET) mechanism is conducted by electron transfer between microorganisms without the direct role of electron carriers like H_2 and formate in the AD process. For many years, it was hypothesised that H_2 and formate transfer electrons between methanogens and their syntrophy are the critical mechanisms for interspecies electron transfer between methanogens and fermentative bacteria. Direct interspecies electron transfer is more efficient in methane-producing reaction times and energy analysis than common electron carriers (Chen et al. 2014; Cheng and Call 2016; Qi et al. 2021). Three types of DIET mechanisms have been identified: conductive pili, electron transport via proteins and electron transfer via conductive materials. Among these mechanisms, conductive materials can be easily implemented on a large scale, including landfills, to improve generation efficiency. The followings are the most critical materials used to change the metabolic pattern in the AD process.

19.5.3.1.1 Activated Carbon (AC)

Activated carbon main properties, high electrical conductivity and surface area and make it popular for various microbial electrochemical systems (Liu et al. 2016). Using AC in different biocathode systems has proved that many microorganisms can accept electrons from AC. Recently, it was proved that AC application could increase the methane-generation rate in an anaerobic digester (Table 19.4), most probably because of the direct electron exchange between syntrophic microbial communities of bacteria and methanogenic archaea (Rasapoor et al. 2021). Liu et al. (2012a, b) developed the concept that AC likely facilitates DIET between bacteria and methanogens. Adding AC to an anaerobic media mitigated the lag phase and increased methane production from ethanol in co-cultures of *G. metallireducens* and *M. barkeri*. Xu et al. (2015) found that introducing AC in an anaerobic digester leads to developing the layered structure of anaerobic sludge granules influenced by bacteria and archaea in the outer and inner layer, respectively. The results illustrated that digester efficiency increased under the effect of an improvement in the microbial population of methanogenic bacteria and syntrophic metabolism bacteria. Methanosarcina and Methanoculleus were the primary species in the reactor operating with powdered AC, with Bacteroidales, Desulfuromonas, and Thermotogaceae also abundant.

19.5.3.1.2 Biochar

Biochar is produced by biomass pyrolysis at temperature ranges of 180–950 °C in an inert atmosphere (Atkinson et al. 2010; Fagbohungbe et al. 2017). It can be used for soil amendment, waste management, carbon storage and, lastly, as a fuel source (Atkinson et al. 2010; Srinivasan et al. 2015). Many researchers have shown that biochar can be beneficial for AD (Table 19.4). It can be an adsorbent of inhibitory digestion elements such as heavy metals and other organic pesticides (Taha et al. 2014). Biochar is helpful to maintain AD buffering capacity, especially those produced by an increase in the pyrolysis operating temperature (Luo et al. 2015). The application of biochar to an AD can adjust nutrient retention and diminish nutrient losses.

Additionally, biochar can absorb organic substrates, phosphate, nitrate, ammonium and metals in the AD (Bagreev et al. 2001). One of the critical parameters of biochar is the promotion of immobilisation, which occurred by the colonisation of microbial cells on the surface of solid materials (Fagbohungbe et al. 2017; Luo et al. 2015). The microbial communities' immobilisation is crucial for the AD process, especially concerning improving the methanogens in DIET (Chen et al. 2014; Cheng and Call 2016). Chen et al. (2014) suggested that biochar can maximise DIET between *G. metallireducens* and *G. sulfurreducens* or *M. barkeri*. Notwithstanding, its conductivity is not comparable with the significant conductivity of AC. One of the main arguments for improving methane generation in the presence of biochar is the substantial enrichment in Geobacter and Methanosaeta species (Lee et al. 2016). The physical properties of biochar can considerably vary the DIET. Luo et al. (2015) reported that biochar with a lower specific surface area could increase Methanosarcina species compared to fine biochar, which has a higher specific surface area.

19.5.3.1.3 Neutral Red

Neutral red (NR) is a synthetic phenazine with multiple applications, from dyeing cloth in the textile industry to ecological marker in biological science and intercellular pH indicator (Cheema et al. 2018; Park et al. 1999). NR structure is formed by a tricyclic aromatic amine, which includes two nitrogen atoms. In 1879, Witt, for the first time, produced NR by condensation of p-nitrosodimethylaniline and 2,4-Daiminotoluene in an aqueous medium and oxidation of the resulting toluene blue by ferric chloride. Since then, various methodologies have been employed, and many companies have synthesised it commercially. NR application as a conducting polymer and redox mediator has raised attention, more importantly for environmental applications (Cheema et al. 2018). NR application affects fermenting organisms by changing metabolic patterns. By reducing CO_2, methane generation might happen via NR application to the anaerobic media through connecting electron donors with a proton-translocating electron transport chain. Consequently, electrically reduced NR can reserve electricity for the electron-driving force essential to generate a proton-motive force and the required electrons for metabolite production (Park et al. 1999).

The higher efficiency is the outcome of optimum NR concentration. The higher NR concentration will result in higher conductivity. However, in a media, concentration is adjusted by the tolerance of microbial species. For example, four different dosages of NR, including 0.15, 1.5, 15 and 30 mM, were employed to produce electricity from wastewater. The results confirmed that 15 mM was the best concentration and could raise the current up to double (Fathey et al. 2016).

Notwithstanding, it is worthy of mentioning that NR can be toxic to microorganisms and plants. Therefore, an accurate dosage of NR needs to be applied. Unfortunately, there is no clear line to highlight the inhibitory level of NR. Some researchers advised that NR at or below a concentration of 0.25 mM would have minimal impact on ecological receptors (Kastury et al. 2015).

19.6 Economics of AD Systems

Economic benefits of anaerobic digestion include energy and by-products. Recently, the energy produced in biogas has reduced fossil fuel expenses by generating renewable sources of heat and electricity. Apart from that, chemical fertiliser has been replaced by solid and liquid fertiliser to improve soil fertility and structure, leading to farm cost management in favour of fewer inputs and more crop yield (Bhatt and Tao 2020). However, many parameters such as feedstock compositions, operating conditions, the scale of the process, government incentives for both energy and fertiliser can affect the economy of AD systems. A tipping fee for solid waste AD plants ranges from $30 to $50/ton in America, lower than landfills to encourage source separation. The source of biogas consumption can impact the economics of AD facilities dramatically. For example, fuelling transportation systems usually generates more revenue than CHP units but needs more capital investments. Transportation of feedstocks and products is another critical element for the economic feasibility of the AD systems, as long-distance carting could increase the biogas production costs. Furthermore, in some regions such as Europe, most AD systems are operated with subsidies from government agencies and various state incentives (Bhatt and Tao 2020; Vasco-Correa et al. 2018).

As the digestion of some feedstock may be challenging and time-consuming, employing physical, chemical, mechanical or combination can improve biogas generation efficiency. Also, using additives proved to be influential on biogas generation in favour of higher income. Converting conventional landfills to bioreactors can increase gas generation substantially as a strategy to raise the benefit of digestion and reduce the environmental impacts. A recent study shows that Neutral red and biochar application in a bioreactor landfill increased the economic benefits of the landfill eight and nine folds, respectively. As a result, new research on improving the AD process can render this technology more attractive to investors (Rasapoor et al. 2021).

19.7 Conclusions

Anaerobic digestion (AD) is a practical technique to transform organic waste materials into valued end-products in an eco-friendly manner. Advantages of this technology include reduced odour and atmospheric greenhouse gas emissions, in addition to bioenergy production and fertiliser recovery. Nevertheless, AD process performance is influenced by several parameters. For example, high concentrations of refractory components such as ammonia, VFAs and H_2S can impair or stop microbial degradation. Therefore, based on the substrate characterisation and degradation index, optimisation of the AD process for energy production may require the incorporation of an extra technique. Pre-treatment, co-digestion and conductive materials may be utilised to accelerate the hydrolysis phase of AD, adjust the nutrient ratio and/or mitigate the negative impact of inhibitory constituents for higher AD productivity and efficiency. However, before technology industrialisation, a comprehensive understanding of the process mechanism and identifying the optimum operational conditions are necessary to support environmental stability and achieve financial gain.

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Chapter 20

Composting Technologies for Biowastes: Environmental and Techno-Economic Feasibilities under Biorefinery Concepts

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Abstract Biorefinery for bio-waste (BW) is now a much-needed strategy for a sustainable energy transition. Although this technology allows for the production of biofuels, biochemicals and biomaterials, its large-scale transportation still suffers from several impeding factors. The instability and incomplete conversion of residues and by-products in some biorefinery processes such as anaerobic digestate restrict the implementation of BW biorefinery. Composting has been widely proposed as a single operational unit for the valorization of agricultural waste and an especially effective method leading to the total stabilization of organic matter and the recovery of nutrients. Integrating this aerobic process can improve the sustainability of the BW biorefinery and yield value-added products in the form of biofertilizers and bioenergy. This chapter describes the potential of composting technology to overcome the organic matter instability issue in BW biorefinery residues. The scope of the integration of composting technology into the BW biorefinery concept will also be explored, with an emphasis on environmental and techno-economic considerations.

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20.1 Introduction

Today, the energy demand has drastically increased, reaching approximately 14,282 Mtoe by 2018, of which 82% is supplied through fossil fuels (IEA 2020). The excessive consumption of fossil resources (i.e. coal, petroleum, natural gas) accelerates its depletion (Qin et al. 2021). Furthermore, the industries of fossil fuels release numerous air pollutants, including greenhouse gases and fine dust, which has led to climate change (Ryu et al. 2020). Besides, one of the best alternative options for fossil-based refineries is biomass (e.g. BW and by-products) biorefinery as it can be seen as a sustainable approach (Sartori et al. 2021). A biomass biorefinery refers to a series of biological and/or chemical processes that transform organic feedstock into bioenergy such as ethanol, biogas, syngas gas, and other value-added products such as biochar, biopolymers, and bio-lipids (Shahbaz et al. 2021).

BW (or organic waste) can be a potential source of bio-energy and bio-products if appropriately and wisely managed (Rehan et al. 2019). Several streams of BW include sewage sludge, food waste, green waste, and manure waste (Sayara et al. 2020; Sánchez 2019). In addition, their quantities have increased rapidly along with population growth, urbanization, and industrialization, making the management of BWs a global challenge (Singh et al. 2014; Fan et al. 2021). Conventional dumpsites or unsanitary landfilling has become major sources of human, air, soil, and water contamination due to greenhouse gas emissions, leachate, and disease-carrying animals and insects (Ayilara et al. 2020). Moreover, one metric ton of organic solid waste can release 50–110 m^3 of carbon dioxide (CO_2) and 90–140 m^3 of methane into the atmosphere during decomposition in uncontrolled landfills (Macias-Corral et al. 2008).

BW biorefineries have recently attracted increased global interest to sustain the energy–environment nexus by tackling carbon management and greenhouse gas emissions. However, the residues generated in the various processing and extraction processes in the biochemical pathway impede the biorefinery development within the circular economy concept. Subsequently, more research and development work is needed to optimize these technologies for achieving maximum economic, environmental, and social benefits.

Composting is an attractive technology to restore nutrients from organic solid waste to agricultural lands. It has many advantages over other methods of managing BW, including lower technical complexity and capital investment and lower environmental burdens because pathogens are usually killed during the thermophilic phase (Atif et al. 2020; Haouas et al. 2020). Additionally, the substantial amount of heat generated inside the compost heap can be recovered and reused (Bajko et al. 2019). Moreover, microorganisms found in the compost medium can be advantageous in various applications, including bioremediation and biofertilization of degraded soils (Haouas et al. 2021a). Finally, when used in an integrated/cascaded manner to treat organic waste from extraction and conversion processes, composting will provide a practical and sustainable solution to achieve zero-waste processes in a biorefining system (Alibardi et al. 2020).

This chapter represents an overview of composting benefits in biorefinery systems, including the transformation of downstream residues into valuable materials and energy. It will discuss the models for integrating composting into biorefineries that use a biochemical pathway to treat BW targeting the environmental and techno-economic feasibilities.

20.2 Underlying Principles of BW Biorefineries

Organic waste valorization is a critical issue that could significantly reduce the world's reliance on fossil fuels (Su et al. 2015; Chaturvedi et al. 2020). In fact, energy from BW will be an important contributor to meeting future energy demands from clean and sustainable sources. BW processing in a biorefinery concept results in a production of a broader range of products like biofuels, chemicals, and biomaterials. In addition, chemicals produced through biorefining processes are more environmentally friendly than those produced by petroleum refineries (Mohr and Raman 2013). Chemicals produced are not finished products in and of themselves; they are used in subsequent processes to produce plastics, fibres, and additives, among other things (De Buck et al. 2020).

Knowing the compositions, the interactions of its components, and the desired end products is essential to select an effective biorefinery configuration (Carmona-Cabello et al. 2018). In addition, the sustainability and profitability factors of the biorefinery are also extremely important and must be assessed to define the energy and environmental issues and the associated costs of any proposed design (Ferreira 2017; De buck et al. 2020).

Actually, biorefinery strategies incorporate multi-step processes after feedstock selection. The first step usually involves pre-treatment of BW followed by biochemical or thermochemical processes (Ferreira 2017). The pre-treatment is one of the most important steps in the entire process, while both the efficiency of the conversion and downstream processing steps depend on it (Cherubini et al. 2009). In biochemical treatment including fermentation and anaerobic digestion (AD), pre-treated BW is converted into a value-added product using enzymes or microorganisms (Coma et al. 2017). The thermochemical pathway includes liquefaction, gasification, and pyrolysis in which BW is treated at elevated temperatures using chemicals as a solvent and catalyst (Ortiz et al. 2020; Tsegaye et al. 2021). Indeed, due to higher conversion efficiencies, combining two or more of the above processes in an integrated/cascaded hybrid system has piqued the interest of many researchers (Strezov and Evans 2014; Lee et al. 2019).

20.3 Biochemical Conversion Platform

Biochemical conversion is a system by which BWs are converted via enzymes or microorganisms into a range of advanced derivatives of biofuels, heat, electricity, and value-added chemicals and biomaterials (Trubetskaya and Matsakas 2021). In comparison to thermochemical processes, biochemical processes are carried out at relatively low temperatures (below 80 °C). Generally, the biochemical platform follows a chain of crucial steps starting with feedstock supply, pre-treatment, hydrolysis, biological conversion, and product recovery (Rabaçal et al. 2017). Enzymes break down the overall structure of organic matter in the hydrolysis step, and the resulting hydrolyzate stream is then fermented by microorganisms (Kucharska et al. 2018). It is worth noting that enzymatic reactions are known for their extreme product selectivity, making this conversion platform ideal for creating specific products (De Buck et al. 2020).

During fermentation, the substrate is converted into recoverable products (alcohols or organic acids) due to the action of microorganisms. Ethanol is the most common fermentation product, and other chemical compounds such as hydrogen, methanol, and succinic acid are beginning to gain research interest (Papadaskalopoulou et al. 2019; Wei et al. 2020). According to the current knowledge about the process, the utilization of BW for fuel production has received a lot of attention due to the low cost of production compared to sugar biomass materials, which will allow fermentation technology to scale up and commercialize more efficiently (Papadaskalopoulou et al. 2019).

Subsequently, AD occurs in controlled reactors without oxygen at temperatures around 35–65 °C, where anaerobic bacteria break down the fermented stream to form biogas (Qin et al. 2021). The main component of biogas, methane, can be purified to a purity of up to 97%, allowing it to be used as a natural gas substitute (Tallou et al. 2020a). The AD-based biogas industry has been implemented in a number of developing countries. However, there are some limitations to this technology in terms of lignocellulose conversion efficiency and productivity (Kainthola et al. 2019).

Therefore, many techniques are already available to develop the current biochemical conversion models depending on feedstock composition. Thermochemical technologies such as slow pyrolysis, thermal treatment, and gasification were found to be among the best pre-treatment options for improving the performance of biochemical conversion by significantly increasing the fraction of fermentable organic carbon (Pardo-Planas et al. 2017; Ghysels et al. 2020; Gallipoli et al. 2021). Otherwise, incorporating post-processing techniques into the biochemical platform to manage residues and by-products will improve its efficiency while lowering its carbon footprint. Composting as a post-treatment in a BW biorefinery model could be promising. Numerous studies have demonstrated the effectiveness of composting treatment to stabilize lignocellulose-rich materials, which are the most resistant to AD, since the chemical structure of these molecules can be cracked aerobically (Song et al. 2021; Bustamante et al. 2013; Preble et al. 2020).

20.4 Composting Integration Aspects

Composting has been widely proposed as a single operation unit for solid organic waste valorization into a high fertilizing product. However, this system is regarded as a low-value process because of the low economic benefit derived from the compost product (0–9 €/t) and also due to not taking advantage of the other compost benefits (i.e. heat energy and compost-derived products) (Evans and Wilkie 2010).

This aerobic process is a simple process that can convert AD and other biochemical processes residues in open-air conditions or in-vessel. The strength of this process is manifested in the capacity to decompose complex organic matter such as hemicelluloses, celluloses, and lignin, which is the main reason for digestate instability (Cheung et al. 2010; Haouas et al. 2021b). Carbohydrate polymers in lignocellulose, which are important energy sources for involved microorganisms, are rather selectively converted in the composting process, leaving a lignin-enriched residue converted to typical lignin-derived composting products, being humic substances (Ansari et al. 2021).

Thus, the composting of the organic fractions generated in the different processes of treatment and extraction can be considered a key element to take full advantage of all the biorefinery fluxes and convert organic matter into high-quality products (Fermoso et al. 2018). Furthermore, compost can be reallocated to the field to recycle nutrients and sequester carbon in an agricultural context.

20.4.1 Composting of Downstream Residues

The digestate obtained after the AD process has a high organic matter and nutrient content (Tallou et al. 2020b). However, solid digestates are the major part of biorefinery fluxes that do not find a way to be valorized and are often disposed of in landfills or burned in waste-to-energy sites, with only a small portion being sent to post-processing (Pecorini et al. 2020). The agricultural valorization of digestate without further treatment could still be unproductive or unsafe according to current standards (Monfet et al. 2018). Even though AD reduces the pathogenic load compared to untreated substrates, prions and spore-forming bacteria may be present in the digestate (Gómez-Brandón et al. 2016; Fermoso et al. 2018). Thus, phytotoxic effects on plants may occur upon its direct land application due to undesirable characteristics, such as odour, viscosity, high humidity, and high content in volatile fatty acids (Orzi et al. 2010; Parra-Orobio et al. 2021). These factors have the potential to harm seed germination as well as plant growth and development. Other minority compounds of the digestate, such as heavy metals, phenolic compounds, or high salinity, can also induce phytotoxicity (Fermoso et al. 2018; Haouas et al. 2021c). On the other hand, fibres (hemicellulose and cellulose) and lignin are barely digested by bacteria, make up a large portion of the organic matter in the digestate solid fraction, and are non-degraded and unstable (Menardo et al. 2011; Romio et al. 2021).

Therefore, additional bio-stabilization is required to turn the raw digestate into a valuable product that can be a beneficial soil amendment within the context of reducing climate change impacts and developing the circular bioeconomy concept (Lu and Xu 2021; Manu et al. 2021; Song et al. 2021). Several authors have studied aerobic post-treatments of digestate, such as pyrolysis (Tayibi et al. 2021), air gasification (Freda et al. 2019), and composting (Chaher et al. 2020). Composting the solid fraction of the digestate could be a viable method for not only managing these materials but also improving the quality of the end product by lowering odour emissions, moisture content, potential phytotoxicity, and pathogen bacteria load (Bustamante et al. 2013; Song et al. 2021). In addition, composted solid digestate was stated as a fertilizer to reduce the need for synthetic inorganic fertilizers while also providing micronutrients that are not normally added to the soil (Haouas et al. 2021b). Furthermore, using composted digestates as a source of nutrients in agriculture, fossil energy consumption in the chemical fertilizers supply chain can be saved, allowing for more sustainable production (Pecorini et al. 2020). However, composting of digestate has received little attention, and there is still much to learn about the process.

Direct composting of the solid fraction of digestate can be challenging and is still dependent on the nature of feedstock (Torres-Climent et al. 2015). In order to improve the compostability of the solid fraction of digestate, process conditions (temperature, C/N, aeration, moisture, pH, and turning frequency) must be optimized. In addition, composting conditions of the solid phase of AD must be adjusted for each scenario, considering specific requirements to maximize the microbial activity (Torres-Climent et al. 2015). Furthermore, in an integrated AD/composting system, another issue worth exploring is the digestion time of the AD process. Not only will the digestion period of the AD process modify the nature of the digestate, but it will also have an impact on compost maturity and gas emissions during digestate composting, as well as the methane yield and power inputs for heat supply in the AD process (Tallou et al. 2021).

The use of additives could be a feasible option to improve the composting operation (Haouas et al. 2020). According to Smidt et al. (2011), subsequent composting of digestate after adding bulk materials achieved a high humification degree. Bustamante et al. (2013) studied the co-composting of the solid fraction of pig slurry digestates with different bulking agents, such as wheat straw, vine shoot pruning, exhausted grape marc, and pruning pepper plants. In an experiment by Song et al. (2021), food waste digestate was co-composted with sawdust and/or mature compost. The results of both studies showed a high enhancement of maturity, stability, and nutrient availability of final composts compared to the untreated digestate of AD and compost of only digestate. Otherwise, hydrolysis solid residue and low-quality fibres from other processes of biochemical biorefinery could constitute suitable additives for composting, hence adjusting the low compostability of AD digestate. However, some BW digestates can produce high-quality compost without the use of other additives in some cases. Wastewater sludge, agricultural solid waste, and municipal solid waste digestates have demonstrated a high capacity for self-composting (Teglia et al. 2011).

20.4.2 Composting Heat Energy Harvesting

During the intensive composting phase at the beginning of the process, the temperature rises and reaches values ranging from 40 °C to 75 °C at the thermophilic phase (Klejment and Rosiński 2008). As a result, a considerable amount of heat is accumulated in the compost and raises its organic matter and water temperature. This increase in temperature was due to microbes' activity quickly degrading the energy-rich and easily degradable compounds (starches, sugar, and fats) and some more resistant substances (proteins, hemicellulose, and cellulose) (Shangguan et al. 2020). The thermophilic phase can last for several weeks (in food waste composting) to several months (in lignocellulosic waste composting) under proper insulation (Fan et al. 2021; Ye et al. 2019). An average of 37.4% of that heat resulted from total bio-oxidation of organic compounds, assumed to be carbohydrates. Other heat was produced due to the incomplete decomposition of organic compounds into simpler organic substances (Klejment and Rosiński 2008).

Generally, heat is metabolically generated according to the basic equation (Finstein et al. 1986):

$$\text{Fresh BW} + O_2 \xrightarrow{\text{microbial activity}} \text{stabilized organic residue} + CO_2 + H_2O + \text{heat}$$

Simultaneously, a small amount of heat will dissipate via convection and conduction, and water evaporation (Fan et al. 2021). Thus, the excess heat must be removed to keep the compost at a good temperature range to achieve high biological activity and maximal heat generation (Mudhoo and Mohee 2007).

Composting could be a source of bioenergy due to the accumulation of heat. However, there is a scarcity of information on the potential heat content of composted biomass, and the results are as diverse as the composted biomass composition (Walling et al. 2020). Klejment and Rosiński (2008) stated that the heat released during the high-temperature phase of municipal waste composting is 1136 kJ.kg.dry matter^{-1}. Values of cumulative energy of 8092 kJ.kg.dry matter^{-1} of biosolid waste and woodchip composting were reported by Ekinci et al. (2006).

Nevertheless, due to low thermal conductivity coefficients between compost and recovery devices, heat recovery from compost is limited. The value of this coefficient is affected by the compost's temperature, humidity, and density. Only 13.4% of the heat generated in a compost pile is contained in hot air. In comparison, 63% of the energy balance is contained in hot water vapour, with the remaining heat being lost from the pile through natural convection and radiation. Various approaches to efficiently extracting heat from composting have been proposed. The simplest method is direct heat utilization of compost vapour. Hydronic heating via within-pile heat exchangers is the second configuration, which uses coiled tubes implanted in the composting mass to heat water flowing through them (Smith et al. 2017). Among the most common technologies used in this configuration is the water jacket method, which consists of a water tube coated on the surface of the reactor/pile, and the heat generated in the reactor heats the water via conduction. Another system involves recirculating water through polyethylene pipes buried in the composting mass, which act as heat exchangers (Fan et al. 2021). Percolation water technology is another conduction-based technology in which water is sprayed, percolated, collected, and recirculated. During the percolation process, the percolated water is heated by conduction, and the heat is removed by a heat exchanger during the collection process. This approach captures the greatest quantity of thermal energy and is most commonly used by commercial composting facilities (Smith et al. 2017). The last type is the low-temperature heat recovery technology, which can efficiently recover heat from a low-temperature heat source (<100 °C) (Fan et al. 2021). Instead, Shangguan et al. (2020) suggested another technology to recover heat in the form of electricity, which produced a voltage of 8.8–18.6 V and a maximum power of more than 7 W by taking advantage of the temperature difference between the compost and the surrounding environment. As a result, the generated electricity was used to power a small aeration pump to speed up aerobic composting.

The bioenergy from composting can be used in agriculture and horticulture, where greenhouses can benefit from both heat and CO_2. Otherwise, the heated water can be directly used for the hydronic space heating or be sent to the domestic hot water accumulation tank and be directly used.

20.4.3 Compost Value-Added Products

In addition to the solid compost product, other marketable products can be extracted from the compost. For example, in composting, microorganisms break down organic pollutants such as polyphenols by the release of extracellular enzymes into low molecular weight compounds and then transform them into heterogeneous and complex carbon macromolecules called humic substances (Vishan et al. 2014; Jurado et al. 2015; Kutu et al. 2019). The humic substances' application via compost can have beneficial effects on plant growth due to their water retention capacity, nutrient uptake, and suppression of various phytopathogens (Guo et al. 2019). In addition, humic substances have the ability to chelate the water-soluble form of heavy metals due to their functional carboxylic, hydroxylic, quinolinyl, and phenolic groups (Guo et al. 2016). Water extracts and humic substances were extracted to act as plant biostimulants and may behave as rhizospheric bio-effectors to stimulate plants' biochemical and physiological activities (Spaccini et al. 2019).

In addition, many researchers focus on the isolation of bacterial strains that have multiple functions and can support abiotic stressors such as temperature, organic matter content, texture, moisture, and pH during compost preparation and soil application. The well-conducted composting process stimulates the development of various types of bacteria and fungi, including beneficial populations of microorganisms that characterize the end product (Haouas et al. 2021a). Many bacterial strains isolated from the compost medium have various applications such as the thermostable degradation of lignocellulose (Ma et al. 2020), the biological control of phytopathogens (Suárez-Estrella et al. 2019), the promotion of the growth of plants (Martínez-Cano et al. 2022), and the bioremediation of heavy metals (del Carmen Vargas-García et al. 2012).

20.4.4 Environmental and Techno-Economic Feasibilities

Evaluating the economy and sustainability of the biorefinery is extremely important to understand the energy, environmental burdens, and costs of any production/ conversion system, giving insight into its sustainability (Ferreira 2017). Integration of composting to produce heat, compost, and compost co-products (compost water extract, humic substances, and bacterial biofertilizers) in a biorefinery system could be a good solution in terms of both cost reduction and decarbonization of the whole system.

The integrated biorefinery incorporates the composting process into its platform design for the continued processing of residues streams and by-products must be modelled in order to guarantee all aspects of feasibility. Comprehensive process models could provide a powerful tool for decision-makers when installing and operating a biorefinery. For this reason, it is of primordial importance to highlight the key success components of the feasibility of models: reactors design, kinetics, and especially life cycle assessment (LCA). LCA is a developed version of mass and heat balances, is a powerful tool recommended for making decisions, and facilitates monitoring mass and energy flows throughout the process chain (Sánchez 2019). LCA analysis was largely carried out to ensure the accuracy of different models and simulated variables of the whole biorefinery design. Also, it is needed to define the environmental impacts that are often expressed as some pollution categories (Yang et al. 2021).

The intensification of efforts to model the integrated biorefinery (including composting technology) is therefore considered highly desirable. Available models of composting technologies found in the literature are limited to only a single process step. However, they may be used as a guide in designing and assessing the conditions under which good compost quality may be expected and could be an effective tool for the scale-up of the process within the framework of BW biorefinery. From an environmental point of view, our focus in this contribution was placed on CO_2 emission as the most striking limit for composting integration in the biorefinery concept technology. The first-order kinetic models of Bonifacio et al. (2017) (Eq. 20.1), Vasiliadou et al. (2015) (Eq. 20.2), and Chen and Hashimoto (1980) (Eq. 20.3) were demonstrated to be efficient in predicting cumulative CO_2 emission.

$$J_{\mathrm{CH_4,ferm}} = \mathrm{KCH_4}\ \mathrm{C_{CO_2}}\ F_{t,\mathrm{ferm}} \tag{20.1}$$

$\mathrm{C_{CO_2}}$: amount of C emitted (kg.C.d^{-1}).

$F_{t,\ \mathrm{ferm}}$: effect of temperature on CH_4 production.

KCH_4: maximum fraction of CO_2–C that can be converted to CH_4–C within a day.

$J_{\mathrm{CH_4,ferm}}$: daily production rate of CH_4 due to fermentation (kg.C.d^{-1})

$$\frac{dV_{\mathrm{CO2}}}{dt} = \frac{1}{P_{\mathrm{CO2}}}\frac{d(\mathrm{CO_2})}{dt} \tag{20.2}$$

$V_{\mathrm{CO_2}}$: Volume of CO_2 emitted.

$P_{\mathrm{CO_2}}$: density of CO_2 (kg-CO_2/m^3 CO_2).

$$\mathrm{CO_2} - \mathrm{C} = 100 - 100 \times \left(R + \frac{(1-R)K}{\mu_m t - 1 + K}\right) \tag{20.3}$$

R: refractory coefficient.

K: Chen and Hashimoto constant.

μ_m: maximum specific growth rate of microorganism (day^{-1}) at time 't'.

Regarding the CO_2 emissions to the atmosphere, the insertion of composting in the biorefinery system will contribute to the reduction of atmospheric emissions thanks to the production of bioenergy. Also, compost products could promote carbon storage in the soil hence improving soil proprieties. It also can be considered a technology that offers the opportunity to produce energy while improving carbon sequestration, enhancing climate change mitigation (Bolan et al. 2012).

As evidenced by Irvine et al. (2010) and Malesani et al. (2021), a full-scale in-vessel composting unit can be useful in terms of the cost implementation, time of the process, greenhouse gases mitigation, energy recovery and utilization, quality of the final product. For the sake of simplicity, Fig. 20.1 represents a schematic configuration of the composting technology within a biorefinery plant that processes BW. In terms of the installation cost-effectiveness, the compost heat recovery system was subjected to an initial cost evaluation to calculate a cost per kWh of energy that could be provided by using the heat of the compost. The capital cost of installing the system is estimated at £11,662, and the annual operating cost at £1039 by Irvine et al. (2010). When compared to solar thermal systems and ground-source heat, the system was found determined to provide the most reliable supply of the three systems and at a very competitive highly affordable price of £0.499 and £0.097 per kWh for domestic hot water supply and spatial heating, respectively.

The cost related to the materials involved with the construction of a compost heat recovery system is low, and it will not add additional costs to the biorefinery implementation. In the study of Malesani et al. (2021), a heat recovery system was implemented, and the energy provided cost was compared with two green technologies (solar thermal panels and geothermal plant) and two traditional technologies

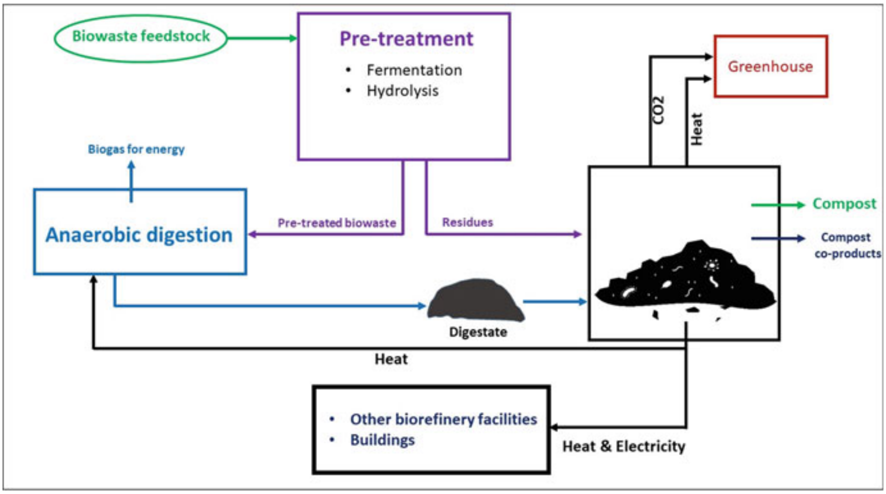

Fig. 20.1 Schematic design of composting integration in the biorefinery

(pellet combustor and natural gas condensing boiler). This system could provide sufficient energy to the biorefinery plant and for domestic usage at competitive prices ranging between 0.087 € $kW.h^{-1}$ and 0,074 € $kW.h^{-1}$, with respect, for example, to the energy generated by a geothermal plant, where the unit price is 0.120 € $kW.h^{-1}$ to 0.124 € $kW.h^{-1}$. Irvine et al. (2010) and Smith et al. (2017) found similar results.

Moreover, revenue from heat, bioelectricity, and other composting products can reduce the initial costs a user must incur when setting up a BW biorefinery. It can therefore be concluded that collecting the composting heat through a heat exchanger and/or as electricity is a realistic solution to contributing to energy demand by the biorefinery facilities (Malesani et al. 2021). More research is needed to determine the economic advantages of composting over other treatment technologies of biorefinery residues.

20.5 Conclusion

The integration of composting in biorefineries that process BW can address the energy sustainability and waste disposal issues in this system. This biotechnology allows obtaining various products by treating downstream residues of different biorefinery processes, mainly the digestate of AD. Also, composting will advance BW biorefinery transition to a circular bioeconomy because of the environmental and techno-economic efficiency of this process.

Obtained compost and its co-products such as extracted humic substances and beneficial bacteria could have wide applications. In addition, the utilization of the energy generated from the composting operation is multipurpose, which can be used in agriculture farms, domestic buildings, and for the biorefinery plant energy supply. Bioenergy provided by composting is predicted to reduce the high capital costs of current biorefinery designs.

More mathematical models are needed to determine the optimal configuration of composting integration in the BW biorefinery concept, based on the principles of sustainable development in which the economic, environmental, and social aspects are considered.

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Chapter 21
Vermicomposting Technology: A Sustainable Option for Waste Beneficiation

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Abstract Intensified food production in response to increased population pressure has resulted in the consequent generation of large quantities of solid and liquid wastes that need to be sustainably managed. Vermicomposting is a process that has gained momentum as a technology that can be used to beneficiate much of the organic waste materials from agricultural and industrial activities. However, in much of the research presented, several authors have used various materials with limited optimization while different methods have also been used to determine the maturity of vermicomposts, which makes this body of knowledge difficult to replicate and practically apply. Our chapter presents research on vermicomposting of various materials using different species and intents to guide the optimized vermicomposting of selected but ubiquitous organic and industrial materials. The chapter also presents the current and effective methods of analyzing vermicompost maturity. In ending, the potential value of the vermicompost and its products in driving climate-smart agriculture and degraded soils restoration is also highlighted. Our chapter, therefore, forms a guide of optimized vermicomposting thus allowing for the effective contribution of this technology in a circular economy.

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21.1 Introduction

The world population has been on an increasing trend with the population estimated to increase from 7.9 billion to 9 billion by 2050. The growing world population has consequently increased food demands which has driven the intensification of food production systems for crops and animals. Furthermore, as electricity and technology became widely accessible, industrial activities and urbanization have also increased to accommodate the growing population moving to the industrial and economic hubs. Though these intensified systems have managed to increase the food output and economic productivity, they have however consequently increased the generation of both solid and liquid waste, thus creating a huge challenge of waste management. As the waste challenge continued to increase, there has been an increase in the inappropriate disposal of waste into landfills and other places, within the linear economy. According to Mupambwa and Mnkeni (2018), these wastes pose a health and environmental pollution hazard through the deposition of harmful toxic elements and pathogens in the environment. In response to the growing waste management challenges, a circular economy model is now being adopted, whose intention is to eliminate waste by optimizing recycling and valorization, thus closing the gap between the production and natural ecosystems' cycles. Vermicomposting is one such technology that is being promoted as an ecologically sustainable waste valorization technology that can be used to recycle organic wastes, thus driving the circular economy agenda.

Vermicomposting is a technology that employs mainly epigeic earthworms in enhancing the biodegradation of waste during the composting process, thus enhancing the mineralization of organic materials into organic fertilizers. With agriculture being amongst the major contributors of solid and liquid organic wastes (mainly animal wastes), vermicomposting is being promoted as an effective technology of converting these agro-wastes into organic fertilizers. These improved organic fertilizers can form an important source of stable organic carbon for use in soils that have been depleted of organic carbon due to heavy tillage practices. Furthermore, there has been an increase in the scientific evidence on the negative influence of inorganic fertilizers in a soil's overall quality and health, which has driven the interest in organic nutrient sources like vermicomposts. Apart from using the earthworms to convert solid wastes like animal manure into fertilizers, there has been a recent interest that makes use of earthworms in the treatment of wastewater, a process called vermifiltration (Arora and Saraswat 2021). Our chapter, therefore, highlights research progress that has been made on the process of vermicomposting and areas where scientific advancement is still desired to allow for the optimized vermicomposting thus allowing for the effective contribution of this technology in a circular economy.

21.2 The Science of Vermicomposting and Earthworms

Vermicomposting is a term that originated from the word "*vermis*" meaning worm and refers to a composting process driven by various types of organic matter feeding earthworms (Das et al. 2016a, b). According to Gomez-Brandon and Dominguez (2014), vermicomposting has thus been defined as "*bio-oxidative process in which detrivorous earthworms interact with microorganisms and other fauna within the decomposer community, thus accelerating the stabilization of organic matter (OM) and greatly modifying its physical and biochemical properties*." Though the term vermicomposting suggests the action of mainly earthworms, the process as described, involves various trophic levels, i.e., primary, secondary and tertiary (Goswami et al. 2021). The vermicomposting process starts with the primary consumers, the bacteria and fungi; followed by the action of the microbe feeders which are the secondary consumers that include the earthworms; nematodes and micro-arthropods and lastly by microbial detritivores (Goswami et al. 2021). During this vermicomposting, earthworms are critical as they drive the increase of the substrate surface area by breaking the original substrate into smaller parts, in processes that have been collectively called gut-associated processes as indicated in Fig. 21.1 (Swati and Hait 2017). The secondary consumers are important as they also act as storehouses of different classes of microbes (Goswami et al. 2021). Unlike traditional composting where naturally occurring micro-organisms are the key drivers of the decomposition process, and thermophilic micro-organisms drive

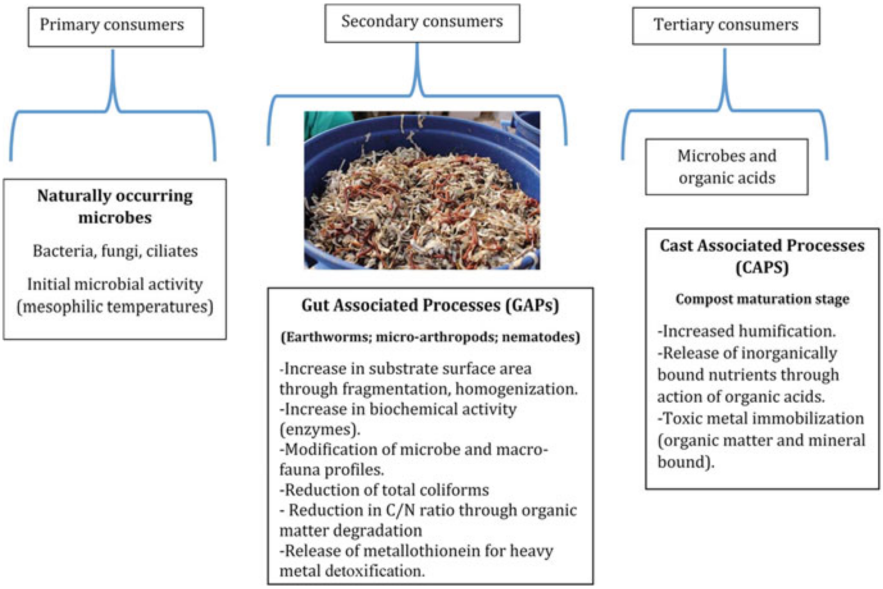
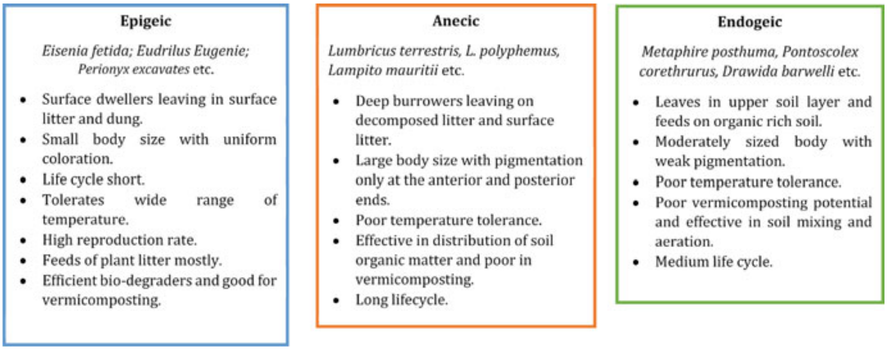


Fig. 21.1 Schematic diagram showing the various stages of the vermicomposting process



Epigeic

Eisenia fetida; Eudrilus Eugenie; Perionyx excavates etc.

- Surface dwellers leaving in surface litter and dung.
- Small body size with uniform coloration.
- Life cycle short.
- Tolerates wide range of temperature.
- High reproduction rate.
- Feeds of plant litter mostly.
- Efficient bio-degraders and good for vermicomposting.

Anecic

Lumbricus terrestris, L. polyphemus, Lampito mauritii etc.

- Deep burrowers leaving on decomposed litter and surface litter.
- Large body size with pigmentation only at the anterior and posterior ends.
- Poor temperature tolerance.
- Effective in distribution of soil organic matter and poor in vermicomposting.
- Long lifecycle.

Endogeic

Metaphire posthuma, Pontoscolex corethrurus, Drawida barwelli etc.

- Leaves in upper soil layer and feeds on organic rich soil.
- Moderately sized body with weak pigmentation.
- Poor temperature tolerance.
- Poor vermicomposting potential and effective in soil mixing and aeration.
- Medium life cycle.

Fig. 21.2 The three categories of earthworms based on their various characteristics and environmental requirements (adapted from Dominguez and Edwards 2011)

the first stage, vermicomposting involves mesophilic microbes throughout the process.

Earthworms are described as macroscopic, clitellate oligochaete annelids that are terrestrially based invertebrates. According to Dominguez and Edwards (2011), earthworms have a segmented body that is bilaterally symmetrical with a cocoon-producing gland called a clitellum that is found in all adults. Earthworms have both male and female organs (hermaphroditic animals), and reproduction occurs through cross-fertilization between two worms, that then each produce eggs that are contained in a cocoon (Dominguez and Edwards 2011).

Earthworms are classified according to the three groups, i.e., epigeic, endogeic, and anecic (described in Fig. 21.2), with the epigeic group having been shown to be effective in degrading organic matter, faster multiplication rates and wide environmental tolerance (Dominguez and Edwards 2011). Of the epigeic earthworms, *Eisenia fetida; E. Andrei* and *Eudrilus eugeniae* have been widely used for vermicomposting (Mupambwa et al. 2016; Ravindran et al. 2015). Though not being effective, the endogeic and anecic earthworms indicated in Fig. 21.1 have also been used for vermi-degradation.

21.3 Current State of Research on Vermicomposting

Various research on vermicomposting has been done in different countries; Table 21.1 presents a summary of the results of this research. The majority of the research has focused on enhanced biodegradation xxxx to sustainably manage municipal, industrial and agricultural wastes, with the intention of creating nutrient-rich organic fertilizers with limited environmental effects.

Table 21.1 Selected research in certain countries on vermicomposting and earthworms

Country	Research drive	Main research results	Selected references
South Africa	• Use of animal manure like cow dung, chicken manure, pig manure, and goat manure. • Optimizing the initial mixture for C/N ratio and earthworm stocking density of animal manures for vermicomposting. • Use of *Eisenia fetida* species for vermicomposting. • Amending organic fertilizers with inorganic amendments like fly ash and rock phosphate for enhanced fertilizer value. • Use of microbial inoculants like effective microorganisms (EM) in increasing the biodegradation and mineralization rate of vermicomposts. • Use of waste paper as a source of carbon in composts.	• Dairy manure with a carbon to nitrogen ratio adjusted to 30 to 1 resulted in the highest compost quality and biodegradation relative to the one with a carbon to nitrogen ratio was adjusted to 45 to 1. • Pre-composting for 1 week eliminated up to 95% of fecal coliforms, *E. coli* and of *E. coli* 0157. • Addition of phosphate rock (PR) enhanced biodegradation and increased the final N and P concentrations of vermicomposts. • A stocking density of 12.5 g-worms per kg of cow manure compost resulted in a highly humified vermicompost. • Fly ash incorporation into cow dung adjusted to a C/N ratio of 30/1 resulted in optimized vermi-degradation. • Effective micro-organisms addition resulted in enhanced vermi-degradation and nutrient mineralization in cow manure amended with fly ash. • Higher earthworm stocking density of between 25 and 37.5 g of worms per kg for fly ash amended cow manure compost resulted in high P mineralization and biodegradation. • Phosphate solubilizing bacteria addition to cow manure vermicompost amended with fly ash or phosphate rock increase	Mupondi (2010); Unuofin and Mnkeni (2014); Mupambwa (2015); Lukashe (2018); Jacobs (2019), Ravindran and Mnkeni (2016)

(continued)

Table 21.1 (continued)

Country	Research drive	Main research results	Selected references
		P release. • For effective vermicomposting of cow manure, a carbon to nitrogen ratio of 40 to 1, was observed to be optimum.	
Spain	• Biology of earthworms used for vermicomposting. • Influence of compost conditions on earthworm survival, growth, and reproduction. • Ecology and genetics of earthworms. • Nutrient and microbial transformations in vermicomposts and plant growth. • Comparison of vermicomposting and composting. • Changes in nutrients, microbial biomass and activity in soils after exposure to three endogeic species of the genus Postandrilus.	• A moisture content of between 80% and 90% was observed to be idea for pig manure vermicomposting using *Eisenia andrei*, with 8 earthworms per 43.61 g of dry compost being effective. • Vermicomposting of pig slurry resulted in the increase in microbial biomass. • *E. Fetida and E. Andrei* which are commonly used as one species are two distinct species. • *Eisenia fetida* is the striped morph with the area between the segments having no pigmentation or is yellow or pale yellow—(tiger worm), while *E. andrei*, the common red worm, is uniformly red in color. • Environmental conditions during vermicomposting strongly affects cocoon production, rates of development, and growth of earthworms. • Most earthworms preferred temperatures for growth ranging between 15 and 25 °C with temperatures below 10 °C resulting in reduced or little feeding activity; below 4 °C, cocoon production and development of young earthworms	Dominguez and Edwards (1997); Dominguez (2004); Aira et al. (2018); Aira and Dominguez (2014); Dominguez et al. (2010).

(continued)

Table 21.1 (continued)

Country	Research drive	Main research results	Selected references
		ceased completely. • The mineral and organic N contents in soil were generally enhanced in casts produced by all three endogeic earthworm species i.e. *Postandrilus majorcanus, P. sapkarevi and P. palmensis.*	
Iran	• Lumbricidae family of earthworm taxonomy based on the phylogenetic analysis.	• The *Philomontanus* gen. was observed to comprise of three different species i.e. *Philomontanus sarii* sp. nov., *P. mahmoudi* sp. nov. and *P. baloutchi* sp. Nov; which look similar in form but different in characters like size, pigment color and clitellum position.	Bozorgi et al. (2019)
India	• Processing of municipal waste using earthworms while evaluating changes in physio-chemical properties and the efficiency of different species. • Vermicomposting of water weeds like water hyacinth (*Eichhornia crassipes* mixed with cattle manure and saw dust); ipomoea (*Ipomoea carnea*) using *E. fetida* and its effects on heavy metals. • Vermicomposting of animal fleshing generated from tannery industries. • Comparison studies on *E. fetida, Eudrilus euginae and perionyx excavatus* earthworms on vermi-degradation efficiency of household wastes. • Vermi-degradation of fly ash using earthworms for sustainable waste	• Based on the compost chemistry, *E. fetida* was observed to be more superior in performance over *L. mauritii.* • Epigeic species of earthworms (i.e. *E. fetida)* was not effective in modifying soil structure to which *L. mauritii* was capable of. • Vermicomposting was shown to be effective in convert tannery waste into nutrient-rich organic fertilizers. • *E. euginae* was observed to have faster growth rate, higher feeding and biodegradation capacity, compared to other two species. • In different combinations of fly ash and cow manure mixtures, bio-available forms nitrogen increase where	Kaviraj and Sharma (2003); Srivastava et al. (2020); Singh and Kalamdhad (2013); Hussain et al. (2016); Ravindran et al. (2008); Bhattacharya and Chattopadhyay (2004); Ananthakrishnasamy et al. (2009).

(continued)

Table 21.1 (continued)

Country	Research drive	Main research results	Selected references
	valorization using different epigeic earthworm species.	earthworms were present, with the 1:1 mixture having the best characteristics. • Vermicompost application significantly improved plant growth parameter.	
China	• Heavy metal bioremediation in acidic soils through vermicomposting. • Influence of biochar on vermi-degradation of sewage sludge and household waste and earthworm growth parameter. • Effects of earthworms during vermi-degradation of sewage sludge on changes in heavy or trace metal concentration. • Effects of adding the biosurfactant rhamnolipid, the lignolytic and cellulolytic fungus *Phanerochete chrysosporium*, and the free-living nitrogen-fixing bacterium *Azotobacter chrococcum* on vermicomposting of green waste using *Eisenia fetida.* • Changes in Chinese cabbage growth, antioxidant and metabolite concentration after the application of cow manure vermicompost.	• Amendment with vermicompost increased soil physical properties like aggregate stability while reducing the heavy metal bio-availability. • Amendment with biochar increased the reproduction rate of earthworm's species *E. fetida*. • Vermi-degradation increased nutrient mineralization as indicated by the higher concentrations in final compost. • Vermidegradation with addition of biochar reduced the heavy metals content. • The bio-accumulation factor for Cu, Ni, Zn, and Pb showed the effectiveness of earthworms in removing heavy metals. • The growth and reproduction of earthworms increased under the addition of the lignolytic and cellulolytic fungus and the free-living nitrogen-fixing bacterium together with the biosurfactant. • Essential amino acids in plants increased under the treatments with vermicompost applied.	Liu et al. (2019); Khan et al. (2019); Liu et al. (2012); Gong et al. (2017).

21.4 Vermicomposts on Plant Growth

In the twentieth century, there was a rush in adopting green revolution technologies that made use of huge quantities of inorganic fertilizers, which resulted in positive increases in crop yield responses throughout the world. However, with the growing realization that in as much as it is important to increase crop yields, the soil is also an important resource that can be degraded if we over-exploit it without feeding it also. This has driven researchers into focusing on organic nutrient sources that not only feed the crop but also feed the soil with organic matter. However, the main limitation with the application of organic fertilizers has been the low nutrient concentration of macronutrients (NPK), which are usually lower than what the crop requirement, relative to that supplied by inorganic fertilizers. Various researchers have thus evaluated the potential nutrient supply of vermicomposts and the subsequent crop responses as summarized in Table 21.2.

21.5 Vermicomposts on Degraded Soil Physical Properties

One of the most significant benefits of vermicompost application on soils is the improvement in soil physical properties. Soil physical properties have significant implications for plant roots penetration, gas exchange, water movement and water holding capacity and hence plant growth and yield. However, most soils in the smallholder sector especially in developing countries are highly degraded with poor soil structure and are highly prone to compaction and high rates of soil erosion. Consequently, crop yields are always lower that possible or expected yield, resulting in high food insecurity. The use of vermicompost in such soils can significantly improve soil physical properties leading to an improved soil environment, which allows for optimum crop growth.

Vermicomposts are high in organic matter particularly humic acids, which function to improve soil aggregation through the formation of clay-humic complexes. The formation of these complexes increasing inter-particle hydrophobicity and cohesion within aggregates. The increased hydrophobicity results in reduced clay wettability and hence reduced aggregate disruption. This in turn improves soil porosity, leading to improved water infiltration as well gaseous exchange. Moreover, an improvement in soil porosity leads to reduced soil bulk density and hence improved plant root growth. The reduction of soil bulk density with application of vermicompost is also attributed to the low bulk density of vermicompost, which mediates the bulk density of soil upon application (Ibrahim et al. 2015). Aksakal et al. (2014) observed significant improvements in soil aggregate stability, porosity and reduced bulk density and penetration resistance after applying vermicompost in soils with different textures. These changes were attributed to increases in soil organic matter with the application of vermicompost. Similarly, Azarmi et al. (2008) attributed reduced bulk density and improved total porosity with the

Table 21.2 Summary of selected studies that have used vermicomposts as nutrient source in crop production

Vermicompost type and crop	Macro-nutrient composition of vermicompost.	Research results	Reference
Pig manure and food wastes vermicompost commercially prepared using *Eisenia* spp. used for the growing of tomatoes and marigold in a substitution (10% and 20%) experiment. The commercial potting mix metro mix was used as a control.	• *Pig manure vermicompost*: Total N (2.36%); Organic C (43.8%); Total P (4.5%); Total K (0.4%); nitrate (4525 μg/g); pH (5.3). • *Food waste vermicompost*: Total N (1.8%); organic C (34.0%); Total P (0.4%); Total K (1.1%); nitrate (665 μg/g); pH (7.3).	• Slight increase in shoot dry weights under treatments containing 10% food waste vermicompost or 20% pig waste vermicompost, compared to the control. • All potting mixtures containing vermicomposts had a significantly greater cumulative microbial activity than the metro-mix control. • Vermicomposted pig solids contained large concentrations of nitrates, which resulted in increased plant growth comparable to where fertilizer had been applied.	Atiyeh et al. (2000)
Commercially produced vermicomposts from dairy cow manure, supermarket food wastes and recycled paper wastes were applied at field rates of 10 or 20 t ha^{-1} for tomato, pepper and strawberry growth. Vermicompost amended treatments supplemented with inorganic fertilizer to make N level equal.	• *Food waste*: NPK; 13 g/kg; 2.7 g/kg 9.2 g/kg. • *Cow manure*: NPK; 19 g/kg; 4.7 g/kg 14.0 g/kg. • *Paper waste*: NPK; 10 g/kg; 1.4 g/kg; 6.2 g/kg.	• The marketable tomato yields in all vermicompost-treated plots were consistently greater than yields from the inorganic fertilizer-treated plots. • Significant increase in plant growth and yield parameters of peppers in treatments where vermicompost had been applied relative to where synthetic fertilizer had been applied. The increased growth was attributed to increase in microbial biomass.	Arancon et al. (2003)
The vermicompost (VC) was prepared from vegetable waste mixed with cow dung in 2:1 ratio by employing epigeic species, *Eisenia fetida*. 4 levels of vermicompost	• Major nutrients (N = 0.92%; P = 1.21% and K = 1.45%).	• Vermicompost application increased plant spread, leaf area, and dry matter, while increasing fruit yield. • Substitution of vermicompost drastically reduced the incidence of	Singh et al. (2008)

(continued)

Table 21.2 (continued)

Vermicompost type and crop	Macro-nutrient composition of vermicompost.	Research results	Reference
at 2.5, 5.0, 7.5, and 10.0 t ha^{-1} were supplemented with inorganic fertilizers to balance fertilizer requirement of strawberry.		strawberry physiological disorders like albinism; fruit malformation and occurrence of gray mold. • Increase in the marketable fruit yield up to 58.6% with better quality parameters. • Best results were achieved at 7.5 t ha^{-1}, though doses higher than these did not significantly increase higher growth and yield parameter.	
Cow manure *and Eisenia fetida* were the sources for the vermicompost. Sweet basil (*Ocimum basilicum*) was grown in peat medium supplemented with different vermicompost (VC) ratio, with water stress during flowering.	• The properties of vermicompost were: Organic matter content (61.37%); pH (6.98); EC (3.55 dS/m); total nitrogen (2.66%); total potassium (1.14%); total phosphorus (0.74%); total calcium (0.23%).	• Vermicompost applications at 10% and 20% concentration significantly improved the plant dry weight, root dry weight, leaf dry weight under water stress. • Essential oil compounds, major compounds (estragole and eucalyptol) decreased with the water stress and vermicompost treatments, while minor compounds increased with the vermicompost and water stress. • Increased nutrients reported under vermicompost amended treatments.	Celikcan et al. (2021)
Fly ash-enriched cow dung vermicompost and its effects on growth of *Chloris gayana* in a gold mine waste-affected soil. Amendment rates to supply 20 mg P/kg soil, 40 mg P/kg soil as vermicompost and 40 mg P/kg soil as triple superphosphate (control) fertilizer.	• The properties of the vermicompost were as follows: pH (8.8); total P (0.03%); total N (0.016%); nitrate (10.7 mg/kg).	• The 40-mg P/kg fly ash vermicompost treatment resulted in a significant increase in shoot height, shoot biomass and root biomass compared to the control treatment. • Amendment effect had no influence on plant tissue N, Pb, Cd and As. • The increased biomass was reflected in the plant	Lukashe et al. (2020)

(continued)

Table 21.2 (continued)

Vermicompost type and crop	Macro-nutrient composition of vermicompost.	Research results	Reference
		tissue analysis where 40 mg P/kg had high P, Ca, Mg, and K, though not significantly different to the 20-mg P/kg treatment. • Applying fly ash-based vermicompost at 40 mg/kg can be effectively used for re-vegetation.	
Fly ash amended cow dung vermicompost incorporated into pine bark at different 5 rates from 0% to 100%, for the growth of ornamental marigold.	• The fly ash amended vermicompost properties were as follows: pH (11.14); Ca (4.5 g/kg); K (4.2 g/kg); nitrate (9.0 mg/kg); P (508.6 mg/kg)/.	• Incorporation of FA up to 75% resulted in significantly high germination percentages above 90% compared to only 22.5% for the 100% PB medium. • After 4 weeks of growth, seedlings in the 25 and 50% FA substituted media had higher plant height and leaf area. • The 25% FA treatment resulted in significantly higher number of flowers and buds relative to the 50 and 75%. • For effective marigold seedling germination and growth, a 50% fly ash amended growing medium is recommended. • For maturity and flower production, the 25% fly ash vermicompost combination is preferred.	Mupambwa et al. (2016)

application of various amounts vermicompost on loam soil in Iran to improved soil organic matter. To further demonstrate the importance of vermicompost in improving aggregates, Zhu et al. (2017) reported that vermicompost improved the formation and stabilization of water-stable aggregates bauxite residue. The residue was converted from a sheet-like structure to a granular macro-aggregated structure, while micro-aggregates were converted from a grain to a granular or prismatic structure.

21.6 Vermi-Leachate

In vermi-degradation, most research has focused on the solid compost chemistry with very limited research having been focused on the liquid leachate that is generated. Furthermore, there has been no research that has deliberately attempted to leach the nutrients from the solid compost, for the development of liquid organic nutrient sources. Unlike the ordinary composts derived leachates, these vermi-leachates are superior as they contain significant concentrations of essential plant growth nutrients, several enzymes, plant growth hormones and can also increase plant disease resistance. However, though anecdotal evidence suggests these positive benefits from the use of vermi-leachates, there has been very limited work focusing on characterizing the molecular composition of these leachates. Such information can be critical in identifying which treatments result in increased specific organic molecules that can be linked to the increased responses in crops. Furthermore, there is need for optimizing the leachate extraction methods of the leachates in vermicomposts, to allow for the development of effective liquid organic nutrient sources. Such research will be crucial in driving the adoption of cheap nutrient sources for hydroponics among resource-poor in developing countries.

21.7 Vermicomposting in Wastewater Treatment

Natural freshwater resources are under increasing pressure due to climate change, population growth coupled with a rise in urbanization and industrialization have led to tremendous increases in the generation of volumes of domestic and industrial wastewater (Singh et al. 2020). The treatment and disposal of these large volumes of wastewater and sludge produced have subsequently become a global concern as this leads to pollution of oceans, lagoons, soils, surface and groundwater and poses environmental threats to aquatic life (Manyuchi et al. 2018; Singh et al. 2020). Overtime, the discharge of untreated or semi-treated sewage in open waterways, has led to increased nutrients such as nitrogen and phosphorus, that may cause eutrophication, resulting in low dissolved oxygen which has intense ecological impacts in water bodies (Kanaujia et al. 2020). Numerous technologies for wastewater treatment have been explored e.g. septic tanks, activated sludge, constructed wetlands, etc. however; they have become inefficient (Chowdhary et al. 2020). Therefore, a need to optimize cleaner technologies for wastewater treatment such as vermifiltration, to safeguard the environment arises.

Vermifiltration is a wastewater treatment process that relies on the use of earthworms and naturally occurring micro-organisms, which are placed inside a bio-filter to convert organic wastes and pathogens present in wastewater into stable compounds (Fig. 21.3).

Studies on vermifiltration technology under various conditions have showed to be effective in the treatment of sewage sludge, with high levels of reducing the

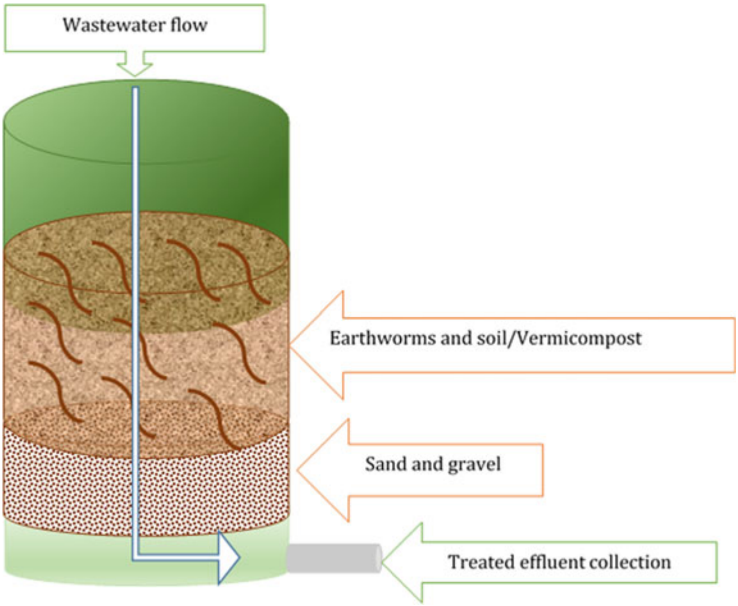


Fig. 21.3 Schematic diagram showing the general structure of a vermi-filtration unit (adapted from Singh et al. 2017)

biological oxygen demand, total solids, as well as some ability to remove N and P (Manyuchi et al. 2018). Studies also show that various earthworm species are capable of treating wastewater and these include *Eisenia fetida, Perionyx sansibaricus, Lumbricus rubellus, Eudrilus eugeniae and Eisenia hortensis,* although *Eisenia fetida* is the most commonly studied (Arora and Saraswat 2021). Domínguez-Crespo et al. (2012) looked at the effects of Ni, Cu, Zn and Cd from wastewater on the adaptability of *Eisenia fetida* earthworms to the treatment process by measuring the growth performance and fecundity of the earthworms. The study found that heavy metal bio-accumulation in the tissues of the worms was difficult, therefore significantly affected the weight of the earthworms and caused mortality. Kumar et al. (2016), evaluated the effectiveness of *Eisenia fetida and Eudrilus eugenia* earthworms in treating domestic wastewater and revealed a significant removal of BOD, TSS, and TDS. Comparatively, *Eisenia fetida* showed the highest potential for use in wastewater treatment during the vermifiltration process. Adugna et al. (2015), used *Eudrilus eugeniae* in a concentrated gray water treatment study relative to fine sand and sawdust reporting effective removal of wastewater parameters such as BOD, though the species showed low removal efficiencies for TSS and coliforms. Ghatnekar et al. (2010), used the earthworm *Lumbricus rubellus* in treating effluent from a gelatin industry and also found reductions in COD (90%) and BOD (89%) in the final effluent, which was then used for irrigation purposes.

These studies indicate that vermifiltration creates an opportunity to naturally recycle wastewater from household and municipal processes, that can be adopted from both household and industrial use. Vermifiltration has the potential in effectively recycling household organic wastes while contributing to waste valorization. In addition, no after-treatment by-products are generated by achieving the aim of minimizing pollution (Liu et al. 2021).

21.8 Conclusion

The use of earthworms to enhance the biodegradation of organic and at times inorganic materials is gaining momentum from a waste management perspective and also as a way of generating nutrient-rich organic fertilizers. During the vermicomposting process, complex linkages exist between the earthworms and naturally occurring micro and macro-organisms, indicating the process of vermicomposting is not entirely dependent on earthworms alone. It is interesting to note that, though various research has been done on vermicomposting, more research is still required to develop optimized protocols that can allow for the production of nutrient predictable organic fertilizers. This variation in nutrient composition and the low macro-nutrient contents have contributed to the lack of commercial adoption of these nutrient sources, and most of them are still confined to local household use. However, positive results on crop growth and soil improvement have been reported by various researchers, indicating the great potential of vermicomposts in sustainable soil fertility management. Furthermore, vermicomposts have now also been adopted in the wastewater filtration process, with great potential in water sanitation among the resource-poor communities.

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Chapter 22
Land Application of Organic Waste Compost

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Abstract The acceleration of urbanization and industrialization has led to a sharp increase in waste production, most of which are biological waste. This is a global challenge because traditional waste management methods (i.e., landfills) have brought environmental issues including greenhouse gas emissions, leachate formation, and toxin release. Composting is a sustainable and effective way to deal with biological waste. This book chapter reviews the compost from the aspects of compost quality and compost application. Introduce the commom application of compost as organic fertilizer or soil conditioner, focusing on the low level of use of organic waste compost in reality. This paper conducts a comprehensive study on the energy content of compost pellets through the analysis of key methods. It also looked forward to the environmental impact and future prospects, providing further insights into the application of this technology in the closed-loop bioeconomy.

22.1 Introduction

Population growth, booming economy, and acceleration of urbanization have caused a crisis of organic waste worldwide. According to incomplete statistics, 2.01 billion tons of municipal waste have been generated in the world so far. If it continues according to the current development momentum, it is estimated that 3.4 billion tons of municipal waste will be generated every year in 2050 (Chen et al. 2020; Wainaina et al. 2020). Treatment of waste in an inappropriate manner will cause serious environmental problems, including environmental pollution, ecological imbalance, harmful to human health, and natural resource exhaustion (Sharma et al. 2019). In addition, extreme climatic conditions and high carbon footprint in agricultural production will cause the government to invest more resources to improve the environment. Therefore, it is necessary to explore an environmentally friendly, sustainable organic waste management method, and it also has important significance in the circular economy. Biotransformation technology has received extensive

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attention in recent years because it can convert organic waste into stable organic fertilizer and value-added products (Huang et al. 2021a).

Since organic waste is rich in organic matter and nutrient elements that can be used by plants, biotransformation can realize nutrient recovery and the production of useful energy through organic supplementation and convert organic waste into organic fertilizer (Matos et al. 2020). It should be pointed out that the biotransformation of organic waste is also an equally important way in the development of biostimulants (Huang et al. 2021b). In recent years, biostimulants or compost products of organic waste containing biostimulants have been proven effective in agriculture and horticulture, mainly including worm compost, betaine, humus substances (HSs), and chitin/chitin sugar derivatives (Dube et al. 2018). Huang et al. (2021a) observed that the compost samples after biotransformation of organic waste contained various betaine, and the biotransformation of larvae could effectively improve this substance. Additionally, the compost after larval transformation contains a variety of biologically active substances, such as antimicrobial peptides, coagulants, and chitin, which are important sources of biostimulants (Lopes et al. 2020; Wang et al. 2020a).

According to United Nations projections, there will be 9.8 billion people on the earth in 2050, and food demand is expected to increase by about 60% in the next few decades. Unfortunately, FAO predicts that global agricultural productivity will decline at a rate of 1% per year (FAO 2017). Therefore, in the near future, the supply of wheat, rice, and corn will be difficult to maintain the current human needs, with shortages of about 38%, 42%, and 67%, respectively (Rehman et al. 2017). Human health and social well-being will be seriously threatened (García-García et al. 2020). The current situation provides an excellent opportunity for plant scientists to apply their knowledge to the agricultural field and try to increase productivity by recycling bio-accelerators in organic waste. In this regard, the use of bioconversion technology to treat organic waste to develop biostimulants is a promising strategy. It provides solutions to the contradiction between population growth, reduced food production, and global environmental degradation, provides opportunities for the utilization of organic waste resources, and brings benefits to consumers, the food processing industry, and the global environment.

However, as far as we know, an advanced literature review and extensive reference framework on biostimulants in organic waste biotransformation composting have not yet appeared. Therefore, this research will focus on studying the biostimulants and their synthesis pathways in the bioconversion of organic waste compost and conduct systematic research on related knowledge to maximize the potential of organic waste bioconversion technology. Finally, knowledge gaps, challenges, and opportunities will be identified in order to further develop and promote these technologies as tools to achieve sustainable development goals.

22.2 Advantages of Organic Waste Compost Application in Farmland

22.2.1 Advantages of Organic Waste Compost in Soil

Use of waste composting methods can provide an opportunity to relocate large quantities of waste, and convert them into usable organic compost resources, which is the preferred choice for resource utilization of agricultural waste. As a main fertilizer that provides nutrients to crops, organic waste compost has been used in farmland to form a great ecological balance system.

22.2.1.1 Enhancement of Soil Nutrients

Organic waste compost contains various large and trace elements necessary for plant growth and development and provides a relatively smooth and lasting nutrient supply to plants, with great after-effects, which is a direct source of plant mineral nutrients (Liu et al. 2019). Most organic waste compost is rich in a variety of soluble organic compounds that make up organisms, such as cellulose, hemicellulose, sugars, proteins, amino acids, amides, and phospholipids. After the mineralization and decomposition by various microorganisms and enzymatic reactions, these compounds would be transformed to simpler substances, which can be directly absorbed and utilized by crops (Mazumder et al. 2021). During the decomposition process, multifarious organic acids would be generated, including oxalic acid, lactic acid, carbonic acid, etc. These organic acids can form stable complexes with calcium, magnesium, iron, and aluminum ions, which can promote the conversion of insoluble phosphates in the soil, thereby increasing the availability of phosphorus (Cid et al. 2020). Furthermore, it is worth noting that organic waste compost application has a positive effect on accelerating the desalination and de-alkalization of the soil, remediating soil contaminated by heavy metals, adjusting soil pH, and improving the quality of agricultural products (Cao et al. 2018; Kulikowska et al. 2015). After organic waste compost application in farmland, various nutrients will be continuously released for plants to absorb and utilize through the decomposition, and also continuously carbon dioxide would be generated to improve the carbon balance of plants (Duong et al. 2013).

22.2.1.2 Improvement of Soil Biological Activity

Inevitably livestock manure contains a variety of active enzymes secreted by the digestive tract of animals and multiple enzymes produced by microorganisms (Acharya et al. 2019). The application of organic waste compost in farmland greatly improves the enzyme activity in soil, which is beneficial to enhance the absorption performance, buffering performance, and stress resistance of the soil and can provide nutrients and energy for soil microbial activities (Baiano et al. 2021; Deng et al. 2020). These enzymes can change the soil microbial flora, increase the beneficial soil microbial community and soil enzyme activity, which is conducive to the transformation of soil materials and the utilization of soil nutrients (Ezugworie et al. 2021). Significantly, microorganisms can produce biologically active substances such as vitamins B_1, B_6, B_3, B_{12}, folic acid, streptomycin, etc., which play an important role in decomposing organic materials and improving the conversion of materials and energy in soil. For example, vitamins B_1 and B_6 can promote the development of plant roots, make crops better utilize the effective ingredients in soil, and promote plant growth and enhance crop resistance. Meanwhile, organic waste compost application can make the microorganisms multiply and increase the total amount of beneficial microorganisms in soil, such as nitrogen-fixing bacteria, ammonifying bacteria, cellulose decomposing bacteria, nitrifying bacteria, etc., so that the metabolic intensity of the soil has been enhanced (Deng et al. 2021).

22.2.2 Advantages of Organic Waste Compost in Plant

Recently, organic waste compost has been widely used as plant growth substrates or soil amendments, opening up new solutions for the resource utilization of organic solid waste. It was found that organic waste compost can provide suitable water, fertilizer, gas, heat, and other environmental requirements for plant growth and pass it to various growth parts through the root system, which can promote the growth and development of plant roots and improve crop biomass and quality.

22.2.2.1 Improvement of Crop Yields

Organic waste compost is an environmentally friendly fertilizer prepared by biologically treating organic solid waste such as animal manure and other organic solid wastes, which is recognized and valued by the public, and the development and application of composting products has gradually become a current research hotspot. Through field experiments, Jeong et al. (2019) found that the overall yield of rice after applying pig manure organic compost was 2556 kg ha^{-1} higher than that without fertilization. Among them, the dry weight of grain, straw, roots, branches and leaves, and rhizosphere deposits was 712, 1247, 195, 108, 294 kg ha^{-1} higher than those without fertilizer. Meanwhile, Lakhdar et al. (2010) studied the effect of different doses (0, 40, 100, 200, and 300 t h^{-1}) of municipal solid waste compost on the yield of wheat (*Triticum durum*) and reported that after applying 40 tons and 100 tons of compost, plant yields increased significantly.

22.2.2.2 Improvement of Crop Quality

Organic waste compost has the advantages of high effective nutrient content, long-lasting fertilizer efficiency, strong disease resistance, etc. Microorganisms in compost will transform and decompose the nutrients in soil when entering the soil environment, turning them into effective nutrients that can be easily absorbed by crops, thereby improving crops quality. Rehman et al. (2017) investigated the effects of different compound composts of sewage sludge, pig manure, and phosphate rock on rice phosphorus absorption, soil phosphorus recovery and growth, and residual effects on wheat crops were studied. They found that the uptake of phosphorus by rice and wheat in the compost treatment is higher than that of the control treatments, indicating the long-term positive residual effect of compost fertilizer. Furthermore, the field experiment study of straw and solid sewage sludge composite compost showed that the nutrient use efficiency of sugar beet and wheat increased significantly, especially nitrogen and phosphorus (Mantovi et al. 2005). Also, Roca-Pérez et al. (2009) reported the significant effects of rice straw and sludge mixed compost on soil properties and plant growth.

22.2.2.3 Promotion of Crop Root Development

Organic waste compost can increase root biomass, expand the range of root growth, improve the ratio of root to shoot, increase the horizontal distribution range of roots, and increase the proportion of roots distributed in deep soil layers (Cucu et al. 2020). Research had found that the use of compost in the soil can improve the degree of carbon mineralization in the rhizosphere soil, improve the environmental problems of soil degradation caused by continuous farming methods, stimulate root growth, and increase crop yields (Zhang et al. 2014). Plants obtain nutrients from the soil mainly through the absorption and utilization of nutrients by the roots. The suitable environment for most plant roots is neutral. The pH of the soil affects the availability of nutrient elements, thereby affecting the absorption efficiency of nutrient elements by the roots. The active substances such as enzymes existing in modern aerobic composting can significantly increase the soil enzyme activity after being applied to the soil and affect the root activity of crops and plant growth.

22.3 Principles and Methods of Applying Organic Fertilizer to Crops

22.3.1 Wheat

China is a largely agricultural country, and the agricultural economy occupies a large part of the proportion of China's economic development. As one of the important crops in our country, wheat has a very important position in social development to ensure its food security. To get more wheat harvests, we need to scientifically and effectively fertilize the wheat in the process of wheat planting. Based on this, the application of fertilization technology in the process of wheat planting was analyzed and the corresponding countermeasures for possible problems in the process of wheat planting were put forward, all to increase the yield of wheat, increase the income of farmers, and promote the development of society.

1. Common problems in wheat fertilization
    (a) Insufficient amount of organic fertilizer
    Fertilizers are divided into ordinary chemical fertilizers and organic fertilizers. The nutritional components of the two are different. Organic fertilizers have certain effects in improving soil quality and can also guarantee the nutrients of crops, which is conducive to the sustainable development of the land. When fertilizing wheat, some farmers, because they do not know much about organic fertilizers, think that it is enough to apply chemical fertilizers to wheat and do not need to apply organic fertilizers, thus ignoring the effect of organic fertilizers on the soil. If the amount of organic fertilizer is not satisfied for a long time, it will lead to changes in the soil structure, which is unfavorable to the growth of wheat and thus affects the yield of wheat.
    (b) Unreasonable use of fertilizer
    At each stage of wheat growth, different fertilizers are needed, and there are differences in the ratio of dosage. This requires different amounts of fertilization in different growth stages according to the needs of wheat, and a certain amount of fertilization cannot be used blindly. However, in actual planting, many farmers did not realize this. They relied on their subjective consciousness to fertilize the wheat and did not fertilize the wheat in a scientific and effective ratio. This affected the normal growth of wheat, thereby reducing the harvest of wheat. For example, farmers know that applying nitrogen fertilizer can increase yield, so they blindly apply more nitrogen fertilizer to wheat, resulting in a decline in the disease resistance of wheat, which still affects the growth of wheat and reduces yield (Akao 2018).

2. Winter wheat in North China
    Principles of fertilization
    (a) Adjust and reduce the amount of nitrogen and phosphate fertilizer appropriately according to the level of soil fertility.
    (b) Increase the application of organic fertilizers, realize the return of wheat straw to the field, and encourage the combined application of organic and inorganic fertilizers.
    (c) Nitrogen fertilizer is applied in stages, and the proportion of nitrogen fertilizer application in the middle and late stages of growth should be appropriately increased.
    (d) According to the soil potassium status, apply potassium fertilizer efficiently; pay attention to the coordinated application of zinc and other trace elements.

(e) Fertilizer application should be combined with high-yield and high-quality cultivation techniques.

Fertilization method

(a) Apply 2000–3000 kg of organic fertilizer based on the yield of wheat per mu.
(b) Under the condition of more than 600 kg per mu: nitrogen fertilizer (N) 10–15-kg/mu, phosphate fertilizer (P_2O_5) 6–8 kg/mu, potassium fertilizer (K_2O) 6–8 kg/mu; yield 500–600 kg per mu Bottom: nitrogen fertilizer (N) 8–12 kg/mu, phosphate fertilizer (P_2O_5) 4–6 kg/mu, potassium fertilizer (K_2O) 4–6 kg/mu; under the condition of 400–500 kg per mu: nitrogen fertilizer (N) 6–10 kg/mu, phosphate fertilizer (P_2O_5) 3–5 kg/mu, potassium fertilizer (K_2O) 0–5 kg/mu; under the conditions of 400 kg/mu yield: nitrogen fertilizer (N) 5–8 kg/mu, phosphate fertilizer (P_2O_5) 3–4 kg/mu, potassium fertilizer (K_2O) 0–5 kg/mu.
(c) If organic compost is applied to the base fertilizer, the amount of chemical fertilizer can be reduced as appropriate. For zinc-deficient soils, 1 to 2 kg/mu of zinc sulfate can be applied. 1/3 of the total nitrogen fertilizer is used as base fertilizer, 2/3 is used as top dressing at the jointing stage; all phosphorus and potassium fertilizers are used as base fertilizer. When the yield level is below 400 kg/mu, the proportion of nitrogen fertilizer as base fertilizer and top-dressing fertilizer can be half. For wheat fields in sulfur-deficient areas, if superphosphate, potassium sulfate, and sulfur-based compound fertilizer are not used as the base fertilizer, ammonium sulfate should be selected for the first topdressing, and about 2 kg of ammonium sulfate per mu. Dryland wheat can appropriately increase the proportion of base fertilizer, fertilize scientifically, and formulate and issue guidelines for wheat fertilization in various regions according to local conditions.

3. Winter wheat in the Yangtze River Basin

Principles of fertilization

(a) Increase the application of organic fertilizers, implement straw returning to the field, and combine organic and inorganic fertilizers.
(b) Appropriately reduce the total amount of nitrogen fertilizer, adjust the proportion of base fertilizer and topdressing, and reduce the amount of base fertilizer.
(c) Phosphorus-deficient soils should be appropriately increased or stably applied phosphate fertilizers. Soils with abundant available phosphorus can appropriately reduce the amount of phosphate fertilizers.
(d) Give preference to medium- and low-concentration fertilizer varieties. Phosphate fertilizers can choose calcium-magnesium phosphate fertilizer and superphosphate, and potash fertilizers can choose potassium chloride.

Fertilization method

(a) Apply 2000~3000 kg/mu of organic fertilizer.

(b) Under the condition of more than 400 kg per mu: nitrogen fertilizer (N) 10–12-kg/mu, phosphate fertilizer (P_2O_5) 4–6 kg/mu, potassium fertilizer (K_2O) 4–6 kg/mu; yield 300–400 kg per mu Bottom: nitrogen fertilizer (N) 8–10 kg/mu, phosphate fertilizer (P_2O_5) 3–5 kg/mu, potash fertilizer (K_2O) 3–5 kg/mu; under the condition of 200–300 kg per mu: nitrogen fertilizer (N) 6–9 kg/mu, phosphate fertilizer (P_2O_5) 3–5 kg/mu, potash fertilizer (K_2O) 0–5 kg/mu.

(c) All organic compost is used as base fertilizer; 50% of nitrogen fertilizer is used as base fertilizer, and 50% is used as topdressing; all phosphorus and potash fertilizers are used as base fertilizer. Weak gluten wheat should increase the proportion of base fertilizer. In zinc-deficient and manganese-deficient areas, 1 kg of zinc sulfate or manganese sulfate is applied per mu, and ammonium molybdate dressing is used for molybdenum-deficient fields. Applying organic fertilizer or planting green manure over pressed fields can appropriately reduce the amount of base fertilizer. For plots where straw is returned to the field all the year round, the amount of potassium fertilizer can be appropriately reduced (Abubaker et al. 2015).

4. Dry farming winter wheat in Northwest China

Principles of fertilization

(a) Determine the base fertilizer according to the soil water storage status.

(b) Increase the application of organic fertilizers and encourage the combined application of organic and inorganic fertilizers.

(c) Fertilization is based on base fertilizer, supplemented by top dressing.

(d) Fertilizer application should be combined with high-yield water-saving cultivation techniques.

Fertilization method

(a) High-fertility soil, with a yield of more than 300 kg per mu: organic compost 1500–3500 kg/mu, nitrogen fertilizer (N) 6–8 kg/mu, phosphate fertilizer (P2O5) 3–4 kg/mu.

(b) Medium-fertility soil, under the condition of 200–300 kg per mu: organic compost 1500–3500 kg/mu, nitrogen fertilizer (N) 5–7 kg/mu, phosphate fertilizer (P2O5) 3–6 kg/mu.

(c) Low-fertility soil, under the condition of <200 kg per mu: organic compost 1500 ~ 3500 kg/mu, nitrogen fertilizer (N) 3 ~ 5 kg/mu, phosphate fertilizer (P2O5) 3 ~ 7 kg/mu.

(d) Organic fertilizer and phosphate fertilizer are applied as base fertilizer at one time, 70% to 80% nitrogen fertilizer is used as base fertilizer, and 20% to 30% ammonia fertilizer is used as topdressing. The guidelines for scientific fertilization of winter wheat in irrigated fields have been formulated and released in accordance with local conditions.

22.3.2 Corn

1. Northeast cold spring corn area. Including most of Heilongjiang and eastern Jilin.
   Principles of fertilization
   - (a) Determine the reasonable amount of ammonia, phosphorus, and potassium fertilizers based on the results of soil testing and formula fertilization.
   - (b) Nitrogen fertilizer is applied in stages, and the proportion of potassium fertilizer is appropriately increased in high-yield fields.
   - (c) Combination of advanced technologies and sustainable agronomy practices according to climate and fertility conditions.
   - (d) Increase the application of organic fertilizers and encourage the combined application of organic and inorganic fertilizers, and the appropriate amount of straw can be crushed and returned to the field.
   - (e) Pay attention to the application of trace elements such as sulfur and zinc, and increase the application of alkaline fertilizers to the soil with severe acidification.
   - (f) It is recommended that corn and soybeans are intercropped, intercropped or rotated, while reducing the amount of chemical fertilizers and increasing the application of organic fertilizers and biological fertilizers (Cucina et al. 2017).

   Fertilization method
   - (a) Apply organic compost 2000–3000 kg/mu; recommended formula fertilizer 14-18-13 (N-P_2O_5-K_2O) or similar formula fertilizer.
   - (b) The output level is 500–600 kg/mu, the recommended dosage of formula fertilizer 14-18-13 (N-P_2O_5-K_2O) is 20–25 kg/mu, and the 7-leaf stage topdressing urea is 8–10 kg/mu.
   - (c) The yield level is 600–700 kg/mu, the recommended dosage of formula fertilizer 14-18-13 (N-P_2O_5-K_2O) is 25–30 kg/mu, and topdressing urea is 10–13 kg/mu at the 7-leaf stage.
   - (d) The yield level is above 700 kg/mu, the recommended dosage of formula fertilizer 14-18-13 (N-P_2O_5-K_2O) is 30–35 kg/mu, and topdressing urea at the 7-leaf stage is 12–15 kg/mu.
   - (e) The yield level is below 500 kg/mu, the recommended dosage of formula fertilizer 14-18-13 (N-P_2O_5-K_2O) is 15–20 kg/mu, and the 7-leaf stage topdressing urea is 6–9 kg/mu.
   - (f) If organic compost is applied to the base fertilizer, the amount of chemical fertilizer can be reduced as appropriate. In fields rich in phosphorus, zinc, and iron trace element fertilizers should be properly applied.

2. The semi-humid spring corn area in the northeast. Including southwestern Heilongjiang, central Jilin, and northern Liaoning.
   The principle of fertilization

(a) Control the application amount of nitrogen, phosphorus, and potassium fertilizers, apply nitrogen fertilizer in stages, appropriately reduce the amount of base fertilizer, and make full use of the after-effects of phosphorus and potassium fertilizers.
(b) For plots with one-time fertilization, select slow and controlled release fertilizers, and appropriately add diammonium phosphate as seed fertilizer.
(c) The plots with high effective potassium content and low yield level can be used with less or no potassium fertilizer under the condition of applying organic fertilizer.
(d) Pay attention to applying zinc fertilizer to plots with high soil pH, high yield, and zinc deficiency. Plots where chlorine-based compound fertilizers have been applied for a long time should be replaced with sulfur-based compound fertilizers or sulfur-containing fertilizers.
(e) Increase the amount of organic fertilizer and increase the intensity of returning straw to the field.
(f) Promote the application of high-yield and density-tolerant varieties and increase corn planting density reasonably.
(g) Use deep tillage to break the bottom of the plow, promote the development of the root system, and improve the efficiency of water and fertilizer use on the plots without straw.
(h) Cover the planting area with plastic film, consider using slow and controlled release fertilizer when applying base (basic) fertilizer to reduce the number of top dressing.
(i) Use the lower limit of the recommended fertilization plan for medium- and high-fertility soils.

Fertilization method

(a) 1500~2000 kg/mu organic compost for base fertilizer; recommended formula fertilizer 15-18-12 (N-P_2O_5-K_2O) or similar formula fertilizer, according to corn yield, soil nutrient status, and organic fertilizer application, as appropriate increase or decrease the amount of fertilizer.
(b) Yield level is 550–700 kg/mu, the recommended dosage of formula fertilizer 15-18-12 (N-P_2O_5-K_2O) is 20–25 kg/mu, and topdressing urea is 10–15 kg/mu during the big bell mouth period.
(c) The yield level is 700~800 kg/mu, the recommended dosage of formula fertilizer 15-18-12 (N-P_2O_5-K_2O) is 25–30 kg/mu, and urea topdressing is 12–15 kg/mu during the big bell mouth period.
(d) The output level is above 800 kg/mu, the recommended dosage of formula fertilizer 15-18-12 (N-P_2O_5-K_2O) is 30–35 kg/mu, and 15–18 kg/mu of urea is applied in the big bell mouth stage.
(e) The yield level is below 550 kg/mu, the recommended dosage of formula fertilizer 15-18-12 (N-P_2O_5-K_2O) is 15–20 kg/mu, and urea topdressing is 8–10 kg/mu during the bell-month period.

3. The semi-dry early spring corn area in the northeast includes the west of Jilin, the northeastern plain of Inner Mongolia, and the southwest of Heilongjiang.

   Principles of fertilization

   (a) Combined fertilization technology with organic fertilizer and inorganic fertilizer for dyeing, and no-till fertilization technology with straw mulching can be used in windy sandy soil area.
   (b) Deep application of nitrogen fertilizer, the depth of fertilization should reach 8–10 cm; fertilization in stages, it is recommended to apply nitrogen fertilizer in the loudspeaker period.
   (c) Give full play to the coupling effect of water and fertilizer, use the synchronization law of the maximum efficiency period of water and fertilizer demand of corn, and apply nitrogen fertilizer in combination with water supplement.
   (d) Grasp the principle of balanced fertilization, coordinate the supply of nitrogen, phosphorus, and potassium, and pay attention to the application of zinc fertilizer on zinc-deficient plots.
   (e) According to the characteristics of the soil in the area, use physiological acid fertilizer, and the seed fertilizer should be ammonium dihydrogen phosphate.
   (f) Use the lower limit of the recommended fertilization plan for medium- and high-fertility soils.
   (g) Drip irrigation planting under the mulch, consider using slow and controlled release fertilizers when applying base (basic) fertilizers to reduce the number of drip irrigation topdressing (Christel et al. 2014).

   Fertilization method

   (a) Use 1500–2000 kg/mu of organic compost per mu; recommend to use formula fertilizer 13-20-12 (N-P_2O_5-K_2O) or similar formula fertilizer.
   (b) The yield level is 450~600 kg/mu, the recommended dosage of formula fertilizer 13-20-12 (N-P_2O_5-K_2O) is 20~30 kg/mu, and the urea topdressing period is 8–12 kg/mu.
   (c) The yield level is above 600 kg/mu, the recommended dosage of formula fertilizer 13-20-12 (N-P_2O_5-K_2O) is 30~35 kg/mu, and the urea topdressing period is 10–14 kg/mu.
   (d) The yield level is below 450 kg/mu, the recommended dosage of formula fertilizer 13-20-12 (N-P_2O_5-K_2O) is 15–20 kg/mu, and 6–8 kg/mu urea is topdressed in the bell mouth stage.

4. Warm and humid spring corn area in the northeast. Including most of Liaoning and northeastern Hebei.

   Principles of fertilization

   (a) Determine the reasonable amount of nitrogen, phosphorus, and potassium fertilizers based on the results of soil testing and formula fertilization.
   (b) Nitrogen fertilizer is applied in stages, and one-time fertilization should not be used as much as possible, and the proportion and frequency of potassium fertilizer application should be appropriately increased in high-yield fields.

(c) Increase the intensity of returning straw to the field and increase the proportion of organic fertilizers.
(d) Pay attention to the application of trace elements such as sulfur and zinc.
(e) Fertilizer application must be combined with high-yield cultivation techniques such as subsoiling and densification.
(f) Use the lower limit of the recommended fertilization plan for medium- and high-fertility soils.

Fertilization method

(a) Apply 100–2000 kg/mu of organic compost; recommend to use formula fertilizer 17-17-12 (N-P_2O_5-K_2O) or similar formula fertilizer.
(b) The output level is below 500 kg/mu, the recommended dosage of formula fertilizer 17-17-12 (N-P_2O_5-K_2O) is 15–20 kg/mu, and 9–12 kg/mu of urea is topdressed in the bell mouth stage.
(c) The yield level is 500–600 kg/mu, the recommended dosage of formula fertilizer 17-17-12 (N-P_2O_5-K_2O) is 20–25 kg/mu, and urea topdressing is 12–14 kg/mu in the big bell mouth period. mu.
(d) The yield level is 600~700 kg/mu, the recommended dosage of formula fertilizer 17-17-12 (N-P_2O_5-K_2O) is 25~30 kg/mu, and the urea topdressing period is 14–16 kg/mu.
(e) The output level is 700 kg/mu or more, the recommended dosage of formula fertilizer 17-17-12 (N-P_2O_5-K_2O) is 30–35 kg/mu, and 15–20 kg/mu of urea is applied in the large bell mouth stage.

22.3.3 Rice

1. Rice in cold regions of Northeast (Heilongjiang, etc.)
   Principles of fertilization

   (a) Promote the return of straw to the field and attach importance to the fertilization of the paddy soil.
   (b) Increase the proportion of basal nitrogen fertilizer, so that the nitrogen in the basal fertilizer accounts for about 45% of the total ammonia application, reduce the fertilizer distribution, and increase the application ratio of ear fertilizer.
   (c) On acidic soils, it is recommended to choose alkaline calcium-magnesium phosphate fertilizer for phosphate fertilizer.
   (d) Potassium fertilizer can give priority to potassium chloride, and the amount of potassium fertilizer can be appropriately reduced in plots where straw is returned to the field.
   (e) Based on the results of soil testing, pay attention to supplementary application of trace elements and silicon-containing fertilizers.

(f) Adopt water-saving irrigation and top dressing to "bring nitrogen with water" to give full play to the coupling effect of water and fertilizer and improve fertilizer utilization.

Fertilization method

(a) Apply 1500–2000 kg/mu of organic compost.
(b) Apply nitrogen fertilizer (N) 6–8 kg/mu, phosphate fertilizer (P_2O_5) 3–4 kg/mu, and potassium fertilizer (K_2O) 3–5 kg/mu in fields with a target rice yield of 500–600 kg/mu. in zinc or boron-deficient areas, basal application of zinc sulfate 1–2 kg/mu or borax 0.5–0.75 kg/mu; in fields with acidic soil, appropriate basal application f silicon-containing alkaline fertilizers.
(c) 40–45% of nitrogen fertilizer is used as base fertilizer, 20–25% as medicinal fertilizer, 30–35% as ear fertilizer; all phosphate fertilizers are used as base fertilizer; 50% of potassium fertilizer is used as base fertilizer, and 50% as ear fertilizer (Zhou et al. 1994).

2. Double-cropping early rice in the middle and lower reaches of the Yangtze River.
   Principles of fertilization

(a) Appropriately reduce the total amount of nitrogen fertilizer and increase the ratio of ear fertilizer.
(b) Deep application of basal fertilizer, topdressing "bring nitrogen with water."
(c) Phosphate fertilizers prefer to choose ordinary calcium or calcium-magnesium phosphate fertilizers.
(d) Increase the application of organic fertilizers and encourage the return of straw to the field.

Fertilization method

(a) Apply 1000–2000 kg/mu of organic compost.
(b) Under the nutrient condition of 400–450 kg per mu; nitrogen fertilizer (N) 6–8 dry g/mu, phosphate fertilizer (P_2O_5) 4–5 kg/mu, potassium fertilizer (K_2O) 4–5 kg/mu, in the absence of zinc or boron-deficient areas, apply zinc fertilizer or boron fertilizer in an appropriate amount, and apply silicon-containing fertilizer as the base.

    40%~50% of nitrogen fertilizer is used as base fertilizer, 25%–30% is used as tiller fertilizer, 20%~—25% is used as ear fertilizer, all phosphate fertilizer is used as base fertilizer, 50%~60% of potash fertilizer is used as base fertilizer, and 40%–50% as ear fertilizer.

    The amount of basal fertilizer can be appropriately reduced when using organic compost or planting green manure over-compressed fields; in the fields where straw is returned to the field all the year round, the amount of potassium fertilizer can be appropriately reduced.

3. A mid-season rice in the middle and lower reaches of the Yangtze River.
   Principles of fertilization

   (a) Increase the application of organic fertilizer, combining organic fertilizer and inorganic fertilizer.
   (b) Control the total amount of nitrogen fertilizer, adjust the ratio of base fertilizer and topdressing, and reduce the amount of nitrogen fertilizer in the early stage.
   (c) Deep application of basal fertilizer, topdressing "bring nitrogen with water."
   (d) Appropriately reduce the amount of phosphate fertilizer for rice in the oil-rice rotation cropping field.

   Fertilization method

   (a) Apply 1500–2500 kg/mu of organic compost per mu.
   (b) In the case of 550–600 kg per mu, the amount of nitrogen fertilizer (N) for japonica rice is 10–15 kg/mu, the amount of nitrogen fertilizer (N) for indica rice is 8–12 kg/mu, and the amount of phosphate fertilizer (P_2O_5) is 3.5–5 kg/mu, Potassium fertilizer dosage (K_2O) 4.5–6 kg/mu; zinc sulfate 1 kg per acre applied to zinc-deficient soil; silicon-containing fertilizers should be applied as appropriate base.
   (c) 40%~50% of nitrogen fertilizer is used as basal fertilizer, 20%~30% is used as medicine fertilizer, and 20%~30% is used as ear fertilizer; organic fertilizer and phosphate fertilizer are all basal application; potassium fertilizer is divided into basal fertilizer (60%~70%) and ear fertilizer (accounting for 30% to 40%) was applied twice.
   (d) Apply organic fertilizer or plant green manure over pressed fields, the amount of base fertilizer can be appropriately reduced (Zhang et al. 2014).

4. One-season mid-season rice in Southwest China.
   Principles of fertilization

   (a) Increase the application of organic fertilizer, combining organic fertilizer and inorganic fertilizer.
   (b) Adjust the ratio of base fertilizer and topdressing to reduce the amount of nitrogen fertilizer in the early stage.
   (c) Deep application of basal fertilizer, topdressing "bring nitrogen with water."
   (d) Appropriately reduce the amount of phosphate fertilizer for rice in the oil-rice rotation cropping field.
   (e) Choose medium- and low-concentration phosphate fertilizers, such as calcium-magnesium phosphate fertilizer and ordinary calcium phosphate, etc.; choose potassium chloride for potassium fertilizer.
   (f) Appropriate application of silicon-containing alkaline fertilizers or basal quicklime to fields with soil pH below 5.5.

   Fertilization method

   (a) Apply 1000–2000 kg/mu of organic compost.
   (b) When the yield per mu is 550–600 kg, the amount of nitrogen fertilizer (N) for japonica rice is 6–10 kg/mu, the amount of nitrogen fertilizer (N) for indica

rice is 6–10 kg/mu, and the amount of phosphate fertilizer (P_2O_5) is 3.5–5 kg/mu, the amount of potassium fertilizer (K_2O) is 3.5–5 kg/mu.

(c) 35%~55% nitrogen fertilizer is used as basal fertilizer, 20%–30% is used as medicinal fertilizer, 25%–35% is used as ear fertilizer; organic fertilizer and phosphate fertilizer are all basal application; potassium fertilizer is divided into basal fertilizer (60%~70%) and ear fertilizer (accounting for 30% to 40%) was applied twice.

(d) In zinc- and boron-deficient areas, apply zinc fertilizer and boron fertilizer in an appropriate amount; apply silicon-containing alkaline fertilizer or quicklime 30–50 kg/mu in the base of the soil with strong acidity.

5. Double-season early rice in South China.

Principles of fertilization

(a) Control the total amount of nitrogen fertilizer, adjust the proportion of base fertilizer and topdressing, reduce the amount of nitrogen fertilizer in the early stage, and implement nitrogen fertilizer.
(b) Deep application of basal fertilizer, topdressing “bring nitrogen with water.”
(c) Appropriate application of silicon-containing alkaline fertilizers or quicklime in fields where the soil is acidified (Hsu and Lo 1999).

Fertilization method

(a) Apply 1000–2000 kg/mu of organic compost.
(b) In the case of 400–450 kg per mu, nitrogen fertilizer 7–10 kg/mu, phosphate fertilizer (P_2O_5) 2–3 kg/mu, potassium fertilizer (K_2O) 5–7 kg/mu; zinc-deficient soil requires appropriate application of zinc sulfate.
(c) Nitrogen fertilizer is applied in stages, basal fertilizer accounts for 30%~35%, split leaf fertilizer accounts for 30%~35%, ear fertilizer accounts for 30% ~40%, organic fertilizer and phosphate fertilizer are all basal applications, and potassium fertilizer is used as basal fertilizer and medicinal fertilizer twice. Application (50% each).
(d) For plots where organic fertilizer is applied, the amount of base fertilizer can be appropriately reduced; for plots where straw is returned to the field all the year round, the amount of potash fertilizer can be appropriately reduced by 30%.

22.4 Principles and Methods of Applying Organic Fertilizer to Fruits

22.4.1 Apple

1. Principle of applying fertilizer
    (a) The amount of nitrogen and phosphorus fertilizer needs to be appropriately decreased due to different condition of soil fertility and the ability of apple production (Tang et al. 2010). Not only could the final compost products be applied to improve the content of nutrient in farmland, but organic fertilizer combined with inorganic fertilizer also may facilitate the growth of crops (Araújo et al. 2009).

    In other aspect, the amendment of micronutrient additives should be attached importance in addition.
    (b) In the season of fall, the application of base fertilizer needs to be paid attention, the dose of nitrogenous fertilizer should be reduced while increasing the application of potassic fertilizer in the course of fruit swelling stage; orchards which have been already applied base fertilizer, the method to apply fertilizer is to apply final compost products or other organic fertilizer in the period of budding as early as possible; otherwise, droughty areas need to improve water content of soil after manuring in order to facilitate nutrient absorption during the period of early spring. What's more, 1%–3% urea (high concentrations of high) need to be applied three times before the budding period (early March), while adding an appropriate dose of white sugar (about 1%), other micronutrient additives and anti-freezing agent to increase nutrients storage in fruits, thus alleviating the harm of frozen in morning and evening of preference (Devos et al. 1995).
    (c) Additionally, the method of manuring organic compost products should be combined with high-yield quality cultivation technology, such as ridges cultivation, grass mulching technology, pruning technique of pendulous fruit branch, and wall bee pollination techniques, etc. Besides, the mulching film (especially gardening mulch) should be able to be covered in arid region (Devos et al. 1995).
    (d) The amendment of alkaline soil modified agents, such as calcium, magnesium, silicon, or lime, could improve acidified planting soil.
2. Methods to apply fertilizer on apple tree planting
    (a) Before and after the period of apple picking, it is the essential time to apply base fertilizer (such as final compost product or organic fertilizer). In other words, base fertilizer should be applied in the middle of September to the middle of October. As for the late-maturing varieties, early and ripe varieties after harvesting, for late-maturing varieties, base fertilizer should be applied before harvesting as soon as possible (Wang et al. 2017a). It is due to

difficulties of practical operation that manure should be able to be amended immediately after harvesting as soon as possible. The usage of clean compost products or commercial organic fertilizer by ditch method or hole application has been suggested about 600–800 kg/mu; or the application of commercial biological organic fertilizer should be added about 400–500 kg/mu. The amount of organic compost or biological fertilizer should be increased by 20%–100%, the amount of compound fertilizer suggested to be reduced by 10%–50%, meanwhile the depth of fertilizer should be 30–40 cm.

(b) The first time of topdressing should be amended before and after the stage of fruits bagging, the producing area of arm temperate semi-humid monsoon climate is recommended to apply 45% formulation fertilizer ($N:P_2O_5:K_2O = 22:5:18$) or similar substantial fertilizer, and every 1000 kg production suggest to add about 12.5 kg fertilizer. The producing area of the semi-arid continental monsoon climate region is recommended to apply 45% formulation fertilizer ($N:P_2O_5:K_2O = 15:15:15$) or similar formulation fertilizer, and every 1000 kg production is suggested to add about 15 kg fertilizer. The depth of fertilization is about 15–20 cm (Meyer et al. 2018).

(c) The second time of topdressing should be amended from late summer to early autumn. The producing area of arm temperate semi-humid monsoon climate is recommended to apply 45% formulation fertilizer ($N:P_2O_5:K_2O = 12:6:27$) or similar substantial fertilizer, and every 1000 kg production suggest to add about 12 kg fertilizer. The producing area of the semi-arid continental monsoon climate region is recommended to apply 45% formulation fertilizer ($N:P_2O_5:K_2O = 15:5:25$) or similar formulation fertilizer, and every 1000 kg production is suggested to add about 10 kg fertilizer. The depth of fertilization is about 15–20 cm. The manuring method is suggested to decrease the dose of fertilizer while increasing the frequency of fertilization (2–3 times) (Devos et al. 1995). The depth of fertilization is from 15 cm to 20 cm.

(d) As for the orchard soil which may be lack of zinc and boron, the dose of $ZnSO_4$ and $Na_2B_4O_7$ should be suggested to apply 1–1.5 kg/mu and 0.5–1.0 kg/mu during the germination stage. 0.3% $Na_2B_4O_7$ solution should be applied by foliage dressing during anthesis and young fruit stage. 0.3% calcium fertilizer should be suggested to be applied for 3 times in the course of fruit bagging stage (Netthisinghe et al. 2011). In addition, soil acidified orchard, administration of not only 150–200 kg/mu lime but 50–100 kg/mu Si, Ca, and Mg fertilizer could suggest to improve the phenomenon of soil acidification in apple orchard (Netthisinghe et al. 2011).

22.4.2 Pear

1. Principle of applying fertilizer
    (a) The application of cleaner final compost product and organic fertilizer should be suggested to increase. In order to improve content of soil nutrient, the method to seeding and covering grass should be taken into account (Wu et al. 2019). The amendment of alkaline soil modified agents, such as calcium, magnesium, silicon, or lime, could improve Acidified planting soil can improve soil by applying other soil modified agents such as calcium, magnesium, silicon, or lime (Abbasi et al. 2013).
    (b) According to the soil fertility conditions and the growth situation of pear orchards, the dosage of nitrogen, phosphate fertilizers is suggested to be decreased, while the potassium fertilizer is applied increasingly. Meanwhile, the medium trace nutrients (Ca, Mg, Fe, Zn, B) should be applied by foliage dressing.
    (c) Combined with optimized cultivation techniques, ability of output, and soil fertility conditions, several key factors (the stage of applying fertilizer, dosage, and the ratio of amending element) which are related to yield of fruits should be suggested to confirmed (Alcoz et al. 1993).
    (d) The method to apply fertilizer should be optimized as soon as possible, which could alter broadcast application to row or hole application, while combining with methods to irrigation (Alcoz et al. 1993).
2. Methods to apply fertilizer on pear tree planting
    (a) Base fertilizer in the orchard which yield is more than 4000 kg/mu, the usage of final compost products should be suggested to amend about 2–3 m^3/mu, or commercial organic fertilizer should be applied about 12 kg/plant. Application of final compost products could be used about 1.5–2.5 m^3/mu, or the dose of commercial organic fertilizer is suggested to amend about 10 kg/plant in pear orchard which yield could reach about 2000–4000 kg/mu (Braun et al. 2009). In the orchard which yield is <2000 kg/mu, the usage of final compost products should be suggested to amend about 1–1.5 m^3/mu, or commercial organic fertilizer should be applied about 7–8 kg/plant (Wu et al. 2019).
    (b) Fertilization in the stage of germination. The usage of urea and KH_2PO_4 is suggested to applied about 0.1 kg/plant and 0–0.5 kg/plant.
    (c) Fertilization in the stage of young fruits swelling. In the orchard which yield is more than 4000 kg/mu, the usage of urea should be suggested to amend about 0.75 kg/plant, $NH_4H_2PO_4$ should be applied about 0.2 kg/plant, while K_2SO_4 should be applied about 0.25 kg/plant (Garrido-Lestache et al. 2005). Application of urea could be used about 0.5–0.75 kg/plant, the dose of $NH_4H_2PO_4$ is suggested to amend about 0.2 kg/plant, meanwhile the application of K_2SO_4 should be applied about 0.2 kg/plant in pear orchard which yield could reach about 2000–4000 kg/mu. In the orchard which yield is <2000 kg/mu, the usage of urea should be suggested to amend about

0.3–0.4 kg/mu, $NH_4H_2PO_4$ is suggested to amend about 0.2 kg/plant, meanwhile the application of K_2SO_4 should be applied about 0.2 kg/plant (Garrido-Lestache et al. 2005).

(d) Fertilization in the stage of the critical period of floral initiation. In the orchard which yield is more than 4000 kg/mu, the usage of urea should be suggested to amend about 0.4 kg/plant, $NH_4H_2PO_4$ should be applied about 0.4 kg/plant. Application of urea could be used about 0.3–0.4 kg/plant, the dose of $NH_4H_2PO_4$ is suggested to amend about 0.3 kg/plant in pear orchard which yield could reach about 2000–4000 kg/mu. In the orchard which yield is <2000 kg/mu, the usage of urea should be suggested to amend about 0.25 kg/plant, $NH_4H_2PO_4$ is suggested to amend about 0.3 kg/plant (Hobbie 2005).

(e) The methods to topdressing. In the orchards which are lack of B, Zn, Fe, and other medium trace nutrients, the dose of 0.2% $Na_2B_4O_7$, 0.2% $ZnSO_4$ + 0.3% urea mixture, or 0.3% $FeSO_4$ + 0.3% urea should be suggested to apply from the period of germination to anthesis for multiple times every 2 weeks. Calcium-magnesium phosphate fertilizer could be used in the soil of pear orchards which are lack of Ca and Mg. According to the condition of soil fertility, which organic manure have been amended, the dose of chemical fertilizer should be suggested to reduce (Wu et al. 2019).

22.4.3 Orange

1. The principle of applying fertilizer on tangerine planting

   (a) The application of cleaner final compost product and organic fertilizer should be paid attention. In order to facilitate the improvement of soil fertility meanwhile promoting the ability of soil water and land conservation, the method to grass covering in the row of tangerine orchard should be suggested to take into account. The amendment of alkaline soil modified agents or organic fertilizer could improve acidified planting soil (Martínez-Alcántara et al. 2012).

   (b) According to the ability of output and soil fertility conditions, several key factors (the stage of applying fertilizer, dosage and the ratio of amending element) which are related to yield of tangerine should be suggested to confirmed. In producing region of which soil may acidize, middle trace nutrients (Ca, Mg, B, Zn, etc.) should be supplied additionally, especially from the period of germination to anthesis (Martínez-Alcántara et al. 2016).

   (c) The fertilization method of orchard was changed to concentrated hole or ditch application.

   (d) Management of irrigation and fertilization is suggested to be integrated with green efficient cultivating techniques. Before applying fertilizers in spring, the sharping and pruning of fruit trees should be paid attention. It is due to high temperature and drought in the season of summer that the technology of grass covering and hole storage of fertilizer and water should be advocated. Furthermore, the application of organic fertilizer (mature compost products and commercial organic fertilizer) should be suggested to amend (Martínez-Alcántara et al. 2012).

2. Methods to apply fertilizer on tangerine planting
    (a) The usage of clean compost products or commercial organic fertilizer by ditch method or hole application has been suggested about 5–10 kg/plant; or the application of commercial organic fertilizer should be added about 2–3 m^3/mu. In order to improve the situation of tangerine growth, a large amount of organic manure should be suggested to be applied as much as possible. As for base fertilizer, compost products and organic manure should be amended in the season of autumn (Canali et al. 2004).
    (b) In the orchard which yield is more than 3000 kg/mu, the usage of nitrogen fertilizer should be suggested to amend about 20–30 kg/mu, phosphorus fertilizer (P_2O_5) should be applied about 6–10 kg/mu, potassium fertilizer (K_2O) should be amended about 15–25 kg/mu. Application of nitrogen fertilizer could be used about 15–25 kg/mu, the dose of phosphorus fertilizer (P_2O_5) is suggested to amend about 6–8 kg/mu, while potassium fertilizer (K_2O) should be amended about 10–15 kg/mu in pear orchard which yield could reach about 1500–3000 kg/mu. In the orchard which yield is <1500 kg/mu, the usage of nitrogen fertilizer should be suggested to amend about 10–20 kg/mu, phosphorus fertilizer (P_2O_5) should be applied about 5–6 kg/mu, potassium fertilizer (K_2O) should be amended about 6–15 kg/mu.
    (c) The calcium-magnesium phosphate can be used to replace other chemical fertilizers to overcome the deficiency of Ca and Mg nutrients in orchards which are lack of Ca and Mg. The usage of $Na_2B_4O_7$, $ZnSO_4$, and $FeSO_4$ should be suggested to amend about 0.5–0.75, 1–1.5, and 2–3 kg/mu, meanwhile combining with organic manure to facilitate the promotion of orchard soil deficiency of B, Zn, and Fe in the season of autumn. If the phenomenon of soil acidification (pH <5.5) has been discovered, silicon calcium fertilizer or lime would be suggested to be applied about 60–80 kg/mu (Orrisi et al. 2013).

22.5 Principles and Methods of Applying Organic Fertilizer to Vegetables

Vegetables are considered an essential part of human diet due to their rich nutrient contents which are essential for the fulfillment of their health requirements. Use of vegetables in the human diet can fulfill the requirements of vitamins, minerals, organic acids, and many other nutrients materials so that fulfillment their health requirements. The most planting area of vegetable crops such as tomato, potato, beans, and leafy vegetables in the world is continuously increasing productivity year by year. In terms of nutritional effects, organic fertilizers have a significant impact on product quality, soil physical properties, and improved biological activity (Courtney and Mullen 2008; Nigussie et al. 2015). Organic agriculture may prove to be a trend in sustainable agriculture with the use of vermicompost, cow manure and pig manure, poultry manure as organic fertilizers release nutrients more slowly, allowing plants to absorb and retain soil moisture more quickly, thereby improving the quality of plant production (Abdelaziz et al. 2007).

It has many advantages over replacing chemical fertilizers with organic fertilizers, such as improving soil fertility, improve soil conditions and microbial communities, and ultimately promote crop growth effectively (He et al. 2020). In this context, the Ministry of Agriculture and Rural Affairs People's Republic of China Affairs Proposes "Action Plan" Organic Substitute Chemical Fertilizers (OSCF) for fruits, vegetables, and tea in 2017. The main goal of the policy is to reduce the use of chemical fertilizers to promote the resource utilization of animal manure, achieve the green development of agriculture. As listed in Table 22.1, organic waste compost, method of application, and overall effect on various vegetable crops. The partial replacement of chemical fertilizer with organic substitutes will lead to an increase in yield potential and also improve product quality without penalizing the environment (Dabing et al. 2018; Duan et al. 2016). The soil oppression of soil-borne diseases is continuously going low by multiple factors, including soil pH, nutrients, and microbial community composition (Wang et al. 2017b; Faoro et al. 2010; Lauber et al. 2008).

22.5.1 Tomato

Tomato is one of the most consumed vegetables in the world and one of the species most requiring pesticides and fertilizers. Soil quality has declined as a result of long-term continuous tomato production and overuse of fertilizers, including soil acidification, low levels of organic materials, declining biodiversity, and changes in the structure of microbial communities (Zhang et al. 2016).

1. The principle of fertilization

   Reasonably apply organic fertilizers, appropriately reduce the application of nitrogen and phosphorus fertilizers, and increase the application of potassium fertilizers. Non-calcareous soils and acidic soils need to be supplemented with calcium, magnesium, boron, and other trace elements. According to the crop yield, stubble area, and soil fertility conditions, chemical fertilizers should be distributed reasonably. Most phosphate fertilizers should be applied as basal fertilizer and nitrogen and potassium topdressing; frequent top dressing should not be used in the early spring growth period. Combine with high-yield

Table 22.1 Organic waste compost, method of application, and overall effect on various vegetable crops

Crop	Organic fertilizer	Method of application	Effects	References
Tomato	Organic biofertilizer	Mulching	Improve the yield, quality, and antioxidant enzyme activity of tomato.	Feng et al. (2020)
	Vermicompost	Field application	Showed 73% better yield of fruits, and dry weight of leaves, dry weight of fruits, number of branches and number of fruits per plant	Meenakumari and Shekhar (2012)
	FYM, compost, and tithonia	Polyhouse application	Increased the level of soil mineral N and tomato yield compared to CB or CP aiming to produce green pods.	Gatsios et al. (2021)
	Tomato pomace and farmyard manure (Tp and FYM)	Field application	A significant increase of yield was noticed under organic fertilization where the highest yield of 8.00 ton ha^{-1}.	Kakabouki et al. (2020)
Potato	Cow manure	Field application	Increase diameter of potato, weight of potato planted, weight of potato per plot, economical and uneconomical yield of potato.	Harti and Sukmasari (2020)
	Bio-fertilizers with mineral fertilization	Field application	Improve not only the potato tuber yield by 21% but also the nutritional value	Wichrowska and Szczepanek (2020)
	Organic compost with charcoal	Field application	Application of organic fertilizer and charcoal during cultivation does not increase significantly of tubers' properties.	Wibowo et al. (2021)
Bean	Nitrogen, biochar, compost, manure	Pot application	It can be concluded that weed interference in red bean crop systems can be reduced by using organic amendments as a source of nutrients.	
	Sewage sludge fertilizer	Land application	The main results found that there were higher responses to the corn and fava bean yields	Elsalam et al. (2021)
	Cow manure with NPS fertilizer	Field application	The main results indicated that organic materials of plant origin alone/integrated with NPS fertilizer are helpful for increased yield of haricot bean (approx. 130%).	Elka et al. (2020)
Cabbage		Field application	Results revealed that the growth and yield of Chinese	He et al. (2020)

(continued)

Table 22.1 (continued)

Crop	Organic fertilizer	Method of application	Effects	References
	Mixed expeller cake (MEC) fertilizer		cabbage increased as more fermented organic fertilizer was used	
	Dried food waste powder (FWP) and organic fertilizer (MFOs)	Field application	Growth factors of lettuce and Chinese cabbage, such as a number of leaf's, leaf length, leaf width, and dry weight were decreased than those of control applying organic fertilizer.	Lee et al. (2019)
	Organic fertilizer (compost)	Field application	The leaf length (12.6–12.9 cm), root length (11.8–15.3 cm), fresh weight (14.7–16.5 g), and dry weight (3.4–3.9 g) were increasing after 4 weeks compared to plants without compost with lower parameters: Length of leaf (11.8 cm), length of root (9.3 cm), fresh weight (13.4 g), and dry weight (11.8 cm) (2.5 g).	Khater (2015)
	Organic waste vermicompost	Pot application	Increase in shoot length (14 ± 0.81 cm), number of leaves (12 ± 0.0), the diameter of leaves (4.76 ± 0.23 cm), length of leaves (9.0 ± 0.40 cm), surface areas of leaves (36.7 ± 0.87 cm2), length of the whole plant (14.33 ± 0.47 cm), and root length (5.66 ± 0.47 cm)	Shafique et al. (2021)

cultivation technology, adopt the principle of "small quantity and many times," and rationally irrigate and fertilize. Old sheds with soil degradation need to return straw to the field or apply organic fertilizer with a high carbon to nitrogen ratio, less poultry manure, increase the number of crop rotations, and achieve the purpose of removing salt and reducing continuous cropping obstacles.

2. Fertilization method
   (a) Seeding fertilization. Increase the use of decomposed organic manure, supplementary application of phosphate fertilizer, spray 30–60 kg decomposed manure, 0.5–1 kg calcium-magnesium phosphate, 0.5 kg potassium sulfate, and 0.5% to 0.1% urea per seedling.
   (b) Base fertilization. Apply best-quality organic fertilizer 1~2 t/mu.
   (c) Fertilization on plant fruiting stage. In the orchard which yield is more than 4000~6000 kg/mu: nitrogen fertilizer (N) 12~16 kg/mu, phosphate fertilizer (P_2O_5) 6~8 kg/mu, potassium fertilizer (K_2O) 15~20 kg/mu; output level 6000~8000 kg/mu: nitrogen fertilizer (N) 15–20 kg/mu, phosphate fertilizer

(P_2O_5) 8–12 kg/mu, potassium fertilizer (K_2O) 20–25 kg/mu. yield level 8000~10,000 kg/mu, nitrogen fertilizer (N) 20–25 kg/mu, phosphate fertilizer (P_2O_5) 10–15 kg/mu.

(d) Calcium, magnesium, and boron deficiency is likely to occur when the soil pH of vegetable field is <6, calcium fertilizer (Ca) 50~75 kg/mu, magnesium fertilizer (Mg) 4~6 kg/mu.

22.5.2 Potato

1. Principle of fertilization
    - (a) Analyze the reasonable amount of nitrogen, phosphorus, and potassium fertilizers based on the results of soil testing and the target yield.
    - (b) Increase the application of organic fertilizers and encourage the combined application of organic and inorganic fertilizers, do not use organic fertilizers that are not fully decomposed.
    - (c) Determine the soil condition and increase potassium fertilizer according to the soil potassium status.
    - (d) Organic fertilizer distribution is mainly based on the combination of base fertilizer and top dressing.
2. Fertilization method. According to the different potato growing regions (south and north of China):
    - (a) According to the yield per acre, it is recommended to apply 1500–2000 kg of organic compost per acre as base fertilizer.
    - (b) In this way recommend compound fertilizer 11-18-16 (N-P_2O_5-K_2O) or similar formula fertilizer as seed fertilizer and urea and potassium sulfate (or nitrogen-potassium compound fertilizer) as top dressing.
    - (c) According to product yield level, if area above 3000 kg/mu: formula fertilizer (seed fertilizer) 11-18-16 (N-P_2O_5-K_2O) recommended dosage 50 kg/mu, topdressing urea 15~18 kg/mu, potassium sulfate 10~12 kg/mu. If product yield area 2000~3000 kg/mu, recommended dosage of formula fertilizer (seed fertilizer) 40 kg/mu, topdressing urea 10~15 kg/mu from seedling stage to tuber expansion stage, potassium sulfate 6–10 kg/mu.

22.5.3 Bean

1. The principle of fertilization
    - (a) Fertilizer application should be based on soil test results to optimize the amount of nitrogen fertilizer and appropriately reduce the proportion of phosphate fertilizer.

   (b) If soil is acidic in nature, then choose physiologically alkaline fertilizers or physiologically neutral fertilizers.
   (c) Application of boron fertilizers was found effective in areas with deficiency symptoms in plants; this fertilizer can be used for seed dressing. It is best to mix seeds with rhizobia to improve the efficiency of modulation.

2. Fertilization method

   (a) Increase the application of organic fertilizer, and the amount of organic compost applied per mu is 1000~1500 kg.
   (b) According to bean nutrient requirements, the application ratio of nitrogen (N), phosphorus (P_2O_5), and potassium (K_2O) in high-fertility soils is 1:1.2:(0.3~0.5) and in low-fertility soils, the amount of nitrogen and potassium can be appropriately increased. The application ratio of nitrogen, phosphorus, and potassium is 1:1:(0.3~0.7).
   (c) Target yield 130~150 kg/mu: nitrogen fertilizer (N) 2~3 kg/mu, phosphate fertilizer (P_2O_5,) 2~3 kg/mu, potassium fertilizer (K_2O) 1~2 kg/mu. If the target yield 150~175 kg/mu: nitrogen fertilizer (N) 3~4 kg/mu, phosphate fertilizer (P_2O_5) 3~4 kg/mu, potash fertilizer (K_2O) 2~3 kg/mu.

22.5.4 Cabbage

1. Principle of fertilization
   Apply organic fertilizer to improve soil fertility. Nitrogen, phosphorus, and potash fertilizers are reasonably combined, and the trace elements are appropriately supplemented.
2. Reinforce top-dressing management after the plant properly set in land

   (a) Calculate the amount of base fertilizer based on the growth of cabbage and the soil nutrient supply capacity and conduct a comprehensive analysis based on the current actual level of cabbage fertilization and apply 2000–3000 kg/mu of high-quality organic compost.
   (b) Under the condition product yield of 5000 kg of clean vegetables per mu, it is recommended to apply nitrogen fertilizer (N) 15–20 kg/mu, phosphate fertilizer (P_2O_5) 5–8 kg/mu, and potassium fertilizer (K_2O) 20–25 kg/mu. The amount of weight loss material can be appropriately increased according to the level of production.

       All phosphate fertilizers are used as base fertilizer; 30% of nitrogen fertilizers are used as base fertilizers, and the other 70% are used as top-dressing fertilizers; 50% of potash fertilizers are used as base fertilizers, and the other 50% are used as top-dressing fertilizers. After the continuous cropping period, topdressing nitrogen and potassium fertilizers can be applied 2 or 3 times.

22.6 Principles and Methods of Applying Organic Fertilizer to Tea

Tea is an important economic crop that is widely planted in China (Xie et al. 2021). The total area of tea plantations in China reached more than 2.85 million ha, which makes China the largest exporter of tea all over the world. While soil fertility, as a vital role in soil, is consistent with the high-quality and high-yield of tea (Ruan et al. 2009). It is confirmed that the soil not only needs to be rich in nitrogen, phosphorus, and potassium, but also requires an appropriate proportion (Venkatesan and Ganapathy 2004). Therefore, it is essential to apply fertilizations into farmlands for improving the yield and quality of tea. However, most of soil is short of organic matter and nutrients, which is caused by serious leaching (Xue et al. 2006; Shen et al. 2012). Meanwhile, with the rapid development of agriculture in recent years, farmers have excessively pursued economic benefits, which not only lead to long-term unreasonable fertilization, but also cause a series of problems such as soil acidification, compaction, and nutrient loss (Braskerud 2002; Duchemin and Hogue 2009). Besides, the unreasonable ratio of chemical fertilizer (nitrogen, phosphate, and potassium fertilizer) and compound fertilizer seriously affects microbial communities and reduces the resistance of tea trees to pathogens, and thus affected the quality of tea (Ji et al. 2018). Meanwhile, irrational fertilizer application has a negative effect on soil ecological environment and the surface and groundwater bodies, which are main contributors for agricultural non-point source pollution. Furthermore, some harmful elements could be enriched in crops and threaten human health through food chain. Therefore, rational fertilization can increase the yield and quality of tea and improve the environment of tea gardens. While ensuring the increase in production and economic development of the tea industry, it also reduces its potential damage to environment, promotes agricultural cost-saving and efficiency, and realizes agricultural sustainable development.CONT

22.6.1 Principles of Applying Organic Fertilizer to Tea

1. The fertilizer application could be mainly with organic compost, combining with proper inorganic fertilizer (Bedada et al. 2014; Huang et al. 2010). Organic compost can provide coordinated and complete nutrient elements, which plays an important role in improving the soil structure, enhancing water retention capacity, and buffering pH condition in a long-lasting time. But the nutrient content involved in organic compost is low, which could not provide sufficient nutrients for plant growth. Different from organic fertilizer, inorganic fertilizer has higher nutrients and fast fertilizer efficiency. However, the application of inorganic fertilizer in a long term could result in soil compaction and serious loss. Therefore, the base fertilizer is mainly with organic compost, while the top application is mainly with inorganic fertilizer.

2. Nitrogen fertilizer is the mainstay, and balanced fertilization is emphasized (Wang et al. 2020b). In order to cultivate a huge root system and a strong skeleton branch, increase the density of side branches and expand the canopy coverage in the younger tea gardens, the demand for nutrients such as nitrogen, phosphorus, and potassium is relatively higher (Wang et al. 2021). Meanwhile, the appropriate ratio of nitrogen, phosphorus, and potassium is 1:1:1. As for adult tea, they require a large amount of nutrients for tea growth, and the suggested proportion of nitrogen, phosphorus, and potassium is 3:1:1. Additionally, the calcium, magnesium, sulfur, and other large elements required by tea trees should be replenished appropriately, and trace elements such as iron, manganese, zinc, copper, molybdenum, boron, and chlorine should satisfy the growth requirements.
3. Pay attention on base fertilizer and topdressing in stages. Generally, basal fertilizer accounts for about 50% of the total fertilization amount, and top-dressing fertilizer accounts for about 50%, and it is suggested to apply all organic fertilizers, phosphorus and potash fertilizers as basal fertilizers. Meanwhile, it is suggested that top dressing should be carried out three times.
4. The application of fertilizer into root is primary, supplemented by foliar fertilization. The root system of tea plants is intertwined and has wide and deep distribution, its main function is to absorb nutrients and water from the soil. Therefore, the fertilization of tea should be the root fertilization, but the tea leaves also have the absorption function, especially in the extreme conditions like drought, wet waterlogged, and others. Besides, foliar fertilization can also activate the enzyme system in the tea tree and enhance the absorption capacity of the tea root system.

22.6.2 *Methods of Applying Organic Fertilizer to Tea*

The amount of fertilization for tea plants should be determined according to the age, tree vigor, the amount and frequency of leaf picking, and soil conditions (Ma et al. 2021). Generally, young tea or those with fewer leaves should be applied less fertilizer, while tea characterized with mature age and high yield should be added more fertilizer. Generally, the annual fertilization amount should be distributed according to the fertilization ratio, which means that the fertilizer amount will change with the number of tea trees. And the added dosage of different fertilizer could be calculated according to the “three elements” (nitrogen, phosphorus, potassium) contained in fertilizer.

1. Base fertilizer. Base fertilizer of tea, mainly with organic compost and phosphate fertilizer, is usually applied in autumn and winter (September to November), which accounts for 40% of the annual fertilizer application. It is confirmed that 600–800 kg organic compost (or 20–25 kg of urea), 40–50 kg superphosphate, and 10 kg potassium sulfate per mu are necessary for tea growth. After mixing them homogeneously, the fertilizer is applied into root system through perforated

method or furrow application. In a word, the application of base fertilizer in tea gardens should be adapted to local conditions and be flexible.

2. Top dressing. After the tea plant grows, the top dressing is carried out in batches from February to September, that is, topdressing is supposed to carry out before spring tea (February to March), summer tea (May), and autumn tea (July). Besides, the top dressing is mainly with nitrogen, and the potassium is applied once before the Spring Festival. And other details are as followed: (1) Top dressing for the first time is carried out in February to March, and 15 kg urea and 8 kg potassium sulfate are applied per mu; (2) Top dressing for the second time is performed in May, and 5 kilograms urea is used per mu; (3) The third top dressing was conducted in July, and 10 kilograms urea 1 mu is applied into farmlands.

In conclusion, it is necessary to provide sufficient nutrients for tea growth through an appropriate way, which not only improve soil structure and make more profits.

22.7 Challenges and Perspectives

If the organic waste is not used for the purpose of organic fertilizer after bioconversion, then there will be competition, which may have a negative impact on the development of organic fertilizer products. The main reason is economic benefits. The value of organic fertilizers is much lower than that of animal feed and biomass energy (Meyer 2017). Therefore, organic waste becomes a suitable raw material for organic fertilizer, and it is best to meet the development of organic fertilizer after biotransformation, and it can also meet the needs of other different uses. Commonly, when the compost product of organic waste undergoes a biotransformation process can be used as a biostimulant. Although there is a lot of interest in the development of new biostimulants recently, there are few relatively reliable products on the market, especially biostimulants extracted from biotransformed compost products. First of all, the biological hormones that promote plant growth have not been fully understood. The biological hormones that promote plant growth may have a synergistic effect, rather than a single substance (Yakhin et al. 2016). Secondly, the mode of action of hormones that promote plant growth is limited, mainly due to the diversification of organic waste sources and the complexity of product characteristics (Brown and Saa 2015). Finally, the dynamic changes of plants after using compost products should also be considered (Yakhin et al. 2016).

At present, the biostimulant extracted from compost has not been actually applied in agricultural production, and scientific researchers have not fully realized its efficacy. Most of the biological hormones rich in compost are substances derived from humic acid, sometimes mixtures or proven biological hormones. This may be related to the difficulty of identifying biological hormones, or because we do not know enough about them, especially those biological hormones that are present in compost. The important feature of compost rich in biological hormones should be paid attention to, in order to give full play to its advantages and potential in agricultural production. Therefore, although many studies have proved that the biological hormones in compost have advantages in agriculture, it is still necessary to establish a theoretical framework to promote the development of coping with biological hormones and provide a scientific basis.

22.8 Conclusion

In order to pursue more profits, more chemical fertilizers were applied into farmlands to increase crop yield. However, excessive application of chemical fertilizer can lead to loss of nutrient elements in soil surface, reduce organic carbon content, microbial abundance, and enzyme activities, and thus resulting in soil compaction and decline of soil fertility. Organic fertilizer, as an alternative of chemical fertilizer, was generated from the management of livestock manure. And the application of organic could improve soil structure, increase soil porosity, strengthen holding water capacity, provide more organic matter and nutrients for plant growth, and thus improved the environmental conditions of crop root growth and create a good soil ecological environment crops growth. Whereas, it needed a long period to release nutrients of organic fertilizer. Therefore, chemical fertilizer was used in conjunction with organic fertilizer is more important for enhancing crop yields. Additionally, due to the different characteristics of different crops and different soil, the ratio of chemical fertilizer and organic fertilizer was supposed to be different. And the results obtained from this manuscript could provide theories for fertilizer application.

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Chapter 23
Thermal Cracking Processes Up-to-dateness for Oil Vacuum Residual and Bio-Raw Materials: A Perspective for Municipal Solid Waste

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Abstract The importance of thermal processes in the processing of hydrocarbons and biomass is growing rapidly. Thermal processes (thermal cracking, pyrolysis, coking) during oil refining make it possible to obtain a wide range of oil products necessary for the energy sector and petrochemical synthesis. Currently, the share of heavy oil in the total volume of oil produced is increasing. As a result, when processing such oils, the amount of low-quality vacuum residues increases, which is a problem for refineries. However, the ever-increasing exploitation of fossil fuels leads to environmental pollution, global climate change, and health problems for living beings. Therefore, in order to meet the energy needs of the future and reduce environmental pollution, it is very important to look for alternative fuels. It is believed that in the future, the global energy infrastructure will be created from energy generated from inexpensive renewable sources, one of which is biomass and municipal solid waste. In recent years, a lot of new data have been obtained on the processing of this feedstock in pyrolysis plants. Biomass can produce a condensable liquid called bio-oil, a solid product called semi-coke, and a mixture of gaseous products containing CO_2, CO, H_2, CH_4, etc. However, the commercialization of biomass pyrolysis technology is still challenging due to the properties of bio-oil such as low calorific value and high instability at elevated temperatures. This chapter discusses the role of thermal processes in the development of heavy hydrocarbon and biomass processing.

23.1 Introduction

Thermal cracking is one of the first processes for refining petroleum feedstock—the history of its industrial application dates back to 1913. Various types of oils were heated under pressure in large drums in order to obtain products with lower

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molecular weights and boiling points (motor gasoline, aviation gasoline, tractor kerosene). In the 1930s, due to stricter requirements for fuel quality, this process was almost completely replaced by catalytic cracking.

From the 1960s to the present, visbreaking and delayed coking are widely used thermal processes. These technologies have not lost their relevance and attractiveness for refineries, since they provide low operating pressure at high operating temperatures, without requiring expensive investments. Also, the keeping of attention of researchers to these processes is due to the possibility of obtaining additional quantities of components of motor fuels from, first of all, heavy oil feedstock, and high productivity and flexibility of installations.

The thermal cracking is most commonly carried out at temperatures of 455–540 °C and pressures of 6.8–68.0 atm. Thermal processing of heavy feedstock can be carried out both in a “soft mode” to reduce viscosity, and in an ultrapyrolysis mode to obtain volatile components (Hulet et al. 2005). It should be noted that a short process time is required to achieve the required degree of high-temperature transformation of feedstock. However, in many cases, an increase in the cracking temperature leads to high yields of by-products (gas and coke) due to a profound change in the chemical composition of the feedstock.

The need to include unconventional heavy petroleum feedstock (HPF), including heavy oils, natural bitumen, heavy residual petroleum fractions (vacuum residues and fuel oil), tar sands, and oil shale, into the refining cycle, is increasing along with the increasing global demand for motor fuels. The most promising technologies are converting vacuum residues and heavy crude oils into light and middle distillates. The high added value of the resulting low-boiling products contributes to the development of these technologies.

High viscosity, increased content of heteroatoms (S, N, O), metals and asphalt-resinous components, together with the almost complete absence of light fractions of hydrocarbons, complicate the work with HPF both at the stage of production and at the stages of their transportation and processing (Sviridenko et al. 2020). The cost of only the stage of production of heavy oils and natural bitumen turns out to be 3–4 times higher than that of light and medium oils (Shah et al. 2010). Due to these features, the reserves of unconventional feedstock are being developed to a lesser extent, while their share, according to experts’ estimates, amounting to 70–80% of the world’s proven reserves (Alboudwarej et al. 2006), will only increase in the future.

It is asphaltenes that impose the main restrictions in the HPF oil refining processes, both thermal and catalytic. In quantitative terms, asphaltenes do not prevail in the composition of oil: their content can vary from trace amounts (~0.01%) in light oils to 20% in heavy oils. At the same time, they have a negative impact on both oil production and their preparation, transport, and processing. For example, oils with a high asphaltene content are characterized by increased viscosity values (30 mPa*s), which requires the use of expensive technologies in oil production and transportation. The high content of asphaltenes during processing is the cause of a number of negative factors:

- Lost of target products due to the intense occurrence of side reactions (primarily polycondensation reactions)
- Increased corrosive wear of equipment
- The need to use harsh processing conditions (at elevated temperatures and pressures)
- Increased consumption of hydrogen (or hydrogen-containing gases)
- Accelerated deactivation of catalysts

The most effective and cost-effective solution to this problem largely depends on the situation in a particular country and in an individual company. For example, in the Russian Federation, the process of continuous coking in a fluidized bed, which has not received commercial implementation, has been developed. Similar technologies from Exxon (Fluid Coking and Flexicoking) are widely used in refineries in the USA.

Thus, thermal processes are the most perspective for the processing of various heavy feedstocks and household waste, which is primarily associated with low implementation costs.

23.2 Thermal Cracking Processes

Thermal cracking is the high-temperature processing of feedstock in order to obtain, as a generally, products with a lower molecular weight. Along with the destruction of feedstock components during thermal cracking, polymerization and condensation processes occur, the products of which are polycyclic and polyaromatic compounds and, ultimately, coke. Depending on the conditions for carrying out thermal processes, release cracking and coking are distinguished.

23.2.1 Visbreaking

In the 1930s, visbreaking became widespread as a “soft” liquid phase thermal cracking. In general, this process offers economical processing of HOF (heavy oil feedstock) into gaseous and distillate products, accompanied by a decrease in viscosity and pour point of the residues (Fig. 23.1). At the present time application of visbreaking is aimed at processing residues in order to increase the yield of light products, i.e., to increase the depth of processing of feedstock. Visbreaking options implemented in industry are presented in Table 23.1. This is due to both the weighting of crude oil and the shift in market demand from fuel oil to distillates.

For the final conversion of any heavy feedstock in the visbreaking process is influenced by the asphaltene content. Visbreaking temperatures must be carefully controlled to prevent asphaltenes condensation to form compaction products (coke). Asphaltenes are held in colloidal suspension by peptizing agents, native surfactants

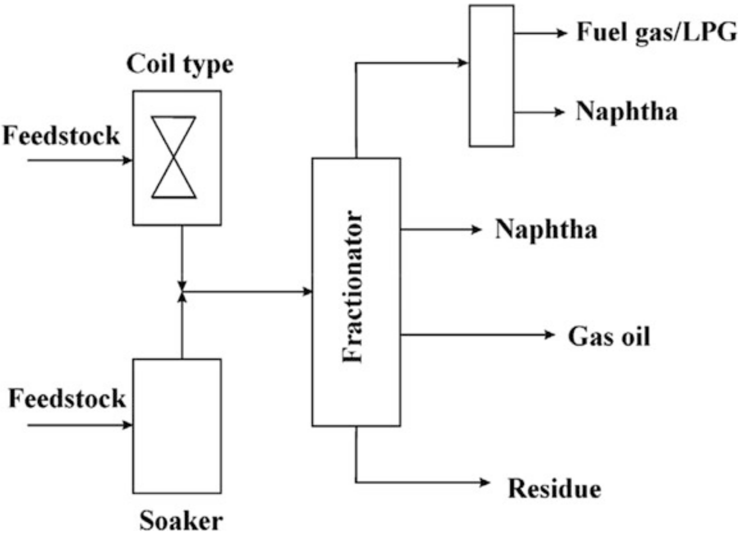

Fig. 23.1 General representation of a visbreaking unit

Table 23.1 Thermal refining processes

Process	Description	Company
HSC process—hydrocarbon soking-camera	Thermal cracking process in a soaker chamber with a high degree of conversion	Toyo Engineering Corp. и Mitsui Kozan Chemical Ltd (Japan)
Heavy-to-light and rapid thermal process	Ultrafast thermal cracking in a circulating stream of a powdered heated inert heat carrier	Ivanhoe Energy (USA)
Heavy oil upgrade process	Thermal cracking by heating feedstock to moderate temperatures, followed by mixing with superheated steam	Red Mountain Energy (USA)
Eureka	Thermal cracking in liquid phase in batch reactors where the desired temperature regime created by bubbling with superheated steam	Chiyoda (Japan)
CHERRY-P	Thermal cracking with the addition of a certain amount of pulverized coal to avoid coke deposits on the inner surface of the reactor	Osaka Gas Co Ltd (Japan)
Conversion of Pierre Jorgensen	Thermal cracking with instant thermal shock to asphaltene molecules using superheated steam	World Energy Systems (USA)

found in crude oil. At high temperatures, these structures tend to degrade, leading to precipitation of asphaltenes. As a result, fuel oil becomes unsuitable for sale. This problem is usually called the instability of the refining products (Giavarini 1981; Joshi et al. 2008) Thus, the degree of conversion of feedstock is proportional to the cracking temperature and residence time in the hot zone and is limited by an increase in the instability of asphaltenes in the residue, which causes the coke formation (Rogel 1998). The resulting coke leads to clogging of technological lines and heating pipes of the furnace, and, accordingly, to premature shutdown of installations.

Visbreaking temperatures range from 455 to 510 °C. The short residence time of the feedstock in the reaction zone avoids significant gas and coke formation. In these conditions, liquid phase cracking leads to the formation of some naphtha, as well as products with a boiling range of kerosene and gas oil. In the process of visbreaking feedstock is passed through the furnace, where it is heated to a temperature of 480 °C at a pressure of about 7 atm. Then the resulting products are sent to the rapid distillation chamber. The gaseous products from this chamber are then fractionated to obtain naphtha and light gas oil, and the liquid products are cooled with a gas oil stream and sent to vacuum distillation, as a result of which a heavy gas oil and a vacuum residue with a reduced viscosity are obtained (Speight 2012). Conversion of 5–10% of the residue into naphtha is usually sufficient to provide at least a fivefold decrease in viscosity, which is also accompanied by a decrease in pour point.

Another version of the visbreaking process in industry is carried out under conditions of lower temperatures and longer contact times. The disadvantage of this approach is the need to remove coke from the reaction chamber. Mild cracking conditions favor high yields of naphtha with low yields of gas and coke. The higher boiling residues are converted decreases with each pass through the thermal zone, and if such fractions are not required as such, they can be coked to increase the yield of light ends or processed using hydro-processes. Thus, in the industry, two types of visbreaking are implemented: in the reaction chamber (low temperature and long stay in the hot zone) and in tube furnaces (high temperature and short contact time).

23.2.1.1 Deep Thermal Conversion Process

The Deep Thermal Conversion (DTC) process is somewhere between visbreaking and coking. DTC process provides maximum distillate yield due to vacuum evaporation of vacuum residue processing products.

In this process, the vacuum residue is loaded first into the heater and then into the reaction chamber. The resulting products are sent to a distillation column at atmospheric pressure for the production of gases, naphtha, kerosene, and gas oil. The remainder of the fractionation is sent to a vacuum evaporator, which extracts additional gas oil and distillate. Depending on the purpose of use, liquid coke (pitch, cracking residues) or solid coke can be isolated.

23.2.1.2 High Conversion Soaker Cracking (HSC) Process

HSC is a process designed for moderate conversion, higher than visbreaking but lower than coking (Joshi et al. 2008; Banerjee 2012). This process is characterized by less gas generation and higher distillate yield compared to other thermal cracking processes. HSC can be used to convert feedstock with high sulfur and metal content, including heavy oil, oil sand bitumen, and heavy feedstock. Of particular interest is the fact that this process uses continuous reactors.

The resulting products enter the rectification column, where they are subjected to fractionation. The gaseous products, after being purified from sulfur, are used as fuel gas for the refinery. Hydro-treated liquid products are used as feedstock for fluidized bed catalytic cracking or hydrocracking. The heavy feedstock is suitable for use as boiler fuel, road asphalt, coke binder and as a feedstock for partial oxidation.

23.2.1.3 Gasification

This process consists of the complete cracking of the residues into gaseous products. Gasification of residues is carried out at temperatures above 1000 °C with the production of synthesis gas, black carbon and ash as the main products (Pindoria et al. 1997). Due to the impossibility of controlling the selectivity during the conversion of feedstock, gasification has not become widespread for processing heavy residues.

Various solid and liquid carbon-containing materials can be used as feedstock for the process, including asphalts from deasphalting units, petroleum coke, and oil sludge. Gasification is achieved due to the complete decomposition of carbon-containing feedstock at high temperatures (more than 1000 °C) in the presence of oxygen (air) and steam.

At the present time gasification is an important intermediate link in the schemes of complex processing of HOF. This process makes it possible to concentrate valuable feedstock in the mineral residue of the process with the possibility of their subsequent extraction, as well as to obtain synthesis gas, which serves as an efficient fuel in the production of electricity or as a feedstock for a number of petrochemical processes. Synthesis gas, which is the target product of the gasification process, is a mixture, the main components of which are carbon monoxide, hydrogen, carbon dioxide, and methane.

The other products are soot—ash and ash slag residues. The soot can contain a significant amount of V (vanadium). With a plant capacity of 800,000 t/year, up to 320 t/year of V can be obtained. The soot is oxidized in a controlled manner in a multi-pass furnace. The product is a V concentrate containing about 75% V_2O_5. Moreover, most of the valuable rare and rare earth elements are concentrated in ash and slag waste, which can be considered as a feedstock for the production of commercial compounds of a number of elements (Magomedov et al. 2015).

In almost all currently implemented gasification projects, preference is given to in-line gasification reactors due to their flexibility, the possibility of processing various carbon-containing a feedstock (liquid and solid) and achieving a high unit capacity, and, consequently, economic attractiveness. The most famous technologies based on in-line gasification reactors are the developments of Texaco (TGP process), Shell (SGP process), Siemens Future Energy, Prenflo (Krupp Uhde), Conoco Phillips (E Gas process). There are about 140 SGP plants and 90 TGP plants in operation worldwide. A promising approach for the gasification of various carbon-containing materials is to carry out the process in a metal (iron) melt, which is located in a crucible of a metallurgical smelting furnace, with oxygen-containing gas blowing through it (Magomedov et al. 2015).

23.2.2 Coking Processes

The possibility of deepening thermal processes is limited by the formation of coke. In general, the yield of light fractions during the cracking of tar or fuel oil is no more than 35–40%. The yield of valuable products is even less when visbreaking is used. Their yield can be increased if the formation of coke is not considered as a disadvantage of thermal cracking. It was this point of view that made it possible to develop and widely introduce into industry the processes called coking (Hsu and Robinson 2017).

During coking, all components of the HOF are decomposed with the formation of distillate fractions and volatile substances; destruction and cyclization of hydrocarbons with the release of kerosene-gas oil fractions; condensation and polycondensation of hydrocarbons and high-molecular compounds with the formation of coke residue.

This process is characterized by a longer reaction time than thermal cracking and takes place at temperatures of 480–560 °C in the absence of air. The highest efficiency is achieved coking provided that upgrade subjected to not only the coke but also liquid and gaseous products of the process are output on the feedstock can reach 70%.

Due to the absence of external sources of hydrogen, the coking process is accompanied by the transfer of hydrogen from heavy to lighter molecules, which leads to the formation of coke and products with a higher hydrogen content. In the course of this redistribution of hydrogen at high temperatures, there is a significant decrease in the H/C ratio at the "donor" part of the feed to values between 0.5 and 1, which significantly increases the yield of coke deposits. It is the low initial content of hydrogen in the HOF that leads to high yields of coke and low yields of more valuable liquid products with this kind of "disproportionation" of the feedstock.

Refining of coke involves several processes. One option is the calcinations, which removes volatile substances and partially heteroatom (S, V). Deep desulfurization of coke requires more severe process conditions than with conventional calcination. Calcined petroleum coke can be used to make anodes, for the production of aluminum and various carbon or graphite products such as brushes for electrical equipment. Currently, the main industrial methods of coking are (Table 23.2)—periodic coking, delayed coking, continuous coking in a fluidized bed and its variant flexicoking.

Table 23.2 Coking processes

Process	Description	Company
Coking	Periodic process of delayed coking at temperatures of 487–505 °C and pressures of 2.0–6.3 kgf / cm^2 abs	CLG/ABB Lummus Global (USA)
LR-coking	Continuous coking process based on rapid heat transfer by feedstock in a fluidized bed of powdered coke heat carrier	Lurgi и Ruhr-Chemie (Germany)
Fluid coking	Continuous coking in a fluidized stream of a circulating powdery heat carrier, which is used as a part of the produced coke	ExxonMobil (USA)
Flexicoking	Combined coking in a fluidized bed of a powdered heat carrier with coke gasification	ExxonMobil (USA)
ThruPlus	Semi-batch thermal delayed coking process with patented distillate and hydrocarbon gas recirculation schemes to increase more valuable products	Conoco Phillips (USA)

23.2.2.1 Periodic Coking

With periodic coking, the feedstock is fed into a cube, where it is heated to 450–490 °C for 6–8 h. The high temperature of the process and the long-term residence of the feedstock in the cube make it possible to obtain lumpy coke, which is of the greatest value for the production of electrodes. The vapors released in this case are continuously removed from the cube and condense. However, the process did not become widespread due to the low productivity of installations associated with their low automation.

23.2.2.2 Delayed Coking

Delayed (semicontinuous) coking is one of the oldest kinds of thermal cracking processes—the first commercial installation put into operation in a refinery Whiting to Standard Oil Co. (Indiana) in 1930 (Valyavin et al. 2007). At the present, the total capacity of delayed coking units is 150 million/t in terms of feedstock, with about 70% of the process capacity being concentrated in the United States. Leading delayed coking technologies have been developed by companies such as Foster Wheeler Energy Corp. (Switzerland), UOP Inc. (USA), C-E Lummus (USA), The M.W. Kellogg Inc. (UK), Koa Oil Co. (Japan).

The name of this process is due to the fact that the reactions leading to coke formation proceed for a rather long time (Fig. 23.2). The feedstock (vacuum residue, deasphalting asphalts, oil refining extracts, etc.) preheated to 350–380 °C are continuously fed to the distillation column trays, the resulting lighter fractions are removed as by-products for further separation. The bottom bed of the fractionating column, including the recycle condensed heavy product stream, then heated in an oven whose outlet temperature ranges from 480 to 515 °C. The heated feedstock enters the coke chambers, which are vertical cylindrical apparatus, where, due to the

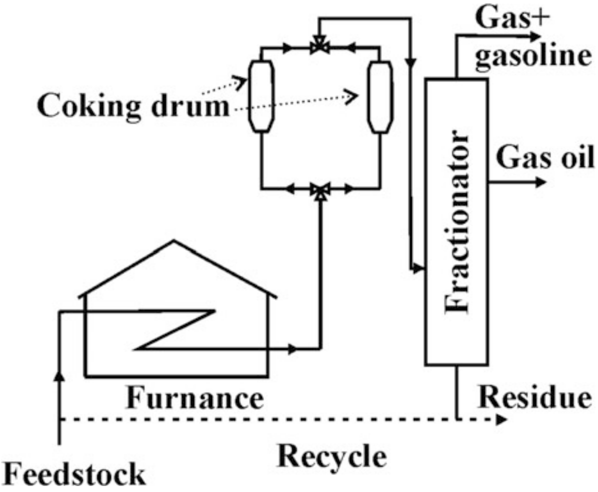

Fig. 23.2 A delayed coker

accumulated heat, it is coked. Coke oven temperatures range from 415 to 450 °C with pressures from 1.02 to 6.12 atm. To ensure continuous operation, two chambers are used: while one is in the flow, the other is cleaned hydraulically (high-pressure water jet). Thus, delayed coking is a continuous process for the supply of feedstock and separation of products, and periodic for the unloading of coke.

This process has established itself as the preferred option for processing heavy residues due to the inherent flexibility of the process (the ability to process any type of residues) and low investment costs (Sawarkar et al. 2007). At the exit, it is possible to obtain up to 60% of liquid products—naphtha and gas oil. In addition, delayed coking makes it possible to obtain various types of coke (including high-density electrode cokes used to produce aluminum, fuel, and needle cokes).

The introduction of delayed coking units in refinery schemes allows to significantly increase the depth of oil refining (Rodríguez-Reinoso et al. 1998). The disadvantages of delayed coking are its semi-periodicity and laboriousness of unloading and transporting coke.

23.2.2.3 Continuous Coking

The fluidized coking (thermal contact cracking) is a petroleum refining process in which heavy oil residues are converted to lighter fractions by thermal decomposition at about 480–590 °C, in most cases between about 500 and 590 °C. Due to the different activation energies, the rate of destruction reactions of feedstock increases faster with increasing temperature than the rate of the polycondensation reaction. As a result, the yield of liquid and gaseous products is higher, and the yield of coke is lower than coking similar petroleum products at a higher pressure. The yield of products is determined by the properties of the feedstock, temperature and residence time in the fluidized bed. An increase in the operating temperature of the reactor of this process by 5 °C contributes to an increase in the yield of such light components as gas and naphtha by about 1% wt. (Speight 2007, 2011).

During continuous coking, the heated feedstock comes into contact with a mobile inert heat carrier heated to a higher temperature, which is powdered coke with a particle size of up to 0.3 mm. The coke deposited on the surface of the coolant is removed from the reaction zone to the regenerator as it is formed, where it is partially burned out. This is the difference between continuous coking and batch and semi-batch processes. The heat released during combustion is used to heat the coolant returned to the reaction zone to preset temperatures.

Heavy petroleum products that can be treated by fluidized coking include heavy residues from atmospheric distillation, residues from vacuum distillation of petroleum, aromatic extracts, asphalts, and bitumens.

In the USA, two technologies have become widespread—Fluid Coking and Flexicoking. With Fluid Coking, continuous coking is carried out in a fluidized stream of circulating powdered heat carrier (Furimsky 2000).

The Flexicoking process, developed in the 1960s and 1970s, has a similar plant. Its key difference is the presence of the gasification reactor providing high conversions of coke for the production of synthesis gas (Roundtree 1997). The units are designed for the gasification of 60–97% of the coke generated in the reactor. In this process, excess coke in a fluidized bed gasifier with steam and air is converted to a gas with a low calorific value. Air is supplied to the gasifier to maintain a temperature of 830–1000 °C. Under these reducing conditions, the sulfur in the coke is converted to hydrogen sulfide. However, even with the gasification process, the resulting coke will contain more sulfur than the feedstock. A typical gas product after the removal of hydrogen sulfide contains: carbon monoxide (CO, 18%), carbon dioxide (CO_2, 10%), hydrogen (H_2, 15%), nitrogen (N_2, 51%), water (H_2O, 5%) and methane (CH_4, 1%). The liquid yield with Flexicoking is the same as with Fluid Coking.

Besides to recovering additional volatile fractions, fluidized bed coking has a number of other advantages. Due to the lack of steam and water, the consumption of utilities is lower. Since there is no cooling process, the energy released from hot coke is saved, etc. Table 23.3 shows a comparative characteristic of the main thermal processes.

23.2.3 Thermal Processes for the Processing of Solid Waste

At present, many developing countries face increasing problems of processing municipal solid waste (MSW) as improper handling poses a risk to the environment and society. MSW can be a source of biogas. At the same time, household waste can be considered as non-biodegradable and biodegradable, which are suitable for thermal and biochemical processes, respectively.

Table 23.3 Comparison of visbreaking with delayed coking and the Fluid Coking process

Parameters	Visbreaking	Delayed coking	Fluid coking
Purpose	To reduce viscosity of fuel oil to acceptable levels	To produce maximum yields of distillate products	To produce maximum yields of distillate products
Conditions	Soft (470–495 °C) heating at a pressure of 3.4–13.6 atm.	Moderate (480–515 °C) heating at a pressure of 6.12 atm	Strong (480–565 °C) heating at 0.7 atm.
Conversion	Low conversion (10%) into products with boiling points below 220 °C.	Complete conversion of feedstock. Coke yield: 20–40% wt. (depending on feedstock). Distillate yield below 220 °C: Approx. 30% (but depends on feedstock).	Complete conversion of feedstock. Coke yield: 20–40% wt. (depending on feedstock). Distillate yield below 220 °C: Approx. 30% (but depends on feedstock).

Table 23.4 Types of Thermal process

Process (Pretreatment)	Principle (Environment)	T, °C	Products		
			Gas	Liquid	Solid
Incineration (Not necessary)	Full oxidative combustion (presence of sufficient oxygen)	850–1200	CO_2, H_2O, O_2, N_2	–	Bottom ash, fly ash, slag, other noncombustible substances like metals and glass
Pyrolysis (Required)	Thermal degradation of organic materials in the absence of oxygen (absence of oxygen)	400–800	Pyrolysis gas	Pyrolysis oil, wax, tar	Ash, char (combination of non-combustibles and carbon)
Gasification (Required)	Partial oxidation (controlled supply of oxygen)	800–1600	H_2, CO, CO_2, CH_4, H_2O, N_2	–	Ash, slag

There are several thermal processes for waste processing: incineration, pyrolysis, and gasification (Table 23.4). Incineration is the most widely used method of high-temperature waste processing (Kumar and Samadder 2017; Miandad et al. 2017). Gasification and pyrolysis are still under research and are largely unsuitable for commercial use. For thermal processes of processing solid household waste, dry feedstock (with a lower water content) and containing a high percentage of non-biodegradable waste are mainly used. For the production of fuel from MSW, recyclable and non-combustible materials are removed from them, followed by crushing and/or granulation of the remaining waste (Zhang et al. 2018).

23.3 Conclusions

Thermal processes have proven themselves long ago and have not lost their relevance to this day. They are constantly being modernized for various feedstocks. Thermal processes can be used to process not only petroleum feedstock but also various household waste and bio-raw materials due to their low cost in comparison with catalytic processes. While the industry requires a variety of volatile and light products from such feedstock, more thermal process units will be commissioned.

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Chapter 24
Chemistry to Technology of Gasification Process: A Close Look into Reactions and Kinetic Models

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Abstract Biomass gasification is a thermochemical conversion process in which diversified solid organic wastes produce majorly gaseous products (syngas) and tarry residue. The availability of sufficient quantities of biomass and effective utilization of municipal solid wastes make biogasification a very important technique. Major focus of gasification technology is to maximize syngas production as it can directly be used for power generation or be utilized as potential feedstock for other chemicals and biofuel production. In this chapter insights into process chemistry of gasification and its key operating conditions are majorly discussed along with various types of available bio-gasifiers. Present-day challenges for the gasification technology are highlighted along with a thoughtful insight to its sustainable growth potential.

24.1 Introduction

Rapid industrialization in developing countries and depletion of fossil fuel reserves have created the demand for energy from renewable sources. According to International Energy Agency, global electrical energy demand is fulfilled by 26% from renewable energy sources in 2018. However, it is expected to increase the renewable energy share due to rising pollution awareness and depleting crude oil reserves. According to International Solid Waste Association (ISWA), approximately 12.5% population are living in megacities across the globe and this share will achieve 50% of total global population by 2050. Growing urbanization and changing consumer patterns are likely to generate the waste in these urban cities. Thus, in line with this, gasification technology is emerged as one of the promising technologies which can

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utilize diversified wastes such as biomass, agricultural residues, municipal solid wastes (MSW), etc. to generate energy (Waste to Energy). Gasification technology has witnessed various challenges since its deployment into commercial-scale operation several decades ago. This technology was adopted for coal and then utilized for biomass as feedstock. Biomass gasification is a thermo-chemical conversion process in which diversified solid organic wastes produce majorly gaseous products (syngas) and tarry residue. Major focus of gasification technology is to maximize syngas production as it can directly be used for power generation or be utilized as potential feedstock for other chemicals and biofuel production. This chapter will provide insights into the process chemistry of gasification in order to develop better expertise on the technology along with an emphasis on the key operating conditions. The conventional gasifiers and their design and operational aspects are reviewed thoroughly with an eye to futuristic technology for sustainable development.

24.2 Biomass Feedstock and Its Pre-Treatment

The quality of biomass feedstock is an essential part of gasification process to ensure the production of good quality fuel. Gasification processes utilize a variety of feedstock materials ranging from coal to biomass but the selection of reactor is mainly dependent on the type and relevant properties of feedstock. A good feedstock will contribute to higher product yield at minimum processing cost and must have easy and large-scale availability (Badgujar and Bhanage 2018). The important desired characteristics of feedstock are higher calorific or heating value, low moisture content, small particle size, uniform particle shape, low volatile solid suspension (VSS), high density, low ash percentage, low nitrogen, phosphorous and potassium content and availability at minimum cost (Kataki et al. 2015). All these properties have significant impact on the performance of gasifier and hence, quality or composition of final gaseous products.

Several researchers have reported a general classification of biomass feedstock into six different groups and subgroups and are illustrated in Fig. 24.1 (McKendry 2002; Vassilev et al. 2010). Based on this classification, biomass feedstocks vary from woody and herbaceous biomass which are derived from agricultural and forest residues to aquatic biomass and finally to human and animal wastes and industrial wastes.

Woody biomass consists of tree stem, branches, leaves, woodchips, bark and trims, shavings, saw dust from saw mills whereas herbaceous biomass includes switch grass, sweet sorghum grass, bamboo whole and other grasses, corn stover, wheat straw, rice straw, husks and shells, grains and seed crops. Aquatic biomass involves mainly algae, water weed, water hyacinth, reed, and others. Human wastes include human dung, whereas animal waste includes various types of animal manures (e.g., cow manure, poultry litter), meat-bone meal. Industrial waste includes municipal solid wastes like paper, cardboard, and discarded food, construction and demolition wastes (wood), waste water treatment sludge, waste materials from food

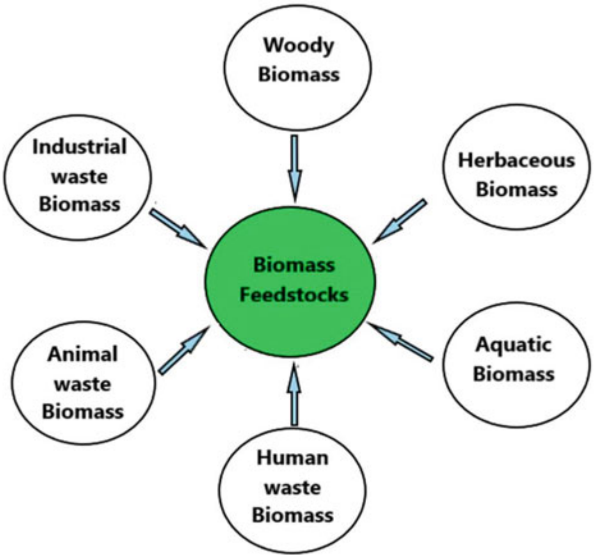

Fig. 24.1 Biomass feedstocks from diversified sources

industry (peelings and scraps from fruit and vegetables, pulp and fibred from sugar and starch extraction) hospital wastes, black liquor from paper and pulp industry, waste papers, paperboard waste, chipboard, fiberboard, plywood, wood pallets and boxes, railway sleepers, tannery wastes, etc. (Vassilev et al. 2010).

All these various types of biomass feedstocks have significant variations in their physical and chemical properties. The quality of produced gas and other products from biomass gasification process and the cost of downstream processing mainly depends on the physical and thermo-chemical properties of biomass feedstocks. A variety of pretreatment methods are typically utilized for efficient utilization of various biomass resources and hence, to increase the efficiency of the gasification process. The main objective of pretreatment method is to make the biomass suitable for specific gasification operation. This is the crucial step prior to gasification. The important physical and thermo-chemical properties of biomass feedstocks are as shown in Fig. 24.2.

As evident from Fig. 24.2, the basic physical properties of biomass feedstocks include particle size and shape along with bulk density. These properties must be maintained within specified ranges in order to reduce difficulty in handling, storage and transportation of biomass and also to make them suitable for subsequent gasification reactions.

Physical pretreatment methods usually include size reduction, drying and densification which are required to convert the raw biomass into useful form before they are fed into a gasifier. Size reduction is essential to obtain the reduced particle size; however, drying is needed to achieve moisture content appropriate for gasification process. In addition, densification method is applied to make the pellets for an increase in density and improved flow of biomass materials (Brar et al. 2012; Kataki et al. 2015).

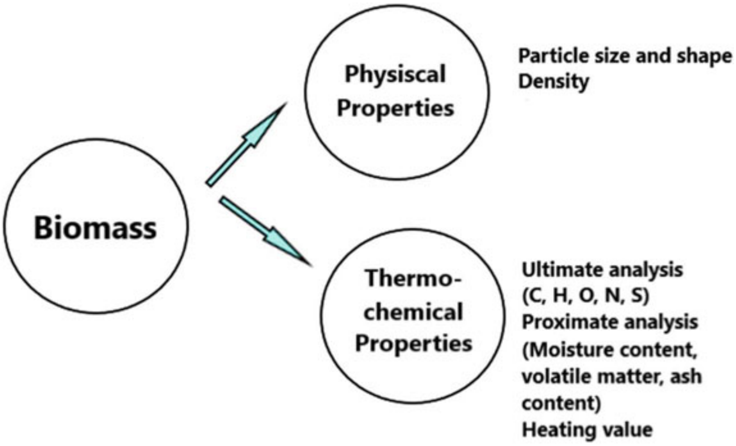

Fig. 24.2 Properties of biomass feedstock that affects the gasification process

The main challenges in handling raw biomass are that after harvesting (at the source) raw biomass typically consists of high moisture content and are mostly irregular in shapes (e.g., chips, straws, grasses), also they have low specific densities. These three factors are responsible for increasing the cost of transportation and hence to add on the overall cost of the gasification process. For example, woodchips have density of 150–200 kg/m^3, grasses having density from 40 to 150 kg/m^3 and moisture content is as high as 40%, moisture content of cereals straw is <15% and more than 90% for the algal biomasses (Sánchez et al. 2019; Jewiarz et al. 2020). Such agricultural biomass namely grasses, wheat straw, rice straw are bulky and fibrous and hence, they require large space for storage and is also difficult to transport to long distance. Hence, densification of biomass using pelletization or briquetting process were utilized to increase their bulk density; for example, pelletizing increases bulk density substantially from 40–250 kg/m^3 to 600–800 kg/m^3 which improves the storability and reduces the transportation cost. In addition, pelletization or briquetting processes yield uniform size and shape of biomass which are easier to handle and amenable feed to conversion unit. However, higher density of obtained biomass using pelletization results in decrease in heat transfer rate during gasification operation which may affect the yield of product gases. On the other hand, the briquetted biomass has moderate density which is easy to break down resulting in higher heat transfer rate and hence helps to increase the conversion into final gaseous products (Theerarattananoon et al. 2011). There lies an inverse relationship between bulk density and moisture content of biomass, such as higher the moisture content of the biomass material indicating having larger volume and therefore leads to low density and vice versa.

Particle size plays a critical role at each stage of subsequent processes namely, storage, transportation, and gasification reaction. Reduced particle size provides a higher specific surface area which accelerates the reaction rate, as well overcome the mass transfer and heat transfer limitations during gasification reactions (Tumuluru and Heikkila 2019). In addition, for some cases, suspension of uniform fine particles in gas is easy as compared to large size particles. For example, particle size of few tens of millimetres is accepted in a fixed bed gasifier, while fluidized bed gasifiers can accept only micron-sized biomass. Smaller particle size provides a shorter residence time for volatiles which leads to reduction in unwanted repolymerization reaction of volatiles and thus, enhances the yield of the gaseous products (Theerarattananoon et al. 2011). Typically, pre-treatment method of biomass feedstocks involves size reduction or grinding along with sieving to obtain a uniform particle size. Rapagna and Latif (1997) have performed the gasification using grounded almond shell and studied the effect of particle size of the product gas yield and tar content. They have reported higher yield of gaseous products (CO, CH_4, and CO_2) and lower percentage of char and heavy tar products, when particle size were reduced from 1 mm to 300μm. The increased gas yield was attributed to an increased heat transfer rate due to the improved surface area of smaller particles.

Size reduction operation helps to improve the physical properties of biomass feedstocks namely size and shape before it is introduced in the conversion unit. Size reduction methods generally involve chipping and grinding operations. The selection of reduction method is mainly dependent on type of feedstock. Two stages are generally involved in woody and herbaceous biomass in which first it is chipped into 5 mm or less followed by grinding that reduces the size of 2 mm or even less (Tumuluru and Heikkila 2019; Dayton and Foust 2019). Hammer mill and knife mill are typical size reduction equipment used for agricultural and forestry biomass. The energy consumption of size reduction equipment depends on various parameters such as type of grinding principle (i.e., shear, attrition, or impact), type of biomass and their moisture content (woody, herbaceous, or municipal solid waste), and capacity of grinder. Generally, more energy is required for size reduction if the moisture content is higher in the biomass and hence, drying is an essential step to remove moisture up to the desired level.

Moisture content is the most critical parameter for efficient thermal conversion of biomass. During gasification process, steam acts as a gasifying agent which is generated from the initial moisture content of biomass; otherwise, additional water is needed to enhance the hydrogen content during the water-gas shift reaction. On contrary, excess moisture content will result in decreasing the reaction temperature due to excess utilization of heat for evaporation of water which causes the partial cracking of hydrocarbons (Chiang et al. 2012; Asadullah 2014). Hence, it is essential to remove the excess moisture content of biomass to a desired level (not more than 40%) using energy-efficient process. The moisture content of municipal solid waste and sludge are generally higher than 50% and hence, pre-treatment by drying is essential prior to gasification. In herbaceous plant like sugarcane, the moisture content is usually much higher (above 50%) and hence not suitable for gasification. Such high moisture content biomass species are processed using fermentation for the production of ethanol. Low moisture content or dry biomass such as woody biomass and low moisture content herbaceous plants are the efficient feedstock for gasification operation (McKendry 2002; Asadullah 2014). Common biomasses and their moisture content are listed in Table 24.1 for ready reference.

Table 24.1 Moisture content in different types of biomass feedstock (data taken from McKendry 2002; Chiang et al. 2012; Kataki et al. 2015)

Biomass	Moisture content (%)
Saw dust	11.30
Rice straw	10.71
Wheat straw	16.00
Barley straw	30.00
Active sludge	56.78
Municipal solid waste (MSW)	53.23
Chicken manure	39.70

Generally, two stages are reported for the reduction of moisture levels in biomass feedstock (Asadullah 2014). The first stage involves initial drying of biomass in open air where sunlight causes natural reduction of moisture at the source location. This is followed by drying using external heat using drying equipment at the gasification plant location. Sun drying is time consuming and sometimes may cause biomass degradation, whereas drying equipment are energy intensive. Selecting an optimal drying operation to achieve desired moisture content and biomass quality is of utmost importance. The combined approach may help to reduce the transportation cost and difficulties as well as load of supplying heat using drying equipment.

Biomass are majorly composed of cellulose, hemicellulose, and lignin along with some extractives and it varies depending on the types of biomasses (Vassilev et al. 2012; Kataki et al. 2015). Cellulose is a linear or straight chain polymer of D-glucose (a six-carbon sugar) linked with β-1,4 linkages; hemicellulose is a branched polymer with both five-carbon and six-carbon sugars, and lignin is a randomly constructed and highly cross-linked structure of phenylpropane units. Herbaceous and woody biomass generally consists of 60–80% (dry basis) cellulose and hemicellulose, and 10–25% lignin (Kumar et al. 2009b). Cellulose content in the biomass group normally decreases in the order of: herbaceous and agricultural biomass > wood and woody biomass > animal biomass. The high cellulose content is found in some subgroups such as wood stems, herbaceous or agricultural stalks and fibers whereas barks and leaves have low cellulose content. The decreasing order of hemicellulose in the biomass group is quite different than cellulose as: wood and woody biomass > herbaceous and agricultural biomass > animal biomass. Lignin content in the biomass group normally decreases in order: wood and woody biomass > herbaceous and agricultural biomass, which is opposite to the group order for cellulose and hemicellulose (Vassilev et al. 2012; Kataki et al. 2015). It should be noted that higher the content of cellulose and hemicellulose in biomass, yields higher percentage of gaseous products. Therefore, softwood, hardwood, wheat straw and bagasse which is having higher percentages of cellulose and hemicellulose are preferred over sunflower seed hull, coconut shell, almond shell, larch plant or poultry litter (Sikarwar et al. 2016; Ren et al. 2019). Guo et al. (2007) have demonstrated that lignin is more difficult to gasify than cellulose based on experimental study of biomass model compounds such as cellulose, xylan and lignin. They have further confirmed based on real biomass gasification study that wheat stalk, corn cob and sorghum stalk are easier to gasify due to presence of less percentage of lignin.

24.3 Gasification Process Chemistry and Technology

The demand from energy and from chemical industries, gasification technology has witnessed high and low growth, since its deployment into commercial-scale operation several decades ago. This technology was adopted for coal and then utilized for biomass as feedstock. The biomass gasification process is a thermochemical conversion process in which solid/organic wastes produces gaseous products and solids. This process produces syngas (a mixture of CO and H_2), which has a considerable heating value and can also be used for power generation or iofuel production. The solid phase produced as by-product is called "char," consisting of majorly higher molecular weight organic matter and some inert material originally present in the initial feed. Gasification takes place in four steps viz., drying, pyrolysis, oxidation and reduction.

24.3.1 Drying

The moisture content of biomass generally ranges between 5% and 35%. Drying occurs at about 100–200 °C. In this zone, biomass feedstock receives heat from oxidation (hot) zone and evaporation of moisture take place to convert into dry biomass (moisture content <5%). Above 100 °C, the loosely bound moisture present in the biomass is vaporized. As the temperature increases further, volatilization process starts for the low-molecular-weight extractives. This process continues until a temperature of approximately 200 °C is achieved.

24.3.2 Oxidation

All the key gasification reactions namely, drying, pyrolysis and reduction are endothermic in nature. In order to provide necessary thermal energy to complete the subsequent key reactions, oxidation reactions are carried out to decompose part of the biomass. The exothermic oxidation reactions are carried out in presence of partial air or oxygen supply. Some of the important reactions are carried out in this zone which are mentioned below:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

$$CH_4 + \frac{3}{2}O_2 \rightarrow CO + 2H_2O$$

Generally, the rate of the reaction is highest for first reaction as compared to other two. Hence, we can say that oxygen preferentially combines with H_2. The remaining amount of oxygen reacts with CO, and CH_4 respectively to produce other oxidation products (four zone modelling). All these oxidation reactions are highly exothermic and results into sudden temperature increase up to 1200–1500 °C in this zone.

24.3.3 Pyrolysis

Pyrolysis is an important pre-step in gasifier. In this zone, thermochemical decomposition of biomass occurs in the absence of air. Dry biomass is thermally decomposed into low molecular weight products such as solid (char), condensable gases and (liquid) tar. In the initial stages, biomass is decomposed into condensable gases and solid char. Then, these condensable gases get converted into non-condensable gases like CO, CO_2, H_2, and CH_4, liquid, and char.

During pyrolysis, following phenomena occur:

- The temperature of the biomass gets increased due to heat transfer from the hot gases. This stage occurs in the temperature range of 120 and 200 °C. This mainly occurs due to some internal rearrangements, such as bond breakage, the appearance of free radicals and the formation of carbonyl groups take place, with a corresponding release of small amounts of water (H_2O), carbon monoxide (CO) and CO_2.
- Due to increase in the temperature, biomass gets converted into volatiles and the formation of char. In the second stage of pyrolysis process, solid decomposition occurs and significant reduction of weight is observed from the initial biomass.
- Heat transfer between the hot volatiles and cooler un-pyrolysed biomass.
- Condensation of some part of the volatiles in the cooler parts of the biomass which produces tar. In this stage, there is a continuous char devolatilization which is caused by the further cleavage of C-H and C-O bonds.
- Auto catalytic secondary pyrolysis reactions due to these interactions.

Studies have been conducted on pyrolysis of biomass and other substances by several researchers (Babu and Sheth 2006). The actual reaction scheme of pyrolysis of biomass is extremely complex in nature due to formation of several intermediate products. Therefore, pyrolysis of biomass is generally modeled based on apparent kinetics.

$$C_nH_mO_p(\text{biomass}) \rightarrow \sum_{\text{liquid}} C_xH_yO_z + \sum_{\text{gas}} C_aH_bO_c + H_2O + C\ (\text{Char})$$

This reaction generally precedes the gasification step.

24.4 Types of Pyrolysis

Pyrolysis process can be classified into slow pyrolysis (intermediate pyrolysis), fast pyrolysis and flash pyrolysis. It mainly depends on the reaction temperature, residence time, and heating rate. Classification of the pyrolysis process is explained below in detail:

24.4.1 Slow Pyrolysis

When time required to heat the fuel up to the pyrolysis temperature is much longer than the characteristic pyrolysis reaction time, then it is considered as slow pyrolysis. In slow pyrolysis, the residence time of vapor in the pyrolysis zone is more than minutes or longer. When there is a requirement of producing a liquid, this process is not used. Slow pyrolysis is mostly used for char production. In slow pyrolysis, biomass is typically heated up to 500 °C at slow heating rates (up to 10–20 °C/min). The vapor residence time varies from 5 min to 30 min. Therefore, the components in the vapor phase react with each other to form solid char and liquid. The main product, char (form of carbon), can be used in a wide range of applications such as for domestic cooking, activated carbon, absorbents, fireworks, soil conditioners and in metallurgical or chemical industry where it can be used as hot utility. As reported by Chhiti and Kemiha (2013), a higher yield of charcoal can be obtained from biomass feedstocks with higher lignin contents and lower hemicelluloses contents. Moreover, for slow pyrolysis, fine feedstock particle size is not required.

24.4.2 Fast Pyrolysis

Fast pyrolysis processes have high heating flux (i.e., flow of energy per unit of area per unit of time is high) in absence of oxygen. Biomass decomposes to generate vapors, liquid (tar) and char. During fast pyrolysis process, biomass gets converted into 60–75 wt% of liquid bio-oil, 15–25 wt% of solid char and 10–20 wt% of non-condensable gas, depending on the feedstock used. No waste is generated because the bio-oil and solid char can each be used as a fuel and the gas can be recycled back in the process.

Some of the essential features of fast pyrolysis process are:

- Process has very high heating and heat transfer rates with requirement of <1 mm particle size of biomass feed.
- Controlled reaction temperature of around 500 °C in the vapor phase, with short vapor residence time <2 s.

24.4.3 Reduction

Product gases from oxidation zone such as carbon dioxide, methane, char, water, etc. undergo reduction reactions (reforming of the char, Boudouard, water gas shift, and methanation reactions). From these reactions, syngas is produced (i.e., CO and H_2).

Water gas reaction:

$$C + H_2O \leftrightarrow CO + H_2 \qquad \Delta H_f^{298} = 131.4\,\mathrm{kJ/mol}$$

Boudouard reaction:

$$C + CO_2 \leftrightarrow 2CO \qquad \Delta H_f^{298} = 172.6\,\mathrm{kJ/mol}$$

Water gas shift reaction:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H_f^{298} = -42\,\mathrm{kJ/mol}$$

Methane formation reaction:

$$C + 2H_2 \leftrightarrow CH_4 \qquad \Delta H_f^{298} = -75\,\mathrm{kJ/mol}$$

The first and second reactions are endothermic in nature, while the third and fourth reactions are exothermic in nature. All these reactions are reversible in nature, and hence, reactants and products co-exist and maintain their concentration ratios according to law of thermodynamics. It can also be stated that endothermic reactions are favored by heat and therefore, as the temperature increases, reactions (24.1) and (24.2) occur preferentially and vice versa. However, increase in temperature responsible for char oxidation which will ultimately result into ash sintering and reduction of energy content of syngas.

Thus, reduction temperature is one of the key parameters to be monitored for the quality and characteristics of the syngas and solid residue.

24.4.4 Catalytic Reforming of Tar

Tar is one of the unwanted products produced during gasification. Tar is a mixture of higher hydrocarbons and it is produced by complex gasification reactions such as devolatilization and pyrolysis process at low temperature and it can be deposited in downstream equipment and reduce the efficiency of the whole system. Generally, temperature plays important role in tar formation. The gasification process ranges between 700 and 1000 °C and at higher temperatures reduced amount of tar is formed and vice-versa. Tar production can lead into severe maintenance problems such as clogging of reactor outlet and failure of other parts of the equipment. It also contains a significant amount of energy which can be considered as a loss of energy. Moreover, presence of polycyclic aromatic hydrocarbons in tar are also hazardous to human beings as well as to other animals if it disposed into river or underground water. This is one of the major problems for the deployment of biomass gasification technology for commercial purposes.

To overcome the problems associated with commercialization of biomass gasification, tar removal or conversion is an important factor that should be taken into consideration. For tar removal/conversion, various approaches are proposed by researchers and it is being reported in the literature, including physical removal, thermal cracking, and catalytic conversion.

Physical tar removal techniques can be done by cyclones, barrier filters, wet electrostatic precipitators (ESPs) or wet scrubbers. Cyclone or ceramic filters are used to separate the particular matter. But due to clogging the pores of the filters, pressure drop is created after certain time which would hamper the efficiency. Under hot gas filtration technique, tar remains in gaseous form which escapes from the ceramic filters. Therefore, it shows poor performance for the removal of the tar. Thus, ceramic filtration is coupled with thermal or catalytic cracking method to remove tar content. Wet ESPs have significant collection efficiency approx. >90% for the particle size <0.5 mm. It has a very low-pressure drop although it has the high capital and running cost. Wet scrubbers are able to achieve high collection efficiency with lower capital cost. However, the efficiency drops sharply with particles <1 mm. They also consume a large amount of spray liquid and fan power, which makes the running cost relatively high.

Catalytic cracking is an advantageous and can be used to minimize tar formation even at low temperatures. Thus, to remove or minimize the tar content in syngas, primarily catalyst is used with steam additive in gasifier to increase the calorific value of the syngas while low production of tar. Moreover, in secondary process, to lower the tar content from syngas, stream of tar contained syngas is sent to catalytic reformer unit in which tar converts into syngas or absorb the tar by catalyst. Catalysts are used in this process are metallic and non-metallic catalysts. Non-metallic catalysts are less expensive and they are dolomite, zeolite, and calcite. Metallic catalysts such as Ni, Ni/Mo, Ni/Co/ Mo, NiO, Pt, and Ru have been applied to various gasification processes with different product gas purity requirements.

24.5 Key Operating Parameters

For the desired product gas composition and higher heating value of syngas, it is necessary to optimize the gasification operating conditions. In line with this, the effects of the main operating conditions on the quantity and composition of the product gas and its impurities are mentioned below:

24.5.1 Particle Size of Biomass

Feed (biomass) particle size is one of the important factors which can affect the gasification results. If the particle size is coarser, more char and less tar will be produced. With an increased particle size, rate of thermal diffusion decreases and results into lower heating rate. Smaller particle size of the feed have greater surface area per unit mass which facilitates more rapid heat transfer and gasification reactions. Lv et al. (2004a, b) observed that gas yields such as CO, H_2, CH_4 etc. have increased with smaller particle size of the feed material. Moreover, Edrich et al. (1985) noticed that the gasification rate depends on particle size. During the gasification of wood in a fixed bed gasifier, the gasification rate increased from 0.1 to 1.0 min^{-1} when the particle size was decreased from 19.05 to 5.00 mm. Rapagna and Latif (1997) noticed that there was an increased gas yield and gas compositions of CO, CH_4, and CO_2, when the particle size was reduced from largest (1.090 mm) to smallest (0.287 mm). By reducing the particle size from 1.2 mm to 0.075 mm, it was observed that syn-gas production increased, i.e., H_2 and CO and attained high carbon conversion efficiencies whereas lesser amount of CO_2 formation. The typical instruments such as Hammermills, knife mills and tub grinders are used for reduction of the particle sizes. Hammer mills are used for dry agricultural as well as for dry forestry residues. Tub grinders are small, mobile hammer mills. Screens are used in the mills to assure the ground particles have certain maximum size. Energy consumption during size reduction depends on the moisture content, initial size of biomass, biomass properties, and screen size of the mill and properties of the mill.

24.5.2 Temperature

Overall performance of the gasifier is dependent on the temperature. It will have an influence on the conversion, product distribution, and energy efficiency of the gasifier. For obtaining energy efficiency, a relatively low temperature and minimum oxygen input is desired (Qin et al. 2012). On the other hand, optimum feed utilization might demand a high temperature above 1000 °C and suitable excess air ratio (say around 0.35) to obtain good yields of syngas along with lower char and tar yield. The conversion of biomass into gaseous products increases when there is an increase in temperature. This is mainly due to high volatile matter content in biomass which enhances the conversion of biomass into syngas at high temperatures. Moreover, with the increase in temperature, char conversion, tar cracking, water gas reaction, water gas shift reaction, Boudouard reaction and methane reforming are favored and hence syngas production increases. The temperature above 750–800 °C, water gas reaction is favored due to its endothermic nature of the reaction and produces H_2 gas content and decreases CH_4 content. At temperatures above 850–900 °C, both steam reforming and the Boudouard reactions are favored and results into an increase in CO content. Gupta and Cichonski (2007) observed that there is a significant increase in H_2 above 800 °C for Steam/Biomass ratio between 0.5 and 1.08. Maximum H_2 yield was obtained at 1000 °C for a feedstock consisting of paper, and at 900 °C feedstocks consisting of cardboard and wood pellets. Balάš et al. (2012) have done on biomass gasification experiments and observed the effect of temperature and pressure on syngas quality. They stated that an increase in temperature results into increase in the proportion of CO and H_2, a decrease in the proportion of CH_4 and CO_2, and an increase in the lower calorific value of the gas. Sadakata et al. (1987) noticed the calorific value of producer gas obtained from crop residue gasification increased steadily up to 700 °C and then decreased. The increase in the gas heating value is due to the increase in concentrations of CO, H_2 and hydrocarbon gases in the gas mixture. The decline at higher temperatures is probably due to the cracking of hydrocarbons. The first-order rate constant of gasification was found to increase with temperature in accordance with the Arrhenius equation (Edrich et al. 1985). Gasification rates are too fast and are controlled by heat and mass transfer rates above 900 °C while in the range of 600–900 °C, the gasification reactions are rate controlling. However, the gasification reaction rates are too slow below 600 °C.

24.5.3 Steam Flow Rate (Steam to Biomass Ratio, S/B)

The effect of the steam to biomass (S/B) ratio has been determined for steam and air–steam gasification. Steam is supplied as a gasification agent which increases partial pressure of H_2O in gasification chambers which encourages the water gas, water gas shift and methane reforming reactions and results in increasing H_2 production. However, gasification temperature should be high enough (750–900 °C) for favoring the steam reforming and water gas reactions (Kumar et al. 2009a). Some researchers have observed that there is a reduction in tar at higher steam to biomass ratios. This is mainly attributed to steam reforming of the tar with an increased partial pressure of steam. Chojnacki et al. (2020) observed that by varying temperatures from 750 °C to 850 °C and steam flow rate from 10 kg/h to 20 kg/h, it has been found that there is an increase in the steam flow rate in the reactor which results in an increase in carbon dioxide and a decrease in hydrogen content. The optimum hydrogen content observed at steam flow rate of 10 kg/h which corresponded to the S/B ratio of 0.5. Moreover, they had observed as heating value of syngas is lowered by increasing temperature up to 850 °C. It can be concluded due to the increase in the percentage of CO_2 and the decrease in the CO and CH_4 contents. Lv et al. (2004a, b) observed that with S/B higher than 2.7, the gas composition did not change significantly but, with S/B between 0 and 1.35, CO yield decreased, and CH_4, CO_2, and C_2H_4 yields increased. With S/B ratio between 1.35 and 2.70, the CO and CH_4 composition decreased and CO_2 and H_2 yields increased which indicated higher steam reforming reactions. Lucas et al. (2004) stated that increasing the temperature of the gasifying agents results into an increase in the heating value of the syngas, and reduces the tar, soot and char residues. Thus, deploying a preheater is recommended before the introduction of gasifying agents (steam and air) in the gasifier which accelerates higher gasification bed temperature.

24.5.4 Gasifying Agents

Gasification reactions are performed by using medium. Thus, the gasification agents such as oxygen, air, steam, CO_2 and others are medium used in the gasification. The selectivity of the gasification reactions depend upon different gasifying agents which affects the composition and LHV of produced gas. Generally, air is used as a gasifying agent due to its low cost and availability. Therefore, LHV of the produced gas is low. This is mainly because of the presence of N_2 Content in the produced gas. Thus, the heating value of the gas ranges between 4 and 6 MJ/m^3. But, when pure oxygen is used as gasifying agent, the heating value is higher and is in the range of 12–28 MJ/m^3. Effect of the air or oxygen as a gasifying agent is discussed below which can affect the yield of the gas.

24.5.5 Equivalence Ratio

The equivalence ratio (ER) is defined as the ratio of the actual fuel to air supplied ratio to the stoichiometric fuel/air ratio. It is commonly indicated that fuel-oxidizer mixture is rich, stochiometric, or lean. The product gas composition strongly depends on the amount of oxygen or air supplied. The gasification products are primarily CO, H_2, CO_2, etc. if the amount of oxygen supplied is rich or stochiometric, then oxidation takes place and production of CO_2 will be more. If amount of oxygen supplied is less than stochiometric then production of CO will be more. Hence, it is necessary to determine the ER where all carbon will be gasified without excess of oxygen or air.

24.6 Design of the Gasifier

The sequence of gasification reactions depends to some extent on the type of gas-solid contacting reactors called as gasifiers. Gasifiers are differentiated mainly on the following factors:

24.6.1 Feed/Air Flow Direction

Biomass and air can both be fed from top of the gasifier or biomass can be fed from side and air provided from top, and then moved by gravity or air flows.

Another type consists of air flow from middle of the gasifier or from the bottom of the gasifier.

- Gasification agent used: It can be air, oxygen, or steam.
- Temperature and pressure range.

Based on the above factors, there are mainly four types of gasifiers.

By considering the aforementioned parameters, gasifiers are mainly categorized into fixed bed, fluidized bed, entrained flow reactor, rotary kiln reactor, and plasma reactor.

24.6.2 Fixed Bed Gasifier

In this category, gasifiers are filled with solid feed bed where the gasifying medium and producer gas either are rising (updraft), in opposite direction (downdraft), or flowing horizontally through the reactor (cross-draft). The gasifying medium can be air, steam, oxygen, or a mixture of them (Fig. 24.3).

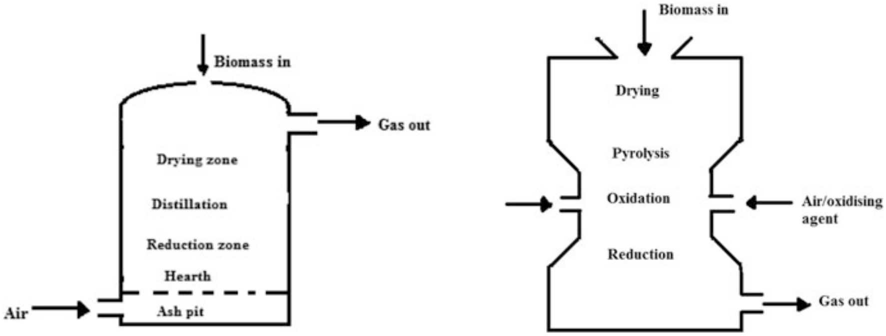

Fig. 24.3 Schematic of fixed bed gasifiers

Gasifier	Advantages	Disadvantages
Fixed bed (updraft)	• Simple construction • Ability to handle high moisture content and different feed material sizes • High thermal efficiency • Cost-effective for small scale applications	• High tar content • Low production/output of syngas • Not suitable for engine and turbine applications
Fixed bed (downdraft)	• High carbon conversion • Simple construction • Low production of tar • Suitable for engine and turbine applications • Uniform distribution of gasifying agent	• Low coefficient of heat transfer • Uniform size distribution of feed is required • Difficulty starting and controlling the temperature • High temperature of the producer gas affects engine efficiency

24.6.3 Fluidized Bed Gasifier

Fluidized bed gasifiers are based on the fluidization principle in which inert bed materials and fuel behave as a fluid. This gasifier is a cylindrical column that contains fluid, has a sufficiently high velocity to suspend the particles within the column and provides large surface area for the fluid to allow heat and material transfer between solid and gaseous phases. Therefore, a fluidized bed maintains a uniform temperature and able to handle wide variations in fuel quality. The advantages and disadvantages are mentioned below (Fig. 24.4):

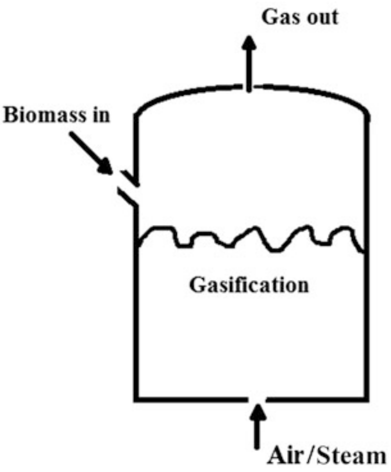

Fig. 24.4 Schematic of the fluidized bed gasifier

Gasifier	Advantages	Disadvantages
Bubbling Fluidized Bed gasifier	• High carbon conversion • Good temperature control • High residence time for mass and heat transfer • Low level of tar • Scale-up is possible • Suitable for pre-treated municipal solid wastes	• High ash production • High investment costs and maintenance cost • Pre-treatment necessary for heterogeneous materials
Circulating Fluidized Bed gasifier	• Low production of tar • High carbon conversion • Load variations are possible • Able to scale up	• Loss of carbon in the ashes • Required the reduced size of feed materials • High start-up cost and investment cost

24.6.4 Entrained Flow Reactor

In an entrained flow reactor, the feed material requires fine size particles (0.1–1 mm particles) and the gasifying agent are injected co-currently. The operating temperature ranges between 1300 and 1500 °C and operating pressures 25–30 bar. Water slurries or dry feed is used as a raw material. Water slurries are atomized and solid feed is injected by pneumatic feeding method, then pulverized fuel is fed into gasifier. In this type of gasifier, fine size particles of biomass, air and steam are fed co-currently. It operates at high temperatures and pressures. Biomass particles flow along with the oxidizing agent and forms a dense cloud of particles. Reactions take place in these clouds of particles, so that syngas will form first followed by ash and tars (Fig. 24.5).

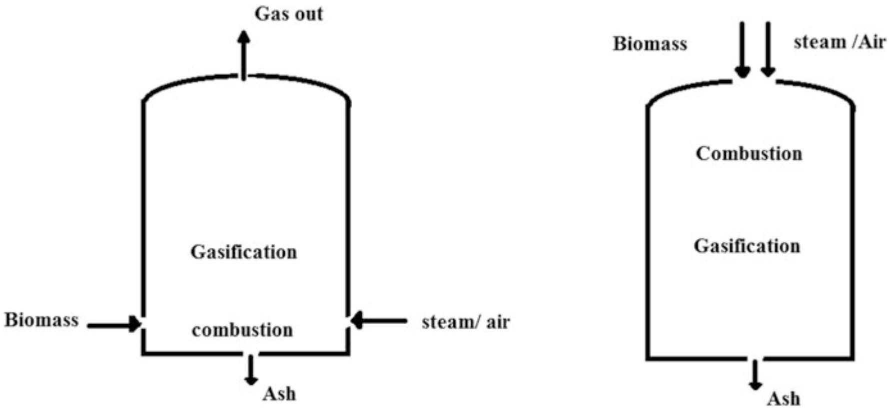

Fig. 24.5 Schematic of the entrained flow gasifier

Gasifier	Advantages	Disadvantages
Entrained flow reactor	• Uniform temperature is obtained • High carbon conversion • Low concentration of tar • Able to scale up	• Low cold gas efficiency • High plant cost and maintenance cost • Size reduction is required • Heat recovery is required to improve efficiency

24.6.5 *Rotary Kiln Reactor*

Rotary kilns consist of cylindrical chamber that slowly rotates around its own axis. The gas–solid contact takes place due to the rotation of the drum that, by continuously stirring, exposes the new solid surfaces to the gasification agent. However, this process of heat transfer and matter exchange is not so effective and hence residence time increases. To improve the efficiency, installations of barriers inside the drum would be effective and increase the mass and heat transfer due to enough residence time for fuel handling. Counter-current configuration is used mostly for gasification. Feed is fed from top of the reactor and gasifying agent is fed from the bottom of the reactor. The advantages and disadvantages are tabulated below.

Gasifier	Advantages	Disadvantages
Rotary kiln reactor	• High carbon conversion • Reduced investment cost • Simple in construction • Suitable for the wastes which can be melted	• Low cold gas efficiency • Difficulty in starting and control temperature • High content of tar and dust • High maintenance cost

24.6.6 *Plasma Technology*

Plasma is an ionized gas stream at high temperatures up to 10,000 °C obtained from electric arc. An electric arc is created between two electrodes spaced apart. The created electric arc or plasma torch disintegrates the biomass feed into their elemental components. Further reduction of biomass, syngas is produced and collected from top of the reactor. The plasma technology for gasification can occur in two ways:

- Direct application of the solid is treated when biomass or municipal solid wastes needs to be degraded.
- The main objective is to produce syngas with lower content of light components and tar.

Gasifier	Advantages	Disadvantages
Plasma reactor	• Short reaction time • Scale-up is possible • Production of vitrified completely inert and non-leachable slag, which include heavy metals	• Presence of nanoparticles in the syngas • Maintenance problem of moving parts • Solidification of the molten materials in the ducts

24.7 Syngas Cleaning

Syngas generated in gasifier often contains impurities like tars, particulate matter, nitrogen compounds, sulfur compounds, halides, and trace metals. The syngas needs to be purified before its usage in internal combustion engine, turbine, fuel cell or in chemical conversion by Fischer–Tropsch synthesis, etc. The purity of syngas required varies based on applications. For example, internal combustion engines can accept particulate matter concentration of <50 mg Nm^{-3} with particle size of <10μm. Gas turbines require this concentration <30 mg Nm^{-3}. Hence there is a need for cleaning the gas for efficient utilization. The contaminants commonly present in syngas are listed below in Fig. 24.6. The types of the impurities actually present depend on the type of feedstock, process conditions, type of gasifier, oxygen supply, and temperature.

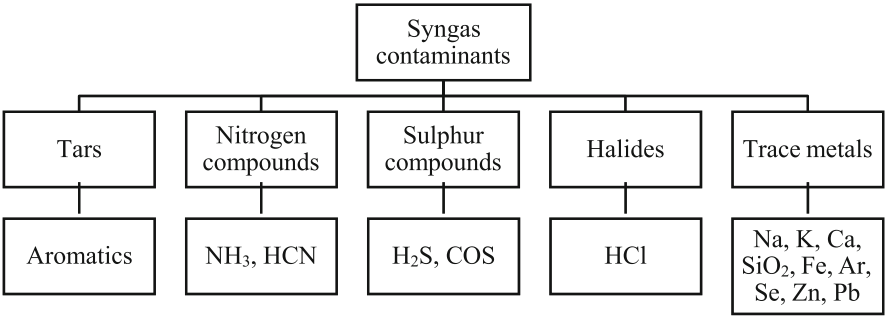

Fig. 24.6 Syngas contaminants

24.8 Methods for Removal of Contaminants

24.8.1 *Physical Gas Cleaning or Cold Gas Method*

It is carried out at an ambient or lower temperature and can be carried out in wet or dry form. Wet form uses adsorption, absorption, filtration, or a combination of these using equipments namely spray towers, wash towers, scrubbers, electrostatic precipitators, or cyclones. On the other hand, dry processes use cyclones, filters, and dry electrostatic precipitators. The wet process has advantage of removing multiple contaminants as compared to the dry process. The solvents used in this process can absorb multiple contaminants. Although this method is simple and easy to use, it suffers a major disadvantage of energy loss. Gasification is carried out at high temperature of around 800 °C whereas the cleaning takes place at room temperature. This results in loss of thermal efficiency. There is an additional cost involved in the treatment and disposal of contaminant streams (Abdoulmoumine et al. 2015).

Recently, Zeng et al. (2020) have described the use of biomass char. The char because of high porosity and activated carbon has been an effective adsorbent. The main advantage is the utilization of by-product from the gasification process itself and no consideration in the items of activation and regeneration after deactivation. Szul et al. (2020) have described the use of mineral sorbents followed by filtration by ceramic filters.

24.8.2 *Hot Gas Cleanup*

The physical treatment methods may not be able to meet the stringent specifications, instead catalytic processes are relied upon. It is generally carried out at temperatures above 300 °C. Methods include thermal cracking, steam reforming or dry reforming and hydrocracking. Various catalysts are used in this method. The choice of catalyst depends on the type of species present in the gas that need to be removed. Abdoulmoumine et al. (2015) have reported guidelines for the use of various elements as catalysts, catalyst promoters, catalyst supports, and sorbents. Recently, Szul et al. (2020) have described a process of simultaneous de-dusting and adsorption of syngas. The process involved high-temperature dry scrubbing using mineral sorbents and rigid ceramic filters.

24.9 Treatment of Various Contaminants

24.9.1 *Tars*

Tars are all hydrocarbons with a molecular weight higher than benzene produced by thermal or partial oxidation of biomass. Tars pose several challenges like blocking of pipelines, corroding downstream wastewater treatment and deactivating catalysts. Shen and Yoshikawa (2013) have reviewed different tar removal methods. The most widely used method to clean tar is wet scrubbing. The choice of absorbent depends on the composition of tars. Water is most commonly used to remove the tars with polar compounds whereas oil-based compounds are used to remove non-polar tars. Although water is a cheap option, it suffers the disadvantage of low removal efficiency and after treatment. Oil-based absorbents can be recovered by regeneration and give high efficiency. A variety of oils including diesel, engine oils, fatty acid methyl esters can be used as absorbents. The disadvantage of oil-based absorbent is the cost and the additional equipment used for regeneration. Nakamura et al. (2016) have discussed the removal of tar using bio-oil scrubber and char bed filter.

Tar removal efficiency of 98% was observed. Unyaphan et al. (2017) have discussed the removal of tar by producing microbubbles of syngas in venturi oil scrubber. This physical method gave a tar removal efficiency of almost 99.2%. Very recently, Calì et al. (2020) have tried to improve the tar management system by minimizing the water consumption and sludge disposal through novel methods so as to recirculate the part of separated tar and exhaust activated carbon to gasification unit. De Filippis et al. (2015) have used highly porous aluminum oxide spheres for efficient tar removal. More than 50% removal of tar was observed in the process.

Thermal cracking converts tar into carbon and hydrogen at elevated temperature of above 1100 °C. The temperature can come down to 650 °C with catalyst. Dry steam reforming can also be carried out. Commonly used catalyst includes alkaline earth metal catalyst like dolomite, olivine, limonite, calcium, magnesium, and nickel-based catalyst. These catalysts give lower recovery. Also, there are challenges in downstream recovery. Dolomites are easily eroded and hence cannot be used in the fluidized bed reactors. Iron and nickel-based catalyst like limonite can be used in in-situ as well as ex-situ mode. When used in-situ mode, they may suffer deactivation by coking. Zeolite-based catalyst can also be used.

24.9.2 Nitrogen

The conventional method to remove nitrogen is water-based scrubbing. Generally, spray and wash towers are used with a removal efficiency of around 99%. Tars are also removed but this complicates subsequent wastewater treatment. Acid-based scrubbing uses sulphuric acid and hydrochloric acid. In this method co-absorption of acidic gases is possible. The major disadvantage is the corrosive nature of acids and lower removal efficiency when the concentration of nitrogen is high. The use of organic acids for removal of nitrogen is still under consideration. Nickel and nickel promoted with Ce and La, Co or Co-Zn mixed oxide is used as catalyst. Limonite is effective for NH_3 decomposition. Alkaline earth, transition metals, nickel can be loaded on different supports. Ruthenium-based catalyst can also be used.

24.9.3 Sulfur

Solvent-based wet and dry cleaning processes are commonly used for sulfur removal. The method can be a chemical reaction or physical absorption. The absorbents used may be alkanolamines, alkaline salts, aqueous ammonia, and organic solvents with high affinity for acid gases. The main advantage is that the solvents can be regenerated. The disadvantage is the low-temperature requirement which adds to equipment cost. New areas for research include ionic liquid-based physical solvents and customizable solvents. Sulfur contaminants can also be removed from syngas using sorbents which are usually metal oxides. These react with sulfur to produce metal sulfides, alkaline earth metals and transition metal-based oxides are frequently used. CaO is the most widely used one as it can simultaneously remove sulfur and halides. Amongst the transition metals, ZnO, TiO_2, and Fe_2O_3 have been found effective. The problem with ZnO is that under reducing environment it gets reduced to elemental zinc which undergoes volatilization at high temperatures. Copper oxide dispersed on oxides of aluminum, zirconium, silicon, vanadium, and cesium have also been used. Some other sorbents include iron oxide, nickel, and ceria-based sorbents. Koido and Iwasaki (2018) have discussed about the removal of sulfur and radioactive nuclides; however, the radionuclides were found to be within acceptable limits by the usual gasification process.

24.9.4 Halides

Hydrogen halides are removed by wet scrubbing using caustic solution (NaOH dissolved in water). HCl is neutralized to NaCl, other acidic gases CO, CO_2, and H_2S can also be removed. The most common hydrogen halide present is HCl and is removed by dehydrohalogenation. Alkali earth metal oxides of Li, Na, and K are found to be most effective at temperatures above 500 °C. The carbonates of alkali metals like $LiCO_3$, Na_2CO_3, and K_2CO_3 have been found to reduce halide content to <1 ppm. These carbonates can also remove traces amount of HBr and HF from dirty gas. The oxides of alkaline earth metals like Mg, Ca, Sr, and Ba are also used as HCl sorbent. However, their carbonates are less effective. Although transition metal oxides (Mn, Co, Zn, and Yi) are also being used; they are found to be less effective.

24.9.5 Trace Metals

Removal of trace metals is facilitated by gas cooling and wet scrubbing with water followed by subsequent filtration. Solid sorbents of metal oxides have been used to remove mercury. These are Pt, Ru, Pd, Rh, Ti, and Ag. The metal oxides can also be removed by the formation of salts like NaCl, KCl, etc. with alkali metals. The other sorbents used are fly ash, bentonite, kaolin, and bauxite.

24.10 Challenges in Syngas Cleaning

Although considerable research has been done on syngas cleanup and many of these are already commercialized, the following challenges remain to be addressed.

- The varying nature of biomass causes reasonable variation in cleaning efficiency.
- Efficiency of cold gas methods often reduced with lowering in temperature while treating the effluent streams.
- Increase in pressure drop and difficulty in removal of deposits during filtration.
- Treatment of large amounts of contaminated water generated during scrubbing.
- Rapid deactivation of catalyst during hot gas treatment methods.

These can be addressed by developing better materials for catalysts that can withstand severe conditions and have a better lifetime. Moreover, methods that are cost-effective and can eliminate multiple contaminants need to be developed.

24.11 Mathematical Modeling and Simulation of Gasifiers

Mathematical simulation is an important and integral part of bio-gasifier research and development. It might predict an accurate prediction for a system or at least provide a qualitative analysis of input variables on desired target for gasifier. It can also identify unsafe operating conditions namely high temperature and high pressure so that we can opt for other operating parameters and optimize the gasification process. Simulation study reduces load on fresh experimentation as well as cost and time. Though it is not a substitute for experimental data for gas solid reactions but still it is used to predict.

Advantages of good mathematical model:

1. It enables to determine optimum operating parameters and design the gasifier.
2. It is used to find areas of operation which should be analyzed for safety.
3. Provide solution at extreme conditions.
4. Used for scale-up studies.

Gasifier simulation models can be classified into four groups:

1. Thermodynamic equilibrium model
2. Kinetic model
3. Computational fluid dynamics
4. Artificial neural network

24.11.1 Thermodynamic Equilibrium Model

It predicts maximum yield of product that can be achieved. If reactants are left for long time, it achieves equilibrium yield. It means the system is most stable. The entropy of the system maximizes and there is a minimization of the Gibbs free energy. Thermodynamic equilibrium models can be approached by two methods, i.e., stoichiometric or nonstoichiometric methods.

24.11.2 Stoichiometric Equilibrium Models

In this type of model, chemical thermodynamic equilibrium reactions are considered. Species are determined by equilibrium reactions. Stoichiometric modeling is done by either one-step reaction or it is sub-modeled by respective zones of gasifier like pyrolysis, oxidation, and reduction zones.

Single-step stoichiometric model

One-step reaction is considered in gasification to avoid complexity. The basic assumption is that one mole of biomass gasified with ω mol of water/steam in presence of "α" mole of air.

$$\mathrm{C_1H}_h\mathrm{O_o} + \omega\mathrm{H_2O} + \alpha(\mathrm{O_2} + 3.78\mathrm{N_2})$$

$$= n_{\mathrm{C}}\mathrm{C} + n_{\mathrm{CO_2}}\mathrm{CO_2} + n_{\mathrm{CO}}\mathrm{CO} + n_{\mathrm{CH_4}}\mathrm{CH_4} + n_{\mathrm{H_2}}\mathrm{H_2} + n_{\mathrm{H_2O}}\mathrm{H_2O} + 3.78a\mathrm{N_2}$$

In the above equation, ω and a are variables that can be changed to get desired amount of product. In product $n_{\mathrm{C}}, n_{\mathrm{H_2}}, n_{\mathrm{CO}}, n_{\mathrm{CO_2}}, n_{\mathrm{CH_4}}, n_{\mathrm{H_2O}}$ are unknowns. These are calculated by stoichiometric balance of carbon, hydrogen, and oxygen.

There are four equilibrium reactions: Boudouard reaction, methane formation, steam reforming reaction (refer Gasification section) and water gas primary reaction. Equilibrium constants are calculated from Gibbs free energy equations of respective reaction.

If the gasification process is assumed to be adiabatic, then the energy balance of the gasification reaction results to a new set of equation, which can determine the final temperature of the system.

$$\sum n_i \left[h^0_{f,i} + \Delta \mathrm{H}^{\mathrm{T}}_{298}\right] i, \mathrm{reactant} = \sum n_i \left[h^0_{f,i} + \Delta \mathrm{H}^{\mathrm{T}}_{298}\right] i, \mathrm{product} \qquad ii$$

Single step reaction using thermodynamic modeling has been done by following authors.

Sl. no	Equilibrium model	Key points	Results	Authors
1	A model developed to evaluate degree of approximation for downdraft gasifier	Consideration of homogeneous and heterogeneous reactions.	The prediction of producer gas composition was in good agreement with experimental data.	Chern et al. (1991)
2	Stoichiometric equilibrium model using Newton–Raphson method of biomass	This is a modified version of Chern et al. (1991) and products formed in the pyrolysis zone completely burn in reduction zone of the gasifier.	The prediction of producer gas and calorific value closely matches with experimental data available in literature for gasification of wood.	Zainal et al. (2001)
3	Stoichiometric equilibrium model using Newton–Raphson method of biomass	Chemical formula of biomass contains S and N. the global reaction contains SO_2 and O_2. And partial correction factor ($\delta/5$) is introduced.	This model is validated with experimental data taken from Jayah et al. (2003).	Melgar et al. (2007)
4	Stoichiometric equilibrium model using Newton–Raphson method of MSW	Nitrogen is incorporated to modify Zainal et al. (2001) thermodynamic model. Also, there is incorporation of a coefficient which is used to multiply with equilibrium constant.	This modified model has been used to simulate the gasification of Thailand MSW.	Jarungthammachote and Dutta (2007)
5	Stoichiometric equilibrium model using Newton–Jacobi iteration method of MSW using MATLAB programming.	Ash is ignored. The process is assumed to be adiabatic.	This model when compared with Senapati et al. is found to be in good agreement. Also if temperature increases, model becomes more realistic.	Bhavanam and Sastry (2013)
6	In one step global reaction, tar has been introduced to match experimental results with Jayah et al. (2003).	Tar is introduced and use of coefficient (3.5) for multiplication with equilibrium constant.	It predicts better results.	Barman et al. (2012)

(continued)

Sl. no	Equilibrium model	Key points	Results	Authors
7	Heterogeneous model of char is developed along with equilibrium reaction modeling.	Char formation is assumed	The producer gas composition matches with experimental data	Sharma (2008a)

Sub-zones for stoichiometric equilibrium modeling:

This model includes separate zones for modeling. There are four sub-models in gasification like sub-model of drying, pyrolysis, oxidation, and reduction. The output of first sub-model becomes input of the next sub-model. This model has an advantage of more accuracy as temperature and composition can be studied at different zones.

Reaction of pyrolysis zone used for modeling

$$\begin{aligned}\mathrm{C_1H}_h\mathrm{O_o} + \omega\mathrm{H_2O} = {} & n_{\mathrm{p,C}}\mathrm{C} + n_{\mathrm{p,CO_2}}\mathrm{CO_2} + n_{\mathrm{p,CO}}\mathrm{CO} + n_{\mathrm{p,CH_4}}\mathrm{CH_4} + n_{\mathrm{p,H_2}}\mathrm{H_2} \\ & + n_{\mathrm{p,H_2O}}\mathrm{H_2O} + n_{\mathrm{p,C_2H_2}}\mathrm{C_2H_2}\end{aligned}$$

Reaction of oxidation zone used for modeling

$$\begin{aligned}& n_{\mathrm{p,C}}\mathrm{C} + n_{\mathrm{p,CO_2}}\mathrm{CO_2} + n_{\mathrm{p,CO}}\mathrm{CO} + n_{\mathrm{p,CH_4}}\mathrm{CH_4} + n_{\mathrm{p,H_2}}\mathrm{H_2} + n_{\mathrm{p,H_2O}}\mathrm{H_2O} \\ & \quad + n_{\mathrm{p,C_2H_2}}\mathrm{C_2H_2} + (\mathrm{O_2} + 3.76\mathrm{N_2}) \\ & \quad = n_{\mathrm{ox,C}}\mathrm{C} + n_{\mathrm{ox,CO_2}}\mathrm{CO_2} + n_{\mathrm{ox,CO}}\mathrm{CO} + n_{\mathrm{ox,CH_4}}\mathrm{CH_4} + n_{\mathrm{ox,H_2}}\mathrm{H_2} + n_{\mathrm{ox,H_2O}}\mathrm{H_2O} \\ & \qquad + 3.76\alpha\mathrm{N_2}\end{aligned}$$

Reaction of reduction zone used for modeling

$$\begin{aligned}& n_{\mathrm{ox,C}}\mathrm{C} + n_{\mathrm{ox,CO_2}}\mathrm{CO_2} + n_{\mathrm{ox,CO}}\mathrm{CO} + n_{\mathrm{ox,CH_4}}\mathrm{CH_4} + n_{\mathrm{ox,H_2}}\mathrm{H_2} + n_{\mathrm{ox,H_2O}}\mathrm{H_2O} \\ & \quad + 3.76\alpha\mathrm{N_2} \\ & \quad = n_{\mathrm{R,C}}\mathrm{C} + n_{\mathrm{R,CO_2}}\mathrm{CO_2} + n_{\mathrm{R,CO}}\mathrm{CO} + n_{\mathrm{R,CH_4}}\mathrm{CH_4} + n_{\mathrm{R,H_2}}\mathrm{H_2} + n_{\mathrm{R,H_2O}}\mathrm{H_2O} \\ & \qquad + 3.76\alpha\mathrm{N_2}\end{aligned}$$

General energy balance formula

$$\sum_i n_i \left[h_{f,i}^0 + \Delta\mathrm{H}_{298}^{\mathrm{T}}\right]_{i,\mathrm{reactant}} = \sum_i n_i \left[h_{f,i}^0 + \Delta\mathrm{H}_{298}^{\mathrm{T}}\right]_{i,\mathrm{product}} + \mathrm{Q_{loss}}$$

The sub-zone thermodynamic modeling has been done by the following authors.

Thermodynamic equilibrium sub-model	Key points	Results	Author
The three zone equilibrium and kinetic free model done by turbo-C program	It does not use thermodynamic equilibrium constant relationships.	This model clearly provides an operating range of equivalence ratio and moisture content for the woody biomass materials.	Ratnadhariya and Channiwala (2009)

24.11.3 Non Stoichiometric Equilibrium Model

This modeling technique totally depends on minimization of Gibbs free energy of the system. There is no specification as to why a particular reaction mechanism is followed. However, moisture content and elemental composition of feed is necessary.

The total Gibbs free energy of gasification contains all gas species ($i = 1\ldots N$) and it is represented by the following equation.

$$G_{\text{total}} = \sum_{i}^{N} n_i \Delta G_{f,i}^{0} + \sum_{i}^{N} n_i \mathrm{RT} \ln \frac{(n_i)}{\sum n_i}$$

where $\Delta G_{f,i}^{0}$ is standard Gibbs free energy of "i" species.

This equation is to be solved for unknown values of ni to minimize Gtotal considering overall mass balance of the overall reaction. This model solved by Lagrange multiplier method.

$$L = G_{\text{total}} - \sum_{j=1}^{K} \lambda_j \left(\sum_{i=1}^{N} a_{ij} n_i - A_j \right)$$

where λ_j is the Lagrangian multiplier for the jth element. And a_{ij} is the number of atoms of the jth element in the ith species, also A_j is the total number of atoms of element j entering the reactor.

$$A_j = \sum_{i}^{N} a_{ij} n_i$$

To find extreme point, dividing by RT and taking derivative

$$\frac{dL}{dn_i} = 0,$$

Substituting above it will become

$$\frac{dL}{dn_i} = \frac{\Delta G^0{}_{f,i}}{\mathrm{RT}} + \sum_{i}^{N} \ln\left(\frac{n_i}{n_{\text{total}}} + \frac{1}{\mathrm{RT}}\sum_{j=1}^{N} \lambda_j\left(\sum_{i=1}^{N} a_{ij}\right)\right)_i = 0$$

Nonstoichiometric modeling has been done by the following author.

Non stoichiometric model	Key points	Results and validation	Author
This type of model has been developed for three types of gasifier gasifiers: a central jet spouted bed, a circular split spouted bed and a spout-fluid bed	Carbon conversion is considered	Results matches with experimental data but this model is less accurate for spouted bed gasification	Jarungthammachote and Dutta (2008)

24.11.4 Kinetic Model

Equilibrium model fails to correlate the reactor design parameter with the product gas composition. This inadequacy leads to the development of kinetic models. This model helps in predicting the time required for a reaction to take place. It also gives the extent to which a reaction proceeds in specified time duration. Kinetic models are applicable when the reaction temperatures are pretty low. As thermodynamic model fails in such cases, kinetic model proves to be an advantage.

It mainly depends on the reactor gasifier geometry and involves parameters such as reaction rate, residence time, length of reactor and reactor hydrodynamics like superficial velocity, diffusion rate, etc. (Patra and Sheth 2015). In determining the conversion during biomass gasification, they provide highly essential information on kinetic mechanisms. Moreover, they are highly useful in designing, evaluating, and optimizing gasifiers (Puig-Arnavat et al. 2010).

Usually, models are derived for reduction reactions and sub-models are formulated for pyrolysis, oxidation, and reduction zones for simplification.

Kinetic modeling has been done by the following authors:

Sl. no.	Kinetic model	Key points	Results and validation	Authors
1	One-dimensional unsteady state model of biomass gasification in a stratified downdraft gasifier for all zones. This model also includes mass and energy balance for	Bed porosity is neglected. Consideration of tar cracking to produce secondary gases. Also for char gasification unreacted shrinking core model is studied.	The prediction of model matches well with dynamic behavior of downdraft gasifier.	Blasi (2000)

(continued)

Sl. no.	Kinetic model	Key points	Results and validation	Authors
	both solid and gas phase separately.			
2	Steady-state kinetic model for predicting the product gas composition and temperature for reduction zone inside a downdraft biomass gasifier	Pyrolysis products get completely combusted in oxidation zone. Pyrolysis and tar cracking neglected. And Char reactivity factor (CRF) is considered.	The result of this model matches well with Chee et al. and experimental data. But concentration of CH4 is predicted more than experimental data.	Giltrap et al. (2003)
3	Steady-state model based on surface reaction mechanism for reduction zone assuming given residence time and reaction temperature			Wang and Kinoshita (1993)
4	Model to predict length of gasification zone, diameter of reactor and operating parameters.	Chen's model is divided into three parts. This model neglected sub zones, instead considered a single zone.	The prediction of this model results gas exit temperature high because of lumped system.	Chen (1987)
5	Kinetic sub-models for pyrolysis and gasification zones	There are two sub-models viz. flaming pyrolysis and gasification	The predicted results are ±5.8% of the experimental studies conducted by Jayah et al. and it is also concluded that reactor temperature and efficiency affects due to moisture content and heat loss.	Jayah et al. (2003)
6	A one-dimensional steady-state model for the gasification process in a fixed-bed downdraft biomass gasifier.	All zones are taken into consideration along with heat and mass transfer. Heterogeneous reactions, heat transfer due to radiation and bed void fraction throughout length of the gasifier are also studied.	Iteration method is used to solve model equations. The obtained results comply with experimental results.	Tinaut et al. (2008)
7	One-dimensional steady-state kinetic model to predict the performance of a downdraft biomass gasifier assuming	Five separate zones are studied. The Char reactivity factor of value 1000 is incorporated. Shrinkage of particle is taken into	The product composition can be determined based on fluid flow module, mass transfer drying model and equilibrium oxidation model. The gasifier	Sharma (2011)

(continued)

Sl. no.	Kinetic model	Key points	Results and validation	Authors
	porous packed bed of gasifier	account in pyrolysis zone.	model complies with experimental data.	
8	Numerical model of a solar downdraft gasifier of biomass char (biochar) with steam based on the systems kinetics	Simulation of biochar gasification is studied in this model. Pyrolysis and tar cracking is neglected.		Gordillo and Belghit (2011)
9	One dimensional (ODE) mathematical model developed for reduction zone of downdraft gasifier.	Phase separation is considered. Char is assumed as a pure carbon.	This model is modeled for reduction zone. The difference between model and experimental data reduced by adjusting parameters, then it shows the behavior of gasifier well.	Simone et al. (2013)
10	A mathematical model for gasification of wood pellets in an open-core downdraft gasifier, with dual air entry.	Various factors are taken into account viz. heat and mass transfer, drying, tar cracking, radiation through porous bed.	The ODE for first two stages solved by first order implicit Euler method and transport equations are solved by semi-implicit method. The model predicts temperature well with experimental literature.	Di Blasi and Branca (2013)
11	A model using an exponentially varying CRF in order to predict better simulation of the temperature profile in the reduction reaction zone.	This model inducts exponential varying CRF for better results.	The study shows good results of reduction zone by varying CRF compared with experimental work carried out by Jayah et.al.	Babu and Sheth (2006)
12	A model for a downdraft gasifier reduction zone using a finite rate of reaction following the chemical kinetics	Char combustion and methane formation neglected.	The water gas shift reaction incorporated at the end of the pyro-oxidation zone and induction of CRF for better results.	Sharma (2008b)

24.11.5 Computational Fluid Dynamics (CFD) Models

It is an important tool for modeling of fluidized bed gasifier and fixed bed downdraft gasifier. In this, set of equations is to be solved for mass, energy, momentum balance. For accurate results, hydrodynamics of reactor must be known. Commercial softwares like ANSYS, Fluent, CFD2000 help in solving equations constituting conservation of mass, momentum, and hydrodynamics. They are highly useful for optimizing the operating conditions for achieving the project specification.

However, anisotropic nature of biomass and lack of broad computational resources have resulted in very few CFD simulations for biomass gasification. Yet, a few researchers have presented simplified CFD models for downdraft biomass gasifiers (Patra and Sheth 2015). There are some CFD models have been discussed in the following table.

Sl. no.	Equilibrium model	Key points	Results and validation	Author
1	A hybrid 1-D + 2-D modeling and simulation of downdraft gasifier for pine wood	This model divided into sub zones. Secondary tar cracking particle size reduction is taken into consideration.	The prediction of syngas composition, gas temperature, particle size reduction and biomass temperature are in reasonable agreement with experimental data.	Rogel and Aguillon (2006)
2	2 D CFD model development of downdraft gasifier	The gas and solid phases solved using Euler-Euler multiphase approach. Turbulence model is used.	The simulation result is matched with experimental results.	Wu et al. (2013)

24.11.6 Artificial Neural Network (ANN)

This is a new simulation technique which consists of multilayer perceptron paradigm (MLP). Further MLP consists of three layers like an input layer, hidden layer, and output layer of neurons. The neurons in input layer consist of input pass to hidden layer and then to an output layer. ANN model can deal with gasification. The enough amount of experimental data is needed as a set of database as an input in ANN simulation. ANN models have salient features like they are non-mechanistic, non-analytical, and non-equilibrium models. Owing to these characteristic features, dynamic modeling aspects are difficult for incorporation into simulation environment. ANN models are used for signal processing, accuracy, optimization, and pattern recognition.

24.12 Present Challenges in Bio-Gasification and Path Forward

Bio-gasification is a promising technology; however, never it catches up to the expected growth potential, majorly due to lack of long-term vision and implementation of policies from Governments and other administrative bodies. In global perspective, there is not much awareness on bio-gasification among industries, consumers, and entrepreneurs. The non-uniformity of knowledge base, bio-literacy and scarcity of proper information puts more hurdles into it. Better coordination and information dissemination related to biomass management and its usage among the bio-energy chain group and sustainable sharing of infrastructure will act as some of the possible antidotes. Some unorthodox approaches on Government policies on pollution standards, licensing requirements and product testing regulations, etc. will surely revolutionize the bio-gasification market and both the matured partners and newcomers will work together in a harmonious environment for a sustainable developmental pathway. Very recently, 11 manufacturers and suppliers of biomass gasifiers are approved by the Ministry of New and Renewable Energy (MNRE) in India (Chojnacki et al. 2020). In Romania, integrated plasma gasification combined cycle plant was investigated thoroughly for its commercialization (Chojnacki et al. 2020). Based on actual data available from sugarcane industries from Brazil, projections for 2030 indicated a substantial cost reduction of 48% for an integrated gasification system coupled with a gas turbine and combined cycle, in order to be competitive with the conventional bagasse burning plants (Dantas et al. 2013). Agro-residue products of crops from South America can conveniently be utilized for electricity generation. This biomass can preferably be transported to other deficient regions with a limited access to agro-residues for energy applications as South America is presently self-sustained in electricity. Africa, despite of its major electrification potential, is unable to tap the global investors on bio-energy sector, majorly due to the sparse rural living conditions. Bio-gasification can be very attractive technology for countries with higher agricultural production like Brazil and also for the developing countries with an ever-increasing demand for electrification and other forms of energy such as those from the Indian subcontinent and other south-east Asian countries.

About 234 MT/year biomass is estimated to be available which can be used for bioenergy generation. However, agricultural biomass of India is majorly used for cooking and other heating utilities; in addition, it is also utilized for fodder for livestock. Scenarios are identical in most of the agriculture-based developing nations. Accordingly, due care to be exercised while planning and designing large-scale bio-gasifier operations; otherwise, gasification plants will run at lower efficiency owing to shortages of available biomass. Uniform availability of biomass feedstock is a prerequisite for smooth operation of any bio-gasifier; hence, proper mechanism of biomass storage during post-harvesting period is an integral component of biomass supply chain management. Generally, biomass is stored in well-ventilated shed and are covered with polythene while transporting to a nearby gasifier. Proper storing mechanism protects biomass from rain, storms, and insects like termites. Some aerobic microbes may cause some biological decomposition of biomass under aerobic condition and hence adversely affects biomass content.

24.13 Conclusions

Biogasification is an emerging sustainable technology with great potential. Better insights to process chemistry and design aspects of gasifiers along with its modeling and simulation aspect will help in the optimal gasifier design and its sustainable operation. Abundant availability of agro-based biomass materials from villages and voluminous amount of untreated solid wastes from urban locations force us to look for suitable alternatives and gasification of biomass acts as a boon which is a two-way green process helping us to treat the wastes in most effective manner to produce electricity and synthesis gas which will surely reduce the load on the ever-increasing energy demand for the future.

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Chapter 25

Open Burning Application to Municipal Solid Waste: Quantification Methods, Emission Inventories, and Uncertainty Delineations

Bhupendra Das

Abstract Open burning is a poorly characterized and under-estimated sources of air pollution, especially in the developing countries. Despite the emerging recognition of municipal solid waste (MSW) open burning, air pollution emission inventories accounts for it in low priority globally. This is because of the large uncertainty in emission inventory. The proposed book chapter highlights the quantification method of open burning of MSW and emission inventory. The detail method of a household survey, a transect walk survey, an experiment to measure the fraction of waste that is combustible, a survey on fraction of population burning waste outside their houses, and a survey of the fraction of MSW burned at dump sites are presented in this chapter. Other parameters include burning/oxidation efficiency, municipal populations, MSW generation rates, and emission factors. Factors that determine uncertainties of MSW open burning and emissions are also reflected.

25.1 Introduction

Developing countries spend 20% to 40% of its municipal revenues just in combating the solid waste management issues, employing 3–6 workers per 1000 members of the population. UNCHS reported that still more than a half of solid waste produced daily is not handled (Alam et al. 2008). Managing solid waste has been conferred a low priority mainly because of the plethora of demand for other public services in many municipalities (ADB 2013). Many cities and towns in the developing countries face severe environmental degradation as well as public health risks due to unmanaged domestic refuse (Alam et al. 2008). There has been an increase in the demand for solid waste management (SWM) in recent years with the expansion of municipalities together with the establishment of new industrial and commercial units. The limited resources, increasing population growth, rapid industrialization,

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intensive, and unplanned urbanization, changing consumption patterns with inadequate and poor waste management have inflated various environmental issues like air and water quality degradation, inadequate sanitation as well as spread of diseases in the municipalities, especially in the developing nations (Dangi 2009; Das et al. 2018; Pokhrel and Vivaraghavan 2005).

The solid waste production has increased in the similar pattern to that of increase in urban population. In Asia, only a few municipalities perform composting, and small percentage of their waste is burnt. Waste burning is done in open fields rather than treating them through proper incineration system (Das et al. 2018). Solid waste burning is also a major contributing factor for increase in emission besides industries. MSW open burning is a major contributor to impairing local and regional air quality, which releases traditional air pollutants (NO_x, SO_2, CO, NMVOC, NH_3), greenhouse gases (CO_2, CH_4), and particulate matter (PM_{10}, $PM_{2.5}$, BC, OC) (Lemieux et al. 2004; Shrestha 2018). Open burning of MSW is now increasingly being recognized in the cities of developing countries (Nagpure et al. 2015; Guttikunda et al. 2014; Hodzict et al. 2012; Wiedinmyer et al. 2014).

Open burning of municipal solid waste (MSW) is very common practice in the developing nations (Das et al. 2018). It has become a major source of PM_{10} and $PM_{2.5}$ emissions in the cities of developing world, causing human health impacts (Nagpure et al. 2015; Park et al. 2013). The solid waste management problem is also a major contribution to local/regional warming because when it burns, it emits different GHGs which have a high Global Warming Potential (GWP) to the environment. Secondly, dumping as well as landfill leakage also contributes in emission of different GHGs (Das et al. 2018). Despite the emerging recognition of MSW open burning, air pollution emission inventories in worldwide accounts for it in low priority. This is because of the large uncertainty in the estimates of the fraction of MSW being burned and the insufficiency of actual field observations of the phenomenon at urban scale (Nagpure et al. 2015). The main sources of uncertainty are the fractions of MSW that is recycled, landfilled, and dumped illegally on riverbanks and empty plots of land. This book chapter presents methods to estimate MSW open burning and air pollution through waste burning parameters and emission factors.

25.2 Systems for Solid Waste Management

The activities that are involved in the management of solid waste from the source of generation to ultimate disposal is known as solid waste management system. They include solid waste generation from various sources (e.g., household, commercial, institutional, industrial, construction, and demolition); waste handling, storage and processing (including waste recovery, reuse, recycle, composting); waste collection (e.g., tilt-frame, truck, tractor, pickup, rickshaw, wheel barrow, labor); transfer-station (locally available space to transfer waste from small collection vehicles to larger vehicles); waste processing and treatment (e.g., component separation for reuse and recycle; volume reduction); and final disposal and landfilling (Peavy et al. 1985).

25.3 Methods to Estimate MSW Open Burning

25.3.1 Municipal Solid Waste Generation

Household, commercial, institutional, and industrial waste generation together represent municipal solid waste (Eq. 25.1). The per capita waste generation (g/capita/day) of each household is calculated by dividing total waste produced by the number of people living in that household on that day (ADB 2013). Total amount of household waste generation can be calculated by multiplying per capita waste generation with total population residing in that area (Eq. 25.2). Likewise, having the census of commercial, institutional and industrial sectors and their average waste generation, total waste generation can be calculated.

$$\mathrm{MSW_{Total}} = \mathrm{SW_H} + \mathrm{SW_C} + \mathrm{SW_{ins}} + \mathrm{SW_{ind}} \tag{25.1}$$

$$\mathrm{SW_H} = \mathrm{W_G} \times \mathrm{Population} \tag{25.2}$$

Where,
$\mathrm{MSW_{Total}}$ = Total municipal solid waste generation
$\mathrm{SW_H}$ = Household solid waste generation
$\mathrm{SW_C}$ = Commercial solid waste generation
$\mathrm{SW_{ins}}$ = Institutional solid waste generation
$\mathrm{SW_{ind}}$ = Industrial solid waste generation
$\mathrm{W_G}$ = Per capita waste generation (g/capita/day)

25.3.2 Estimation of the Waste Combustible Fraction

To calculate waste combustible fraction (δ), field experiment is required. The experimental samples should be the mixture of household, commercial, institutional, and industrial waste. There are four basic steps during the experimental study (Figs. 25.1, 25.2, 25.3, 25.4, 25.5, and 25.6). First, the composition of experimental waste pile has to be studied. Second, initial mass of MSW should be measured using a digital weighing balance. Third, collected waste piles should be ignited and carefully monitored until the combustible material is turned to ash. Lastly, the burnt trash (ash) and the residual trash should be segregated carefully, and their masses have to be measured separately (Das et al. 2018).

The burnt mass of MSW is calculated by subtracting the mass of residual trash left after combustion from the total initial mass. The ratio of burnt mass of MSW to total

Fig. 25.1 Measurment of sample mass of trash

Fig. 25.2 Arrangement of sample of trash to be burnt

initial mass of MSW is referred to as the waste combustible fraction (Eq. 25.3) (IPCC 2006).

$$\delta = \frac{\text{Burnt Mass of Trash}}{\text{Total initial mass of Trash}} \tag{25.3}$$

This experimentally-derived parameter is used in the subsequent calculations of MSW open burning (Table 25.1).

Fig. 25.3 Sample of trash burning

Fig. 25.4 Sample of trash burning

25.3.3 *Estimation of the Fraction of Population Burning MSW*

A transect study is required to obtain fraction of population burning MSW (P_{frac}). During transect walk, a total number of trash piles and burning incidence along a study route should be identified and noted down. Simultaneously, household surveys should be conducted to know status of total population residing in trash piles burning route and whether they are participating to the waste collection services. Those piles

Fig. 25.5 Measurment of sample mass of trash and burning

Fig. 25.6 Segreggation of unburnt trash from burnt trash

which are not participating to waste collection services, the information on methods of waste management practices (e.g., burning, bury, and composting) should be obtained while interviewing with the households. The household perception information of waste burning has to be tabulated. P_{frac} is calculated through a ratio of population who is not participating at waste collection to population whose waste is collected for disposal or landfilling (IPCC 2006). There is a likely chances of population who is not participating at waste collection burn their waste and therefore can be taken into account for P_{frac} calculation. While considering it, some uncertainty might prevail. To validate the findings, P_{frac} has to be correlated with observation-based waste piles burning incidence during the transect walk (i.e., waste piles burning per household) (Das et al. 2018).

Table 25.1 MSW Open Burning Parameters

Parameters	Value	Country	Source
Population (pc)	Respective value of the location/nation	Respective country	–
MSWGR	Respective value of the location/nation	Respective country	–
δ	0.57	Nepal	Das et al. (2018)
P_{frac}	0.13	Nepal	Das et al. (2018)
λ	0	Nepal	Das et al. (2018)
η	0.4	Developing nation	Shrestha (2018)
ε	Respective value of the location/nation	Respective country	–

Fig. 25.7 Quadrate method to estimate fraction of MSW burning at disposal sites

25.3.4 *Estimation of the Fraction of MSW Burning at Disposal Sites*

There are few basic steps to estimate fraction of MSW burning at disposal sites (λ). Waste collection vehicles can be tracked from waste collection points to disposal point in the early morning or during the time of waste collection. After the vehicles are followed, visual inspection can be made thoroughly at the disposal sites to check whether there are any signs of MSW open burning practices. The quadrate method can be applied to estimate λ (Fig. 25.7). In case, there is no sign of MSW open burning practices in the disposal sites, λ can be estimated as zero (Das et al. 2018) (Table 25.1).

25.3.5 Emission Factors

The emission factors (EFs) can be obtained from various literatures (i.e., country's specific as well as global-based measurement) (Table 25.2). EF is expressed as grams of pollutants emitted per kilogram of trash burned. For estimating the mass of MSW open burning, EFs for CO, CO_2, NO_x, BC, $PM_{2.5}$, CH_4, OC, NH_3, and EC are reported in NAMASTE campaign in Nepal (Stockwell et al. 2016; Jayarathne et al. 2018). Likewise, EF of SO_2, a laboratory based measurement can be found at Akagi et al. (2011). EFs for PM_{10} and NMVOC are reported in USEPA (1995). The activity data (e.g., MSW generations) are the baseline for the emission estimation.

25.3.6 Calculation

To calculate MSW burned at source and disposal sites of the urban and sub-urban neighborhood, guidelines from different literatures can be used (e.g., Das et al. 2018; IPCC 2006; Shrestha et al. 2013; Shrestha 2018).

25.3.6.1 Solid Waste Open Burning at Source

$$M_s = \mathrm{Pc} \times \mathrm{MSWGR} \times \delta \times P_{\mathrm{frac}} \times \eta \times 365 \qquad (25.4)$$

Where,

Table 25.2 MSW open burning parameters

Pollutant	Emission factor (g/kg)
SO_2 (a)	0.67
NO_2 (b, d)	1.06
NO (b, d)	1.52
CO (b, d)	84.7
NMVOC (c)	15
PM_{10} (c)	8
CH_4 (b, d)	3.97
BC (b, d)	3.3
OC (d)	5.67
CO_2 (b, d)	1602
$PM_{2.5}$ (d)	7.37
NH_3 (b, d)	0.76
EC (d)	0.19

Source: (a) avg. of Akagi et al. (2011), USEPA (1995), Yokelson et al. (2013); (b) Stockwell et al. (2016); (c) USEPA (1995); (d) Jayarathne et al. (2018)

M_s is the amount of open-burned MSW (kg/year); Pc is population (capita); MSWGR is per capita MSW generation rate (kg/capita/day); δ is fraction of combustible MSW; P_{frac} is fraction of population burning waste; and η is burning/oxidation efficiency (fraction), which is 0.4 (compiled by Shrestha 2018).

25.3.6.2 Solid Waste Open Burning at Disposal Site

$$M_s = \text{Pc} \times \text{MSWGR} \times \varepsilon \times \lambda \times \delta \times \eta \times 365 \tag{25.5}$$

Where,

M_s is amount of open-burned MSW (kg/yr); Pc is population (capita); MSWGR is per capita MSW generation rate (kg/capita/day); ε is MSW collection efficiency (fraction that is disposed/land filled); λ is fraction of the waste that is actually burned relative to the total amount of waste disposed at a disposal site; δ is fraction of combustible MSW, and η is burning/oxidation efficiency (fraction).

25.3.6.3 Estimation of Emissions from MSW Open Burning

The total emission from MSW open burning can be estimated by multiplying activity data with emission factors (Eq. 25.6) (Das et al. 2018; IPCC 2006; Shrestha et al. 2013; Shrestha 2018; Defra 2009).

$$\text{Em}_i = M_s \times \text{EF}_i \tag{25.6}$$

Where, Em_i is emission of pollutant i; EF_i is emission factor of pollutant i; M_s is amount of MSW burned.

25.4 Factors that Determines Uncertainties of MSW Open Burning

There are various factors that determine uncertainties of MSW Open Burning. First factor is waste composition. The range of waste composition (%) such as food waste, paper, cardboard, plastics, textiles, rubber, leather, glass, metal, etc., determine uncertainties of MSW Open Burning. The ranges vary region or country wise. Second factor is chemical composition, such as moisture content, volatile matter, fixed carbon, hydrogen, oxygen, nitrogen, and sulfur. Third, particle size can also affect MSW open burning. Lastly, climatic condition (e.g., rain, wind, relative humidity) has profound impact on MSW open burning estimation too (Das et al.

2018). While calculation, all above factors should be well considered to minimize uncertainties.

25.5 Conclusion

MSW open burning and air pollution can be estimated through waste burning parameters like population (capita), solid waste generation rate, waste combustible fraction, fraction of population burning MSW, fraction of MSW burned at dumping sites, waste collection efficiency, burning/oxidation efficiency, and emission factors. These parameters are crucial for emission inventory work in the sector of solid waste management. Various factors that determine uncertainties of MSW open burning estimation are waste composition, chemical composition, particle size and climatic condition, which have to be considered during calculation.

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Chapter 26

Overview of Torrefaction Technologies: A Path Getaway for Waste-to-Energy

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Abstract The ever-increasing demand for cleaner energy to meet the rising demands of the technologically advancing population coupled with the serious impact of climate change has opened the door for research on different renewable energy sources to be researched and commercialised. Most of the power used for industrial and household use has been generated using mostly coal, water and nuclear over the years. However, all these energy sources are finite and beside water, they cause pollution mostly leading to greenhouse gases (GHG) emissions that are accelerating global warming. To reduce our reliance on coal as an energy source, biomass can be used alongside coal or as a direct substitute of coal. Torrefaction helps us to achieve this aim and the torrefied biomass has the net effect of reducing GHG emissions. Even without any significant upgrades to existing coal-fired power stations, torrefied biomass has the distinct advantage of working in those power generation boilers as well. Nowadays, large-scale biomass-based boilers with a rating of over 500 MWth are being operated to produce power.

Another advantage of biomass is that it does not usually contain a lot of sulphur and chlorine making it attractive for use in boilers as this reduces corrosion effects from such deposits. Torrefaction improves biomass properties by increasing the C/H and C/O ratios through removing permanent gases (CO_2, CO, etc.) and volatile liquids (H_2O, organic compounds, etc). In addition, torrefaction can be used to improve municipal solid waste, sewage sludge, food waste, agricultural waste, livestock waste, forestry residues and other waste generated thereby improving the recycling rate and promoting a circular economy.

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26.1 Introduction

The use of renewable sources of energy like plant biomass for energy generation has gained momentum over the past decades. This is because of the adverse effects such as global warming that are caused by non-renewable sources like coal (Abdeljaoued et al. 2020; Aravind et al. 2020). Using renewable sources of energy is in line with the target for circular economy which aims to replace non-renewable energy sources with renewable sources and it is also in line with some of the United Nations' Sustainable Development Goals (Arodudu et al. 2020). In addition, some of the non-renewable sources of energy are close to being depleted as they have been in use since the first industrial revolution (Arodudu et al. 2020).

Biomass is an organic feedstock that comes from plant material either directly or indirectly through photosynthesis (Aravind et al. 2020). Energy from biomass is now the fourth largest primary energy resource showing how important it is becoming (Arodudu et al. 2020; Enaime et al. 2020). Waste can also be used in the process to achieve the same end in addition to using plant biomass and this is a bonus since it allows us to generate energy while processing waste that was supposed to be otherwise burned or landfilled where it may have resulted in air, water and soil pollution (Gabhane et al. 2020; Niinipuu et al. 2020). Waste and biomass sources that are mostly used to produce energy are lignocellulosic biomass, non-lignocellulosic biomass, agricultural waste (crop residues), organic wastes (food waste), energy crops, sewage sludges and municipal green wastes or municipal solid waste (MSW) amongst other sources (Abdeljaoued et al. 2020; Aravind et al. 2020).

Renewable sources of energy can be used to produce solid, liquid, and gaseous products as highlighted in literature through torrefaction/mild pyrolysis, pyrolysis, and gasification, respectively (Bach et al. 2019; Direktor et al. 2020a; Olugbade and Ojo 2020). In this chapter focus will be on torrefaction only, the other technologies can be found in other literatures dedicated to them.

26.2 Principle of Torrefaction

Torrefaction is a thermochemical process that usually occurs in a non-oxidative environment within a temperature range of 200 and 300 °C (Bach et al. 2019; Cao et al. 2020). Torrefaction allows sustainable processing of raw biomass into heat and power, thereby increasing its economic value for our benefit (Brachi et al. 2017).

There are three different types of torrefaction processes, namely dry torrefaction, wet torrefaction and ionic-liquid-assisted torrefaction, Fig. 26.1.

Dry torrefaction is the most common method used, followed by wet torrefaction and then ionic-liquid-assisted torrefaction. Dry and wet torrefaction can be used to improve the properties of lignocellulosic biomasses and even waste. Dry and wet torrefaction results in the degradation of mostly hemicellulose and to some extent

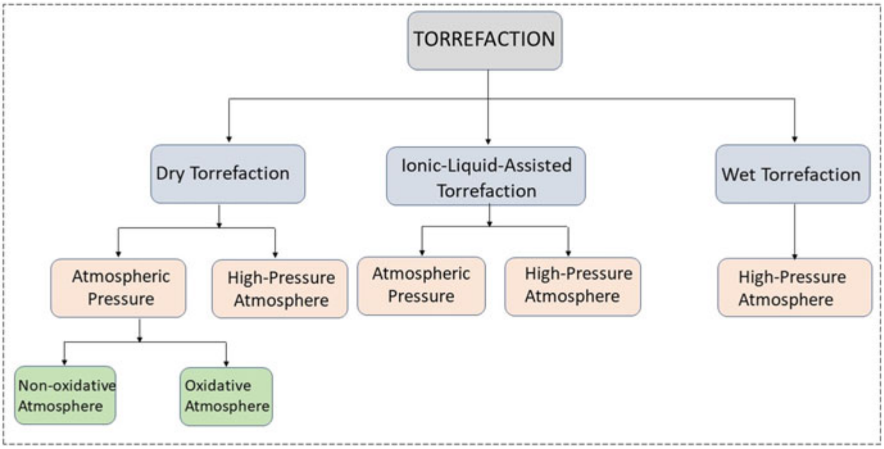


Fig. 26.1 Torrefaction classification. Adapted from Chang (2020), Olugbade and Ojo (2020)

cellulose into their monomers and oligomers (Chang 2020). Once these two degrade, it leads to an increase in the lignin content of lignocellulosic biomasses. Torrefaction leads to decreased bulk density and pelletisation of torrefied biomass becomes very possible. However, pelletisation may require binders because of the degradation of bonding forces between the torrefied biomass particles as well as the loss of natural lignin-binding features after torrefaction (Grycova et al. 2020).

26.2.1 Dry Torrefaction

It is the conventional torrefaction process mostly used (Fig. 26.2). Dry torrefaction is generally characterised by low heating rates (usually <50 °C/min) and higher residence times (usually ranging from 30 to 120 min) depending on the biomass available (Brachi et al. 2017; Gent et al. 2017). Dry torrefaction process takes in raw biomass that has either been dried naturally or dried using a dryer and convert it into biochar (or sometimes called bio-coal) which has properties similar to those of non-renewable coal (Abdeljaoued et al. 2020).

Dry torrefaction is more suited to biomass with lower moisture content like some agricultural waste and lignocellulosic biomass. As the temperature increases, it leads to a decrease in oxygen content when volatile compounds are lost thereby reducing the O/C ratio. Also, from the same volatile compounds being lost, they also contain hydrogen and this leads to a decrease in the H/C ratio as well. The raw biomass usually can be green or in some instances light-brown in colour but after torrefaction it becomes dark-brown in colour at temperatures around 270 °C and sometimes black like coal at temperatures of 300 °C (Campbell et al. 2020). The biochar is devoid of volatile compounds and permanent gases that are driven off during first

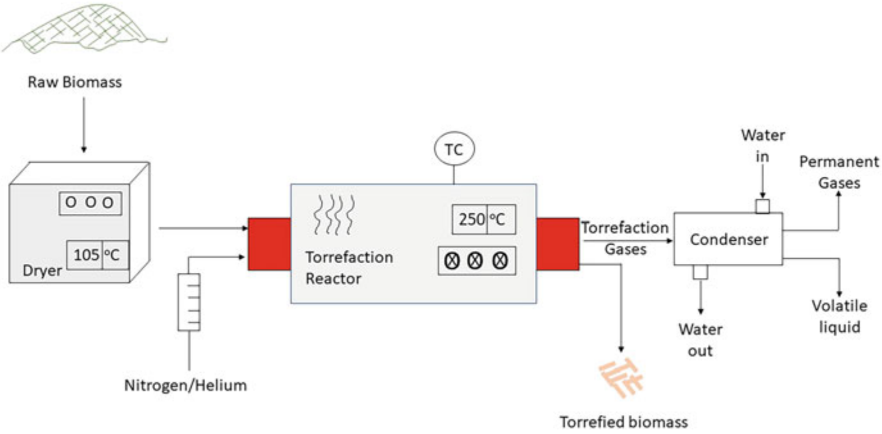


Fig. 26.2 Dry torrefaction process

drying (mainly H_2O) and then torrefaction (mainly H_2O, CO_2, CO, acetic acid and other organic and inorganic compounds) (Olugbade and Ojo 2020).

Irreversible chemical reaction that occurs lead to the formation of permanent gases, volatile compounds and the solid biochar that is left behind. The volatile compounds can be converted into liquid form by cooling them in a condenser leaving the permanent gases that can be vented off or driven to secondary processing plant depending on their concentration (Aravind et al. 2020; Braghiroli et al. 2020). Alternatively, to improve on heat usage, the gases produced can be sent to a burner where energy can be generated from the combustion of some of the gases like CO, $CH_{4,}$ and so on. The heat is recovered and recycled back into the process for drying the biomass (Aravind et al. 2020; Braghiroli et al. 2020). The non-oxidative atmosphere provided by nitrogen prevents side reactions or secondary reactions from volatiles produced during torrefaction, i.e. during solid thermal degradation of the biomass (Gent et al. 2017).

During dry torrefaction of lignocellulosic biomass at temperatures of 270–300 °C, hemicellulose fully decomposes while cellulose and lignin partially decomposes, and in the process alter the morphology of the biomass (de Abreu Neto et al. 2020). For lignocellulosic biomass, the following decomposition reactions occurs: (a) devolatilisation and carbonisation of hemicelluloses, followed by (b) depolymerisation and devolatilisation of lignin and cellulose (Sri Shalini et al. 2020). As torrefaction is progressing, properties of lignocellulosic biomass like cell wall density, mechanical strength (bending strength and elasticity), volume (which decreases) and chemical composition are all modified irreversibly mainly from the action of temperature (de Abreu Neto et al. 2020). This is more pronounced at higher temperatures ($\geq$250 °C) as these temperatures affect most lignocellulosic biomass properties negatively (Basu 2018a).

It sometimes results in slagging and fouling together with corrosion in industrial plants. In addition, depending on the type of biomass it can lead to high ash content

(Olugbade and Ojo 2020). The torrefied biomass which results is hydrophobic in nature (Gent et al. 2017). The torrefied biomass also has improved energy content after torrefaction. However, torrefied biomass from this process will have more alkali metals than in wet torrefaction (Olugbade and Ojo 2020).

26.2.2 *Wet Torrefaction*

Wet torrefaction is also known as hydrothermal carbonisation (HTC) and it is an exothermic process (Nunes et al. 2018). The principle of operation is that wet biomass is inserted in water and then heated in a pressurised reactor/vessel (Enaime et al. 2020; Olugbade and Ojo 2020). The water in use under these conditions will be subcritical as it is still below its critical point of 374 °C (Nunes et al. 2018; Niinipuu et al. 2020). Wet torrefaction is more suited to biomass with high moisture content like animal manure, sewage sludge and municipal waste, i.e. there is no need for a drying stage under wet torrefaction and this eliminates the energy needed for that stage, Fig. 26.3 (Enaime et al. 2020).

The torrefied biomass which results is called hydrochar and it is also hydrophobic in nature as in dry torrefaction (Braghiroli et al. 2020). The torrefied biomass also has improved energy content after torrefaction. The torrefied biomass from this process will have less alkali metals than in dry torrefaction (Basu 2018b; Islam et al. 2019). HTC occurs through hydrolysis which is caused mainly because of the presence of compressed water, forming smaller molecules; followed by dehydration reactions when eliminating volatile substances and decarboxylation; and lastly undergoing polymerisation; aromatization and condensation or polymerisation reactions (Chang 2020; MacDermid-Watts et al. 2021; Mendecka et al. 2020; Sri Shalini et al. 2020).

Just as in dry torrefaction, the O/C and H/C ratios decrease with an increase in temperature through the loss of volatile compounds (Braghiroli et al. 2020; Nunes et al. 2018). The residence time for wet torrefaction is longer than for dry torrefaction

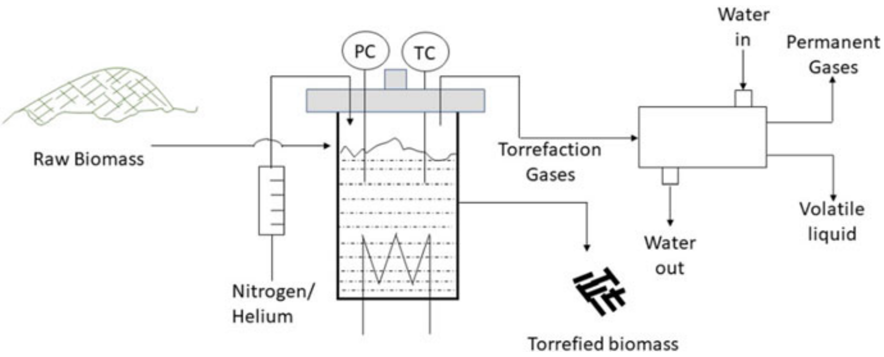


Fig. 26.3 Wet torrefaction process. Adapted from Enaime et al. (2020); Mendecka et al. (2020)

and this leads to the conclusion that the reactions happening in wet torrefaction are slower than those happening in dry torrefaction (Chang 2020).

Temperatures for HTC are in the range of 180–300 °C, but beyond 300 °C, the process produces mostly liquid or gaseous products, and it is then referred to as hydrothermal liquefaction (HTL) or hydrothermal gasification (HTG), respectively (MacDermid-Watts et al. 2021; Moyo et al. 2020).

Another kind of HTC process termed hydrothermal co-carbonisation has been developed where different feedstocks are mixed to make biochar with required or targeted properties (Moyo et al. 2020). This can be useful in making hydrochar for targeted applications.

26.2.3 *Ionic-Liquid-Assisted Torrefaction*

Ionic-liquid-assisted torrefaction or Ionothermal carbonisation (ITC) is applied to lignocellulosic biomass where its components, hemicellulose, cellulose and lignin are pre-treated with ionic liquid (ionic water) instead of pure water as in HTC, Fig. 26.4 (MacDermid-Watts et al. 2021). The ionic liquid assists in converting these complex polysaccharides into smaller units making them easier to process further (Olugbade and Ojo 2020). Ionic water has ionic salts at liquid state and these acts on lignocellulosic components when added. The ionic liquid allows the process to occur at reduced operating pressure or even operating at ambient pressures (MacDermid-Watts et al. 2021). This torrefaction method is not commonly used as much as dry torrefaction and to some extent wet torrefaction as the cost of the ionic liquid is prohibitive and this has slowed its progress to commercialisation.

Comparisons of the three different torrefaction processes are shown in Table 26.1.

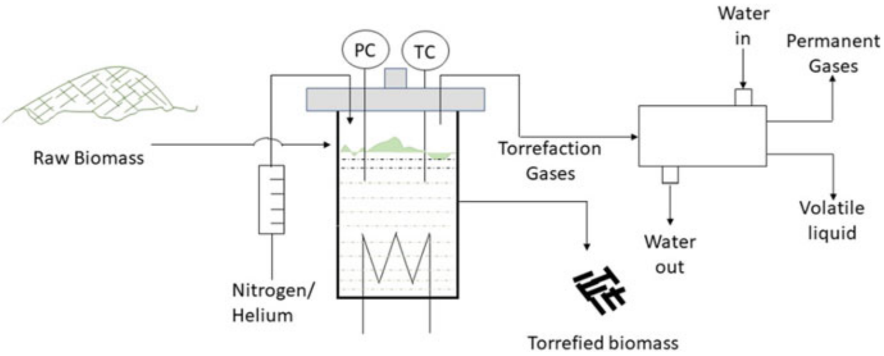


Fig. 26.4 Ionic-liquid-assisted torrefaction process. Adapted from MacDermid-Watts et al. (2021)

Table 26.1 Comparisons of the three torrefaction processes (Basu 2018a; Braghiroli et al. 2020; Bushra and Remya 2020; Campbell et al. 2020; Chang 2020; Gabhane et al. 2020; Hagner et al. 2020; Heidari et al. 2020; MacDermid-Watts et al. 2021; Mendecka et al. 2020; Moyo et al. 2020; Ndukwu and Horsfall 2020; Negi et al. 2020; Nunes et al. 2018; Olugbade and Ojo 2020)

	Dry torrefaction	Wet torrefaction (hydrothermal carbonisation)	Ionic-liquid-assisted torrefaction
Type of biomass required	Low moisture content biomass	High moisture content biomass	High moisture content biomass
Pre-treatment step	Drying of biomass	No pre-treatment	Using ionic salts to convert lignocellulosic components
Drying stage	Drying a prerequisite	No drying as biomass is inserted in water	No drying as ionic salts are added to lignocellulosic biomass
Temperature range	200–300 °C	180–300 °C	180–300 °C
Pressure	1 atm but high pressure has been trialled as well.	1–60 atm	1–60 atm
Inert conditions	Use of inert gases to provide inert conditions	No use of inert gases during process but due to pressurised conditions, oxygen content runs out at some point	No use of inert gases during process
Residence time	5 min–4 h	5 min–24 h	5 min–24 h
Heating rate	5–50 °C/min	2–10 °C/min	2–10 °C/min
Solid yield	$\geq 75\%$	45–90%	45–90%
O/C and H/C	Reduced with an increase in temperature	Reduced with an increase in temperature	Reduced with an increase in temperature
Slagging and fouling	Has potential problems	Not significant	Has potential problems due to the ionic salts
Corrosion	Has potential due to moisture eliminated	Has potential due to wet conditions prevailing	Has potential due to ionic salts used
Product	Biochar/bio-coal	Hydrochar	Hydrochar
Torrefied biomass	Hydrophobic in nature	Hydrophobic in nature	Hydrophobic in nature
Higher heating value (HHV) of torrefied biomass	Lower energy content than for wet torrefaction	Highest increased energy content	Higher as in wet torrefaction
Capital costs	High capital costs	Higher capital costs due to pressurisation. High design costs	Highest capital costs due to pressurisation and ionic water. High design costs
Operating costs	High operating costs	Higher operating costs	Highest operating costs

26.3 Easy of Size Reduction Before and After Torrefaction

Before torrefaction, some biomasses may need to be reduced in their size through crushing and/or grinding/milling (Alves et al. 2020). This step is dependent on the type of biomass and the desired particle size distribution and this normally directs the researcher to the size reduction equipment that is suitable (Amer et al. 2020; Direktor et al. 2020b). Usually, due to high moisture content, it is difficult to crush or grind the biomass as it will be sticking to the walls of the equipment. That is usually the purpose of the initial drying stage in dry torrefaction as well as the torrefaction process itself as they remove the unbound moisture (through initial drying) and bound moisture (during torrefaction) to leave biomass with minimal moisture, and easy to crush and grind (Fodah et al. 2021; Sh et al. 2020). Size reduction only has an effect on dry torrefaction as size reduction and sieving is not necessary for wet torrefaction or ionic-liquid-assisted torrefaction. Also, size reduction is key when torrefied biomass is applied in energy generation, but it depends on the type of reactor which is being used in the energy production plant (Grycova et al. 2020; Kizuka et al. 2021).

26.4 Characterisation Before, During and After Torrefaction

The raw materials and products need to undergo different characterisation methods which are suited to them and the properties that are required. The solid reactants and products together with volatile liquids and permanent gases, which are the raw and torrefied biomasses are analysed by different equipment/techniques. The characterisation can be sub-divided into physical (morphological) characterisation, chemical characterisation, thermal degradation and fuel characterisation (Pathomrotsakun et al. 2020). The procedures used by the equipment/techniques conform to different American Society for Testing Materials (ASTM) standards based on the methods on analysis (Alves et al. 2020; Mamvura and Danha 2020).

26.4.1 Physical (Morphological) Characterisation

- Scanning electron microscope (SEM) shows the surface topography and elemental distribution, i.e. changes on the biomass surface structure or microstructure (Gabhane et al. 2020; Mokrzycki et al. 2019; Nunes et al. 2018).
- Brunauer–Emmett–Teller (BET) test is used to determine the surface area and the bore volume of the raw and torrefied biomass (Grycova et al. 2020; Nunes et al. 2018; Niinipuu et al. 2020).

- Mercury Porosimetry is used to determine the pore volume, porosity and bulk density (Mokrzycki et al. 2019). Alternatively, the bulk density of the raw and torrefied biomass can be determined by using a graduated cylinder and electronic scale (Grycova et al. 2020).

26.4.2 Chemical Characterisation

- Moisture analyser which is used to determine biomass moisture content (MC) (Brachi et al. 2017).
- Elemental analyser (CHN, CHNS or CHN/S analysers) is used to determine elemental composition i.e., ultimate analysis which is carbon (%C), hydrogen (%H), nitrogen (%N), sulphur (%S) and oxygen (%O), %O is determined by difference (Cao et al. 2020; Grycova et al. 2020; Guimarães and Tannous 2020; Islam et al. 2019; Kizuka et al. 2021). The ultimate/element analysis can be represented on a van Krevelen diagram that is a plot of H/C versus O/C (Fig. 26.5).

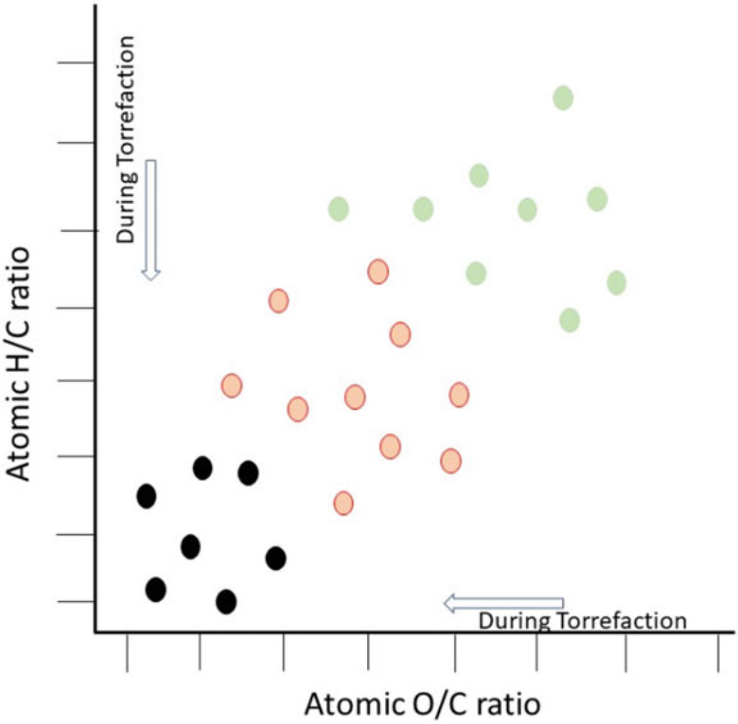


Fig. 26.5 An example of a van Krevelen diagram for biomass. Adapted from Brachi et al. (2017); Cao et al. (2020); Grycova et al. (2020); Nunes et al. (2018)

- Inductively coupled plasma optical/atomic emission spectrometry (ICP-OES) analyser is used to determine the sulphur content (%S) if not determined above (Tafur-Marinos et al. 2016).
- Fourier transform infrared (FTIR) spectroscopy is used to determine the structural and chemical changes of biomass before, during and after torrefaction i.e. the surface chemical functional groups (or chemistry) of the biochar/hydrochar (Cao et al. 2020; Mokrzycki et al. 2019; Pathomrotsakun et al. 2020).
- X-ray powder diffraction (XRD) is used to determine the structural changes of the biochar/hydrochar so that we can identify the biochar/hydrochar based on its diffraction patterns (Heidari et al. 2020).
- X-ray photoelectron spectroscopy (XPS) is used to determine the surface composition of the biochar after torrefaction, i.e. the metal oxide composition of the biochar/hydrochar (Niinipuu et al. 2020).
- Total Organic Carbon (TOC) metre is used to determine the TOC of the hydrochar from HTC and ITC (Heidari et al. 2020).
- Energy dispersive X-ray spectroscopy (EDX/EDS) is used to determine the mineralogical analysis of the biochar, i.e. the quantitative elemental composition (Nyakuma et al. 2019).
- Gas chromatography (GC) is used to determine volatile liquids and torrefaction gas compositions (Hagner et al. 2020).
- Gas chromatography coupled to a flame ionisation detector (FID) is used to determine the volatile liquids faction composition (Mulyana et al. 2019).
- Gas chromatography coupled to mass spectrometry (GC-MS) is used to determine volatile liquids and torrefaction gas composition and identification of the different components (Hagner et al. 2020; Nunes et al. 2018).
- Moisture titrator is used to determine the moisture content of the volatile liquids (Tavčar et al. 2012).

26.4.3 Thermal Degradation

- Thermogravimetric analysis (TGA) is used to determine the thermal degradation and proximate analysis on a dry basis as MC (%MC), ash (%Ash), volatile matter (%VM) and fixed carbon (%FC), %FC is found by difference (Heidari et al. 2020; Kizuka et al. 2021). TGA is also used to determine kinetic data: apparent activation energy (E_a), the frequency factor (A) and the reaction model [$f(\alpha)$] as it can give kinetic curves which show the conversion rate as a function of time or temperature (Brachi et al. 2017; Cao et al. 2020; Grycova et al. 2020; Nyakuma et al. 2019).

The proximate and ultimate analysis once determined, can be used to determine the heating value of raw and torrefied biomass (HHV and LHV) by using experimentally determined correlations that can be found in different literature (Guimarães and Tannous 2020; Kizuka et al. 2021; Xuanzuo et al. 2020).

26.4.4 Fuel Characterisation

- Adiabatic bomb calorimetre is used to determine biomass heating values mostly higher heating value (HHV). Lower heating value (LHV) can be determined by removing the heat of condensation/vaporisation of water (Brachi et al. 2017; Guimarães and Tannous 2020; Xuanzuo et al. 2020).
- Particle size analyser is used to determine the particle size distribution of the biomass especially after crushing and grinding tests. This can be done for biomass blends or blends between biomass and coal before co-firing (Sh et al. 2020).

26.5 Different Measures of Torrefaction Efficiency

The efficiency of the torrefaction process has to be measured to determine the effectiveness of the process. There are different techniques that are used to measure the efficiency of the torrefaction process. Some of these measures are listed below from these literatures (Cao et al. 2020; Guimarães and Tannous 2020; Maia et al. 2020; Mokrzycki et al. 2019; Pathomrotsakun et al. 2020).

(a) Mass yield of biomass ($\mathrm{MY}_{\mathrm{biomass}}$) which measures how much biomass mass is left after torrefaction process:

$$\mathrm{MY}_{\mathrm{biomass}}\,(\%) = \frac{m_{\mathrm{torrefided\ biomass}}}{m_{\mathrm{raw\ biomass}}} \times 100\% \tag{26.1}$$

The value of the mass yield of biomass is from 0 to 1 (or 100%).

(b) Mass yield of volatiles ($\mathrm{MY}_{\mathrm{volatiles}}$) which measures how much torrefaction volatiles are generated by the torrefaction process:

$$\mathrm{MY}_{\mathrm{volatiles}}\,(\%) = \frac{m_{\mathrm{condensable\ liquid}}}{m_{\mathrm{raw\ biomass}}} \times 100\% \tag{26.2}$$

The value of the mass yield of torrefaction volatiles is from 0 to 1 (or 100%).

(c) Mass yield of torrefaction gases ($\mathrm{MY}_{\mathrm{gases}}$) which measures how much torrefaction permanent gases are produced by the torrefaction process and are separated from volatiles in the condenser:

$$\mathrm{MY}_{\mathrm{gases}}\,(\%) = \frac{m_{\mathrm{gases}}}{m_{\mathrm{raw\ biomass}}} \times 100\% \tag{26.3}$$

The value of the mass yield of torrefaction gases is from 0 to 1 (or 100%).

(d) Energy densification ($ED_{biomass}$) which measures how much energy of the torrefied biomass per that of raw biomass is left:

$$ED_{biomass} = \frac{HHV_{torrefided\ biomass}}{HHV_{raw\ biomass}} \tag{26.4}$$

The value of the energy densification of biomass is from 0 to 1 (or 100%). However, this can be above 100% as HHV for torrefied biomass increases with loss of volatiles to be greater than the HHV of the original biomass.

(e) Energy densification ($ED_{volatiles}$) which measures how much energy of the torrefaction volatiles per that of raw biomass is gained:

$$ED_{volatiles} = \frac{HHV_{volatiles}}{HHV_{raw\ biomass}} \tag{26.5}$$

The value of the energy densification of volatiles is from 0 to 1 (or 100%).

(f) Energy densification (E_{bgases}) which measures how much energy of the torrefaction gases per that of raw biomass is gained:

$$ED_{gases} = \frac{HHV_{torrefaction\ gases}}{HHV_{raw\ biomass}} \tag{26.6}$$

The value of the energy densification of biomass is from 0 to 1 (or 100%).

(g) Energy yield of biomass ($EY_{biomass}$):

$$EY_{biomass} = MY_{biomass}\left[\frac{HHV_{torrefided\ biomass}}{HHV_{raw\ biomass}}\right] \tag{26.7}$$

The value of the energy yield of biomass is from 0 to 1 (100%).

These different measures can be used but the most important ones are mostly those linked to biomass as torrefaction process is mostly undertaken to produce a solid product, i.e. torrefied biomass (Bach et al. 2019).

26.6 Torrefaction Reactors

The efficiency of the torrefaction process is mostly dependent on the type of reactor used. This is critical especially when moving from laboratory-scale reactors to commercialised processes. There are different reactors that can be used to achieve torrefaction and these can be grouped using different category systems (Fig. 26.6). Torrefaction reactors can either be indirectly heated or directly heated depending on

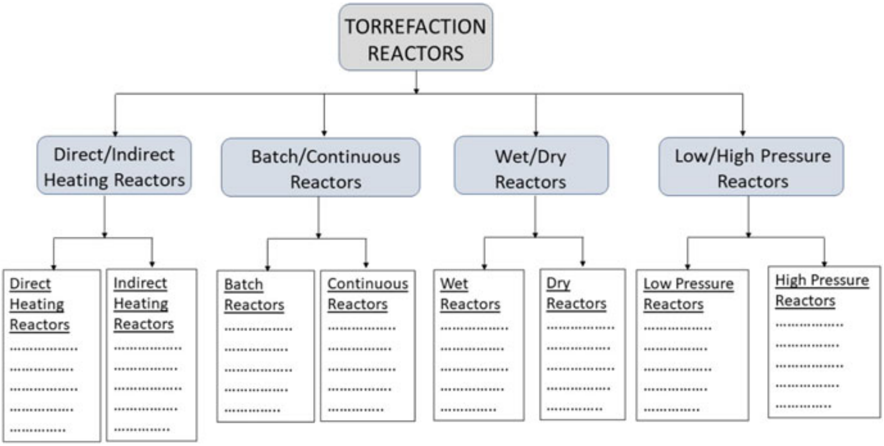


Fig. 26.6 Torrefaction reactors classification. Adapted from (Kuzmina et al. (2016)

the setup. For indirect heating, the heat is transferred via the reactor wall into the reaction zone (Direktor et al. 2020b). This relies heavy on heat transfer mechanism and heat losses to the environment (Basu 2018a). Direct heating is when gases are first heated and then send to the reactor to heat the biomass in the reactor. This process is more efficient in heating than indirect heating and gives a more uniform product (Direktor et al. 2020a).

26.6.1 Directly Heated Reactors

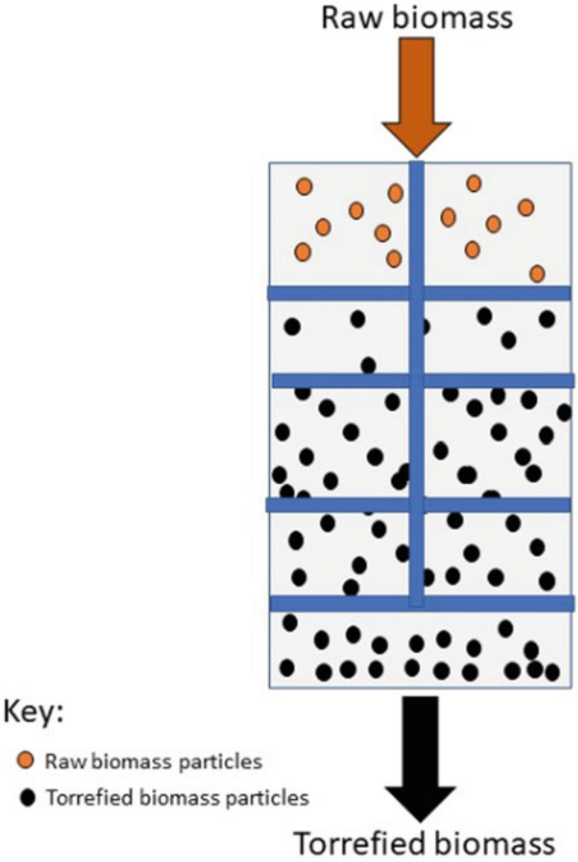
There are many directly heated reactors such as fluidised bed reactors, moving bed reactors, oscillating reactors, multiple hearth reactors and hydrothermal reactors. These will be briefly explained and examples of such reactors in operation will be given.

26.6.1.1 Compact Moving Bed Reactor

Compact moving bed reactors are the simplest and easiest reactors and they are used more frequently. In these reactors, as the name suggests, biomass moves by gravity towards the ascending flow of the hot heat-transfer medium, Fig. 26.7 (Adeleke et al. 2021).

This introduces a disadvantage of high hydraulic resistance as well as non-uniform heating of the biomass if the reactors are of large volume affecting the reactor efficiency (Adeleke et al. 2021). Some moving bed reactors being used are 10,000 tons per year capacity for Andritz/ECN in Stenderup, (DK); 20,000 tons per year for Grupo Lantec in Urnieta, (SP) and 20,000 tons per year LMK Energy in Mazingarbe, France (Negi et al. 2020).

Fig. 26.7 Moving bed reactor. Adapted from Negi et al. (2020)



26.6.1.2 Fluidised Bed Reactor

In fluidised bed reactors, biomass particles of certain size range are suspended using the action of a fluidising gas (Fig. 26.8). There is uniform heating in this setup significantly intensifying the heat-exchange process (Direktor et al. 2020b).

Some of the fluidised bed reactors in existence are 60,000 tons per year capacity for Topell Energy in Duiven, (NL) and unknown capacity for Bio Energy Development and Production in Nova Scotia, Canada (Negi et al. 2020).

26.6.1.3 Oscillating Bed Reactor

Oscillating bed reactors have a symmetrical oscillation that is superimposed to the net flow of reactants and products through the reactor. This improves mixing and maintains excellent heat transfer (Bianchi et al. 2020). An oscillating bed reactor in use is the 30,000 tons per year for Clean Electricity Generation in Derby, UK (Negi et al. 2020).

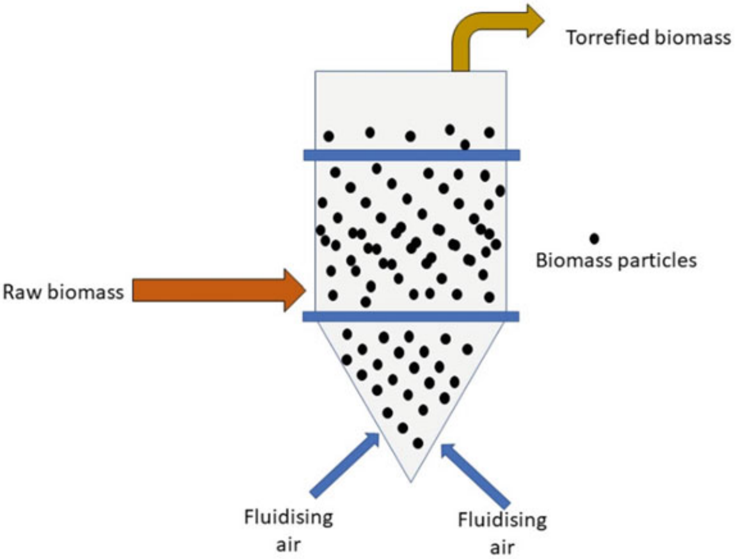


Fig. 26.8 Fluidised bed reactor. Adapted from Ndukwu and Horsfall (2020)

26.6.1.4 Multiple Hearth Reactor

In this type of reactor, biomass is fed at the top of the reactor and it moves down through the different hearths. A centralised shaft drives the arms at each hearth either clockwise or counterclockwise (Adeleke et al. 2021). The flue gas will also flow downhill as the biomass. Steam injections result in very good temperature control and a high product quality with minimal energy loss, giving the process a relatively high efficiency (Ndukwu and Horsfall 2020). Figure 26.9 shows a multiple hearth reactor.

Some multiple hearth reactors being used are an undefined capacity for CMI NESA in Seraing, (BE); 11,000 tons per year for Integro Earth Fuels, LLC in Greenville, USA and pilot and laboratory scale reactors for Terra Green Energy and CEA in McKean County, USA and Paris, France, respectively (Negi et al. 2020).

26.6.1.5 Hydrothermal Reactor

Hydrothermal reactors are used for wet torrefaction, but they are just on laboratory scale only. There has not been any commercialisation or pilot-scale plants built as the mechanism for hydrothermal reactors are still unclear. This is still the stumbling block for reaching pilot-scale and/or commercialisation stage (Heidari et al. 2020). In addition, the development of a continuous feeding system of biomass/water

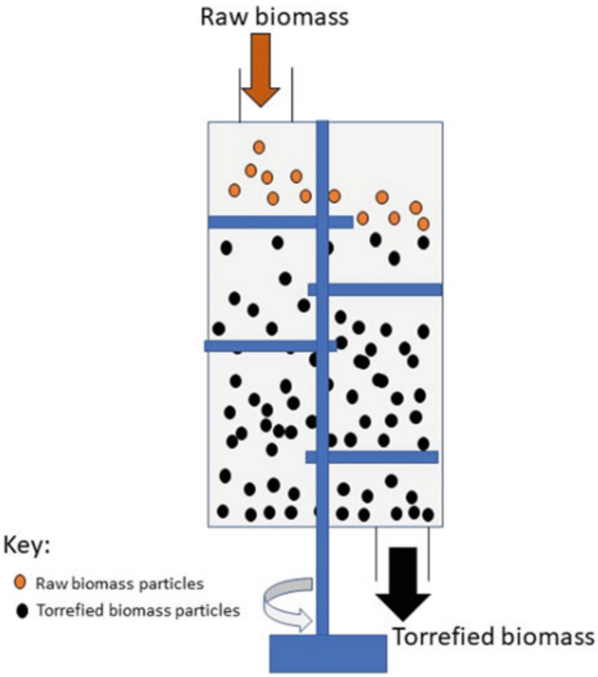


Fig. 26.9 Multiple hearth reactor. Adapted from Ndukwu and Horsfall (2020)

mixture against the high pressures used is another reason for slow commercialisation. However, if the hot process steam/water can be recovered then this can be used to pre-treat the incoming biomass/water mixture thereby making the process economical (Heidari et al. 2020).

26.6.2 Indirectly Hearted Reactors

Indirectly heated reactors come in different forms. Some of these reactors are discussed below.

26.6.2.1 Fixed Bed Reactor

Fixed bed reactor is a reactor with a fixed bed in which biomass is torrefied as a batch reaction, Fig. 26.2 (Awang et al. 2019). This type of reactor is simple, reliable and proven technology for drying biomass feed particles of uniform size but its batchwise nature is its weakness as it makes it uneconomical (Aravind et al. 2020; Awang et al. 2019; Ndukwu and Horsfall 2020).

26.6.2.2 Rotary Drum Reactor

A rotary drum reactor is a reactor in which biomass is heated indirectly with superheated steam or exhaust emission of volatile compounds while the drum rotates about a fixed point with the help of a rotating shaft, Fig. 26.10 (Negi et al. 2020).

Some rotary drum reactors in existence are 30,000 tons per year for Torr-Coal B. V in Dilsen-Stokkem, Belgium; 10,000 tons per year for Andritz in Frohnleiten, (AT); and 20,000 tons per year for Earth Care Products in USA (Negi et al. 2020).

26.6.2.3 Screw Conveyor Reactor

For the screw conveyor reactors, the wall of the reactor is heated and this may result in unequal heat distribution on the reactor especially because some of the biomass will be in contact with the walls being heated, Fig. 26.11 (Adeleke et al. 2021).

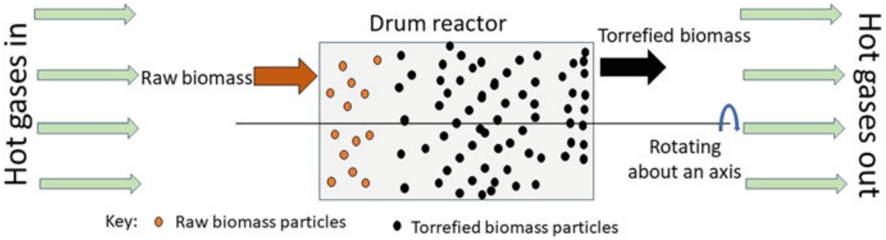


Fig. 26.10 Rotary drum reactor. Adapted from Negi et al. (2020)

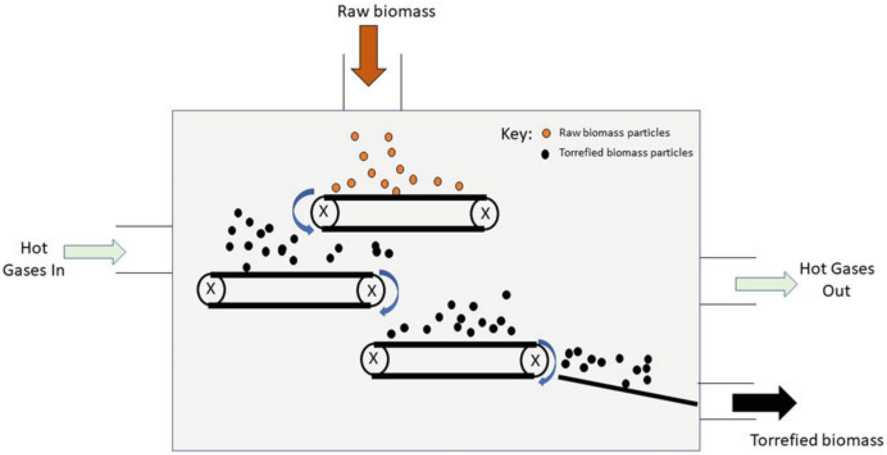


Fig. 26.11 Screw conveyor reactor. Adapted from Ndukwu and Horsfall (2020)

Some screw reactors that are being used are 80,000 tons per year for Solvay/New Biomass Energy in Quitman, USA and a 13,000 tons per year capacity reactor for Agri-Tech Producers LLC in Allendale, USA (Negi et al. 2020).

26.6.2.4 Microwave Reactor

Microwaves are electromagnetic waves in the range 300 MHz to 300 GHz that interact with water molecules in biomass thereby heating up the biomass and resulting in torrefaction (Fig. 26.12). This process occurs in less time as with tubular furnaces, but it results in high electrical energy consumption, therefore high costs (Adeleke et al. 2021; Fodah et al. 2021). In addition, the process may not be efficient as biomass is a poor conductor of heat energy. This means that the process is unsustainable as it goes against the principles of why torrefaction was introduced in the first place (Fodah et al. 2021). As a result, the reactor can be used as a pre-treatment process like drying the biomass and then proceeding to torrefaction using tubular furnaces (Adeleke et al. 2021; Fodah et al. 2021).

Most microwave reactors work at a frequency of 2.45 GHz (Basu 2018a). Microwave reactors can be made to suit both wet and dry torrefaction. Currently, there is one microwave reactor of laboratory scale which is of unknown capacity, which is situated at Rotawave Ltd. in Chester, UK (Negi et al. 2020).

Once the torrefied biomass is produced it is applied mostly in energy production processes and some non-energy production processes.

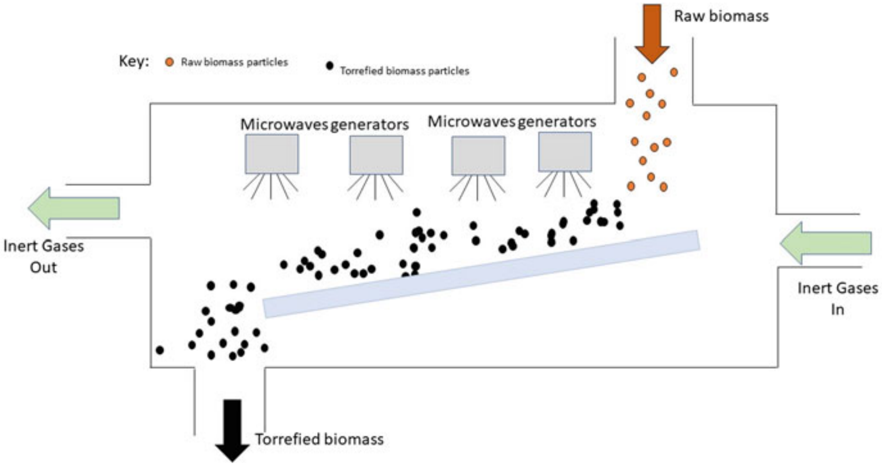


Fig. 26.12 Microwave reactor. Adapted from Ndukwu and Horsfall (2020)

26.7 Non-Power Applications of Torrefied Biomass

Torrefied biomass is usually applied in energy production in power generation alone or co-fired with coal. This has been widely researched and reported in literature (Mamvura and Danha 2020). However, other applications include (1) in iron and steel Industry but in the steel production plants as a replacement for coking coal, pulverised coal and fossil fuels or co-fired with coking coal, (2) in chemical or petrochemical in gasification processes, (3) in pulp and paper mills where it is used in lime sludge kilns and also as a substitute for coal in energy production and (4) in non-metallic minerals as a substitute for fossil fuel being used in kilns (Braghiroli et al. 2020).

Biochar/hydrochar can also be used to amend agricultural soil because biochars/hydrochars contain non-carbonised materials as well as several functional groups which can bind to and interact with contaminants and organic matter (Gabhane et al. 2020; Hagner et al. 2020). Some of these functional groups contain oxygen as carboxyl, hydroxyl and/or phenolic molecules (Gabhane et al. 2020; Kumar and Bhattacharya 2021).

The biochar/hydrochar also finds application in production of activated carbon, as superconductors, as a microwave absorber, as adsorbents like activation carbon for adsorption of inorganic and organic compounds because they have high cation exchange capacity together with high surface area and a porous carbon matrix (Mukherjee et al. 2011; Ahmad et al. 2014), in water purification, in making nanotubes, for supercapacitor fabrication, as feed additives for livestock, as pesticides and in the synthesis of carbon quantum dots (Amer et al. 2020; Fodah et al. 2021; Hagner et al. 2020; Islam et al. 2019; Kumar and Bhattacharya 2021; Racek et al. 2020). For application as activated carbon, the porous structure of the biochar/hydrochar has a higher surface area which will increase the tendency of the biochar/hydrochar to absorb ambient moisture and to adsorb any compounds that it is set to do so (Gabhane et al. 2020). However, this porous structure (high porosity) that encourages high moisture uptake can work as a disadvantage when the biochar is used as a fuel as it may degrade its quality by accelerating its contamination (Amer et al. 2020). This is so because the purpose of torrefaction is to reduce water-attracting power of biomass for it to be stored longer and react less. The porous structure reduces the torrefied biomass' ability to repel the water thereby making it hydrophilic/hygroscopic again (Amer et al. 2020; Braghiroli et al. 2020).

The biochar/hydrochar can also find use in exhaust filters, indoor air filters, carbon fibres, energy storage in batteries, reducing agent in metal processing, cosmetics, healthcare and in building materials in both concrete and asphalt (Racek et al. 2020; Sri Shalini et al. 2020).

26.8 Kinetics of Torrefaction Process

As torrefaction of biomass proceeds, the process can be modelled by different equations. However, torrefaction process of biomass is not yet known completely and also it is very complicated to describe through simplified modelling equations (Grigiante et al. 2020). Therefore, the kinetic data used is usually based on one-step kinetic process, but it is well known that torrefaction occurs via complicated process routes. This means the data determined is reliable to a certain extent and can be used with caution as it does not accurately depict all the process steps which occur. On top of this, there is usually not enough data to validate the kinetic models that are derived, and this simply means the models need to be used with caution as they are only based on limited conditions and limited biomass or biomass of similar type.

The following one-step global equation is used to model the torrefaction process. The kinetics is adapted from Amer et al. (2020), Awang et al. (2019), Grigiante et al. (2020), Guimarães and Tannous (2020), Maia et al. (2020); Ndukwu and Horsfall (2020), Xuanzuo et al. (2020):

$$\text{Chemical Reaction}: \quad \text{Biomass} \begin{array}{l} \xrightarrow{k_B} \text{Biochar/Hydrochar} \\ \xrightarrow{k_V} \text{Volatiles} \\ \xrightarrow{k_G} \text{Gases} \end{array}$$

where: $k = k_B + k_V + k_G$

Then:

$$\text{Kinetic Equation}: \frac{d\alpha}{dt} = kf(\alpha) = k(1-\alpha)^n \tag{26.8}$$

where:

$$\alpha = \frac{m_{\text{initial}} - m_{\text{instantaneous}}}{m_{\text{initial}} - m_{\text{torrefied}}} \tag{26.9}$$

where α is the mass conversion ratio, $d\alpha/dt$ is the rate of change of the mass conversion, m_{initial} is the initial mass (g) i.e. dried biomass mass, $m_{\text{instantaneous}}$ is the mass at given time t (g), $m_{\text{torrefied}}$ is the final mass when reaction is completed for the biochar or hydrochar (g), n is the order of the reaction (n can be 0, 1, 2,. . ., n) and k is the temperature-dependent rate constant (s^{-1}) which is modelled by the Arrhenius equation as follows (Awang et al. 2019; Maia et al. 2020; Nyakuma et al. 2019; Xuanzuo et al. 2020):

$$k(T) = Ae^{-E_a/RT} \tag{26.10}$$

where A is the frequency or pre-exponential factor (s^{-1}), E_a is the activation energy (kJ mol^{-1}), R is the universal is constant (kJ mol^{-1}·K^{-1}) and T is the thermodynamic temperature (K).

The combined equation becomes (Awang et al. 2019; Xuanzuo et al. 2020):

$$\frac{d\alpha}{dt} = \left[Ae^{-E_a/RT}\right](1-\alpha)^n \tag{26.11}$$

This equation has to be integrated to determine the kinetic parameters as:

$$\int \frac{d\alpha}{(1-\alpha)^n} = \int Ae^{-E_a/RT}dt \tag{26.12}$$

However, it is not this easy as we have to account for thermal decomposition under multiple heating rates, and this is usually accounted for by introducing (β):

$$\beta = \frac{dT}{dt} \tag{26.13}$$

And this gives the final equation as:

$$\int \frac{d\alpha}{(1-\alpha)^n} = \int \frac{A}{\beta}e^{-E_a/RT}dt \tag{26.14}$$

Kinetic data can be used to determine thermodynamic data [the enthalpy change (ΔH), the Gibb's free energy change (ΔG) and the entropy change (ΔS)] by making use of the kinetic rate constant k and some equations from literature (Nyakuma et al. 2019). This allows us to conclude on the torrefaction process, its equilibrium nature and how likely it is to occur at different conditions.

The kinetic data determined can be used to simulate and change experimental parameters without performing the experiment again in the laboratory. Knowing the kinetic and thermodynamic data of the torrefaction process is very important for the design and scaleup of the process, as well as to choose the best reactor setup (Awang et al. 2019).

26.9 Summary of the Chapter

Torrefaction is becoming an important technology that will assist in reducing the carbon footprint by reducing the greenhouse gas (GHG) emissions as it improves biomass properties to be close to those for coal. All countries should start adopting biomass and make it part of their energy mix to save our planet and hopefully reverse the impact of emissions that have been generated by non-renewable fuels since the first industrial revolution.

The lockdown that occurred in 2020 due to the global pandemic resulted in a reduction in GHG emissions which were felt globally. However, it will be difficult for the world to go to such a standstill so as to avoid the catastrophe which will occur if we continue to be unresponsible to the emissions we send to the atmosphere. Torrefaction can play a vital role in the mitigation, and it is good that the process is now understood more and more with each passing year due to the research being undertaken!

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Chapter 27
Hydrothermal Carbonisation of Waste Biomass: Current Limitations, Strategic Success and Market Position Analysis

Eloise Alice Rose Bevan

Abstract Hydrothermal carbonisation is comparatively the newest thermochemical conversion technique used on a large scale, and is arguably the most promising due to its unique ability to convert biomass with a high moisture content. There exists a variety of valuable end-products that can be derived from its carbon-dense product coined hydrochar and its process water for applications in the energy, material, agriculture and chemical industries. The main direct applications of hydrochar include soil conditioning and bio-coal, whereas subsequent conversions can include activated carbon, heat and electricity, doped catalyst, super capacitor and electrode material. This chapter explores the current limitations imposed on the technology and the application of its products, drawing recommendations for strategic success through an analysis of its current market position.

Like most new technologies, the main limitation regarding the deployment of hydrothermal carbonisation is the high capital costs required. In addition, operating costs can be high where long-distance waste transport, energy supply and manual labour is required. The application of hydrothermal carbonisation is limited by competing technologies which are now well established in the biomass conversion industry. The high costs in this early stage of development limit its use as a solid fuel, in addition to the competitively lower costs associated with the renewable energy produced from advanced developments in solar and wind. To circumvent limitations imposed by competing technologies, and to ensure market growth, hydrothermal carbonisation should be strategically targeted to centralized, high-moisture waste biomass producing plants such as those in the waste treatment and paper and pulp industries. Whereas the hydrochar should be economically evaluated for the most feasible and value-added applications to ensure efficient use of resources to benefit the circular economy and success of the technology. Activation of the hydrochar for adsorption, use as a catalyst and as a sustainable electrode material look to be the promising applications at this time.

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27.1 Introduction

The process—or technology—of Hydrothermal Carbonisation (HTC) can be easier discerned through deconstruction of its name: hydro, meaning water, thermal, meaning heat, and carbonisation meaning to form carbon. To elaborate, HTC is the process to which organic biomass feeds are mixed with water and subjected to elevated temperatures, which over time results in the carbonisation (carbon densification) of the biomass feed. Biomass can be defined as any organic matter, derived from biological processes such as plants or animal matter. Plant-based biomass is most commonly referred to as lignocellulosic biomass, and on a molecular level it consists of cellulose, hemicellulose, lignin, water extractives and ash (Reza et al. 2013a). Lignocellulosic biomass can be further categorized into one of the three subcategories, depending upon its origin: virgin biomass, energy crops (grown for energy production) and waste biomass. As a thermo-chemical conversion process, HTC is unique in its ability to carbonise any type of biomass in the presence of water. In turn, HTC is able to convert biomass with high-moisture contents, which would otherwise lead to inefficiencies or require an intensive thermal drying stage pre-treating stage prior to torrefaction, pyrolysis, gasification or incineration.

Notable high moisture streams arising from cities include sewage waste, food waste, green (garden) waste and biodegradable municipal waste. Alternatively, niche but ever-abundant examples of high-moisture waste biomass streams include orange peel waste (Xiao et al. 2018), coconut shells (Tu et al. 2019), olive mill wastes (Poerschmann et al. 2013), paper and pulp sludge (Mäkelä et al. 2016), palm husks (Sabzoi 2014), corn stover (Machado et al. 2018) (Mohammed et al. 2020), algae (Park et al. 2018), macadamia nut shell (Fan et al. 2018) and poultry litter (Ghanim et al. 2017). As waste biomass streams with high moisture contents are plenty in supply in the twenty-first century, it becomes clear as to why a technology first referenced in 1914 (Sackur 1914) has been growing in academic and industrial interest since 2005 (Nicolae et al. 2020).

The characteristics of the final products resulting from HTC are a function of the process conditions, this includes the feedstock type, the solid loading (or dry biomass to water ratio), the reactor temperature (and associated pressure), the residence time and the reactor/processing type (size, continuous, batch, stirred, etc.). During HTC, dry biomass to water ratios of 75–90% (Libra et al. 2011) can be processed, with typical HTC temperatures being within 200–275 °C instigating and maintaining pressures above the saturation pressure to ensure the liquid state of water (Reza et al. 2013a). The primary product that results from this process is a solid-form product, coined hydrochar. The carbonisation of biomass in the presence of both heat and water allows for physical and chemical changes of the biomass structure, forming a solid in which the carbon content, atomic ratios (O/C) and energy densification can be compared to lignite (Reza et al. 2014) or peat (Seyedsadr et al. 2018). Beyond these properties, hydrochar can have many advantageous properties over its originating feedstock, with the majority of research observing increased mass densities, friability, homogeneity and hydrophobicity (Hoekman et al. 2011), alongside improved grindability (Sharma et al. 2019).

These properties have identified hydrochar as a viable material for a range of applications. This includes in direct-use application opportunities, such as for soil amendment (Islam et al. 2021), as a solid biofuel (Lucian and Fiori 2017) for domestic heating or for contaminant adsorption (Takaya et al. 2016). Alternatively, upgrading opportunities include its use as a precursor in the production of activated carbon (Diaz et al. 2019), carbon nanoparticles (Shang et al. 2017), carbon dots (Congsomjit and Areeprasert 2020), super capacitors (Rey-Raap et al. 2019), super capacitor electrodes (Gao et al. 2015), as a filler in rubber (Peterson et al. 2015), thermoplastic (Sabzoi 2014) and doped catalysts (Gai et al. 2019).

In order to determine the viability of hydrochar for the aforementioned applications, academics within the field are working to propose mathematical models to predict the properties of hydrochars from different feedstocks. Examples of some of hydrochars properties that are of interest to predict include the carbon content, solid yield, higher heating values (HHV), H/C (hydrogen/carbon) and O/C (oxygen/carbon) ratios (Román et al. 2018). By establishing relationships between a property and the process conditions (time, temperature, solid loading), HTC can be assessed on its applicability for specific feedstock processing and eventual hydrochar applications before investment. Despite the number of variables that are involved with establishing such relationships there have been several mathematical models proposed to better predict the properties. Listed in order of growing complexity, this includes reaction kinetic models (Reza et al. 2013a; Keiller et al. 2019; Lucian et al. 2019a), statistical models (Heilmann et al. 2010; Álvarez-Murillo et al. 2015; Sabio et al. 2016) and computational models (Álvarez-Murillo et al. 2016). In addition to reaching the advanced stages of research, numerous industrial and commercial-scale hydrothermal carbonisation plants have now been in operation across the world since 2010 (Bevan et al. 2020).

This chapter gives an overview of the hydrothermal carbonisation and products, the recent research that has been conducted by academics in the field, what progress and advancements have been made in both academic and industrial settings, and what are the current limitations faced in the development of this technology. In identifying the limitations, recommendations for future research can be effectively investigated to ensure the successful development and deployment of the HTC process and its products. For a broad oversight, the hydrothermal carbonisation process is explained along with an outline of the progressions made by current technology manufacturers in Sect. 27.2. The influence of processing conditions on hydrochar properties along with some of the postulated reaction mechanisms are reviewed in Sect. 27.3. In Sect. 27.4, the different applications of hydrochar and the process water are reviewed. Lastly, Sect. 27.5 explores the main limitations associated with the deployment of hydrothermal carbonisation and its primary product hydrochar, with the recommended solutions or areas for further research to overcome these.

27.2 Process and Technology Developments

27.2.1 Hydrothermal Carbonisation: Process

As previously mentioned, hydrothermal carbonisation is a thermo-chemical process in which water-soluble and water-insoluble carbon fractions are converted under elevated temperatures and pressures into an insoluble carbonaceous product known as hydrochar. The specific temperature and pressure of the reactor are often as such to achieve subcritical or super critical conditions of the water within in the feedstock (Mohammed et al. 2020). The typical reactor temperature in which 'hydrothermal carbonisation' is generally agreed to take place at is 200–275 °C (Reza et al. 2013a), which would result in a water vapour pressure of approximately 15–60 bar. These conditions cause the biomass to decompose through hydrolysis, dehydration and decarboxylation reactions (Kruse et al. 2013). By means of these reactions, the physical and chemical properties of the resulting solid product (hydrochar) are significantly different to its originating feedstock. Properties of the biomass which are changed during the HTC process include an increase in the carbon content from the elimination of volatile oxygenated compounds (furans and low molecular fatty acids) into the aqueous phase (Volpe et al. 2018) and an increase in the higher heating value (HVV), which can be compared to those of lignite coal (Reza et al. 2014). In addition, other properties which can be optimized include porosity, homogeneity, friability and hydrophobicity (Hoekman et al. 2011). However, the extent to which these properties are altered is determined by the process conditions (Sect. 27.3).

A typical simplified hydrothermal carbonisation process is shown in the block-flow diagram presented in Fig. 27.1. However, it is important to note that there exist a variety of alternative process and reactor configurations, as well as plant designs, as parameters are optimized for a variety of reasons, including energy efficiency, reactor geometry, the conversion of a specific feedstock and/or the desired characteristics or eventual applications of the different product applications (Sect. 27.4).

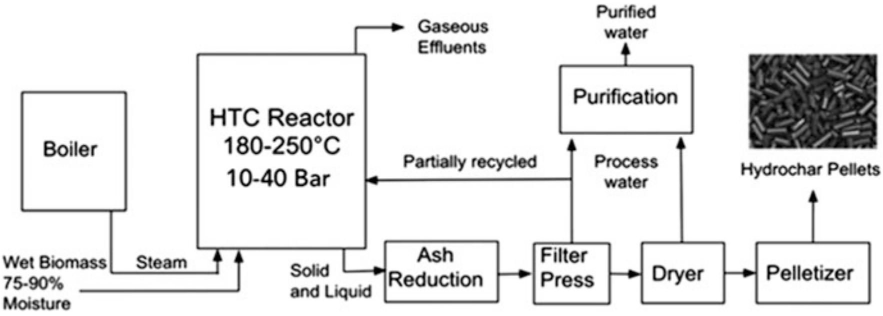

Fig. 27.1 Block-flow diagram of a typical hydrothermal carbonisation process. Reprinted (adapted) with permission from (Bevan et al. 2020)

In order for continuous HTC operation, the biomass needs to be easily transportable through the process, with an appropriate solid loading for pumping. Depending upon the type of biomass feedstock, pre-treatment steps such as milling to reduce the particle size and washing (in the instance that sand, stone, glass and/or metals may be present in the feed) may be required to take place before processing. In the case that the biomass feedstock requires a greater moisture content than it holds naturally for effective pumping, water or recycled process water may be added to the biomass at this stage. In addition, in the instance that a catalyst is to be used in HTC, the biomass and catalyst would be first mixed together. After any necessary mixing, the slurry is pre-heated to the reactor temperature (industrial scale), or the mixture is heated within the reactor (lab-based scale), which is likewise often dependent on the process (referring to continuous and batch, respectively).

In the reactor, the mixture is exposed to the elevated temperature, as such the properties of water are altered so dramatically that it is as if it behaves more as an organic solvent causing a complex reaction network to take place (Reza et al. 2013a). The exact details of all reaction pathways are not yet fully understood, however, inference and comparison of infrared spectroscopy charts for feedstock and their respective hydrochars have led to a common agreement amongst academics that hydrolysis, dehydration, decarboxylation, condensation polymerization and aromatization reactions are most likely to occur during the HTC process (Funke and Ziegler 2010) (Sect. 27.4).

Following the reactor, the mixture of carbonised biomass and process water (typical moisture content of 80 wt.%) is cooled, and on an industrial scale, the extracted heat is most likely optimized elsewhere in the process, for example, pre-heating the feedstock mixture. After cooling and depressurization of the mixture, it is subjected to an energy-efficient filtration stage (mechanical dewatering) to produce a stream of process water and a filter cake of carbonised biomass. The resulting filter cake has a typical moisture content of 50 wt.%, and the process water can be partially recycled back into the process in order to increase the energy efficiency (European Biomass Industry Association 2016) of the process and both the mass yield (Uddin et al. 2014) and higher heating value (Heidari et al. 2018) of the hydrochar. The remaining fraction of the process water that is not recycled is often sent for additional processing, which can vary depending on the intended application, location and technology provider. For example, technology developer Antaco Ltd. purify the process water (Antaco 2019), alternatively TerraNova Energy LTD (2021), C-green Technology AB (C-Green 2021) and Ingelia SL (2021) optimize the soluble organics in the process water for the synthesis of fertilizers in their HTC processes. Following the mechanical filtration, the filter cake is thermally dried, typically to a moisture content between 2 and 5 wt. % (Danso-Boateng et al. 2015) (Malaťák and Dlabaja 2016) before being shaped into cylindrical pellets of hydrochar.

27.2.2 Feedstock

Biomass is a broad term used to encompass any type of matter which is made from organic substances. For HTC, the source of biomass can be categorized into one of two types: lignocellulosic biomass and non-lignocellulosic biomass. Lignocellulosic biomass refers to plant-derived biomass which can be broken down into its macro components of lignin, cellulose, and hemicellulose (Yang et al. 2014). Types of biomass that are categorized as lignocellulosic biomass that has been experimentally trialled through HTC are summarized in Table 27.1. As shown, this category can include commercial green wastes such as garden wastes or industrial plant-based wastes such as olive trimmings and corn stover. Alternatively, non-lignocellulosic biomass refers to biomass that is not directly obtained from a plant source, and has most likely been either processed or had some human intervention, examples include sewage sludge, the organic fraction of municipal solid waste, food waste, paper and pulp sludge. Results of the mass yields and proximate analysis from the hydrothermal carbonisation of non-lignocellulosic biomass are likewise summarized in Table 27.1.

More recently, the coupling of hydrothermal carbonisation with anaerobic digestion (AD) has been investigated as a synergistic method to maximize the energy products (Urbanowska et al. 2020), particularly the increase in biogas and methane when recycling the HTC's process water to AD (Danso-Boateng et al. 2015; Ischia and Fiori 2020). In addition, dewatering and upgrading the digestate to hydrochar provides an alternative disposal method of digestate. Table 27.1 summarizes the results of a recent literature regarding the HTC of different digestates, namely agricultural waste, municipal solid waste, sewage waste and vegetable, garden and fruit waste (Parmar and Ross 2019). As can be observed, the fixed carbon in the resulting hydrochar is significantly lower when compared to the HTC of non-digested lignocellulosic or non-lignocellulosic feedstock's as the carbon has been pre-extracted to produce methane and carbon dioxide in the anaerobic digester.

27.2.3 Products

As shown in Fig. 27.1, the overall product streams that result from the hydrothermal carbonisation process are in gaseous, liquid and solid states. The typical weight distribution for the product stream is 50–80 wt. %, 5–20 wt. %, and 2–5 wt.% for solid, liquid and gaseous products, respectively (Bevan et al. 2020). It is important to note that the final composition between the three physical states described is highly dependent upon the feedstock type and processing conditions (temperature, residence time, biomass/water ratio) (Román et al. 2018).

Table 27.1 Summary of different experimental hydrothermal carbonisation feedstock's: process conditions, mass yields and fixed carbon results from proximate analysis

	Process conditions				Mass Yields			Proximate Analysis		
Biomass feed	Solid Loading	Temperature	Time	Catalyst	Solid	Liquid	Gas	Fixed Carbon—Hydrochar	Fixed Carbon—Raw Biomass	Reference
	%	°C	min	g/g	wt. %	wt. %	wt. %	wt. %	wt. %	
Lignocellulosic:										
Miscanthus	10%	200	240	–	65	–	–	21.74	6.77	(Wilk and Magdziarz 2017)
Pinus radiata	8.3%	220	60	0.5 (NaOH)	52	–	–	41.81	13.44	(Carrasco et al. 2020)
Corn stover	14%	200	240	–	62.24			24.18	17.15	(Zhang et al. 2019)
Olive trimmings	25%	220	180	–	58	33	9	31.4	17.6	(Volpe et al. 2018)
Defective coffee beans	10%	200	40	–	41.7	–	–	13.2	12.4	(Santos Santana et al. 2020)
Wood	25%	225	60	–	68.7	–	–	13.9	24.9	(Stirling et al. 2018)
Apple Chip pomace	8.3%	260	15	–	27	–	–	23.28	15.88	(Zhang et al. 2018)
Orange peel	12.5	240	120	–	41	25	18	N/A	N/A	(Xiao et al. 2018)
Non-lignocellulosic:										
Kitchen wastes	10%	190	240	–	42.3	–	–	68.86	46.22	(Malaťák and Dlabaja 2016)

(continued)

Table 27.1 (continued)

	Process conditions				Mass Yields			Proximate Analysis		
Biomass feed	Solid Loading	Temperature	Time	Catalyst	Solid	Liquid	Gas	Fixed Carbon—Hydrochar	Fixed Carbon—Raw Biomass	Reference
	%	°C	min	g/g	wt. %	wt. %	wt. %	wt. %	wt. %	
Paper and pulp; primary sludge	11.1%	260	30	–	30.3 ± 1.1	58.1 ± 2.4	11.6 ± 1.4	44.3 ± 3.3	34 ± 0.4	(Sharma and Dubey 2020)
Co-HTC green and food waste	5%	220	60	–	14.54	–	–	N/A	N/A	
Digestates of:										
Agricultural waste	20%	200	60	–	67.8 ± 1.5	26.9 ± 4.6	5.3 + 3.1	17.3 ± 1.9	13.8 ± 0.0	(Parmar and Ross 2019)
Municipal solid waste	20%	200	60	–	87.1 ± 0.2	9.5 ± 2.1	3.3 + 1.9	5.6 ± 0.7	8.3 ± 0.0	(Parmar and Ross 2019)
Sewage sludge	20%	200	60	–	76.1 ± 0.3	19.2 ± 0.4	4. + 0.7	6.5 ± 0.2	2.1 ± 0.1	(Parmar and Ross 2019)
Vegetable, garden and fruit wastes	20%	200	60	–	80.9 ± 1.0	16.6 ± 0.2	2.5 + 0.8	9.0 ± 0.7	9.0 ± 0.2	(Parmar and Ross 2019)

27.2.4 Solid-Form Product: Hydrochar

The majority of HTC-related papers are focused on the analysis and understanding hydrochar. Hydrochar is a carbon-rich, energy-dense solid whose properties can be likened to that of lignite (Reza et al. 2014). Table 27.1 summarizes some of the literature and the different process conditions trialled, along with the resulting mass yields and fixed carbon content of the raw biomass and its hydrochar. Observing these, it becomes clear that varying process conditions (and feedstock) can lead to large differences in the properties of the final product(s). For example, when comparing the HTC of miscanthus by Wilk and Magdziarz (2017) to that of defective coffee beans by Santos Santana et al. (2020) they differ only by feedstock and residence time as solids loading and temperature are the same at 10% and 200 °C, respectively. However, the HTC of miscanthus for 240 min, compared to the HTC of defective coffee beans for 40 min leads to a large discrepancy between the solid yield and fixed carbon in the hydrochar, where these were found to be 65 wt. % and 21.74 wt. % for miscanthus and 41.7 wt. % and 13.2 wt. % for defective coffee beans, respectively. What's more is that the longer reaction time for miscanthus resulted in a higher percentage of fixed carbon and a higher mass yield of hydrochar. This increase could be explained by the formation of a secondary char from the soluble extracts (Lucian et al. 2019a), with more secondary char forming with time. Alternatively, the greater reduction in mass for defective coffee beans could be the result of the rapid hydrolysis of a greater mass hemicellulose and amorphous cellulose present in this biomass.

As shown, the predictability of hydrochars properties is not a clear linear trajectory because of the numerous process parameters and complex reaction mechanisms. This can be a limiting factor in the deployment of this technology as outcomes are not certain or guaranteed. As such, it becomes evident as to why research into the understanding of these mechanisms and the mathematical modelling to achieve optimization of the process conditions and the predictability of product properties continues to be a focal point of interest amongst academics in the field (Álvarez-Murillo et al. 2015, 2016; Lucian et al. 2019a; Sabio et al. 2016).

27.2.5 Methods for Hydrochar Analysis

The most common characterization methods of hydrochar in the literature is elemental analysis (or ultimate analysis), proximate analysis and solid mass yield. Elemental analysis can be performed through standard EURO EA elemental analyzers (Sharma et al. 2019; Sharma and Dubey 2020), with most HTC-related studies reporting on elemental carbon, nitrogen, hydrogen and oxygen contents. The results from elemental analysis of hydrochars formed under different temperatures and time show that the elemental oxygen content is dependent on time and temperature through an inverse correlation with the increase in either reaction time (Zhang

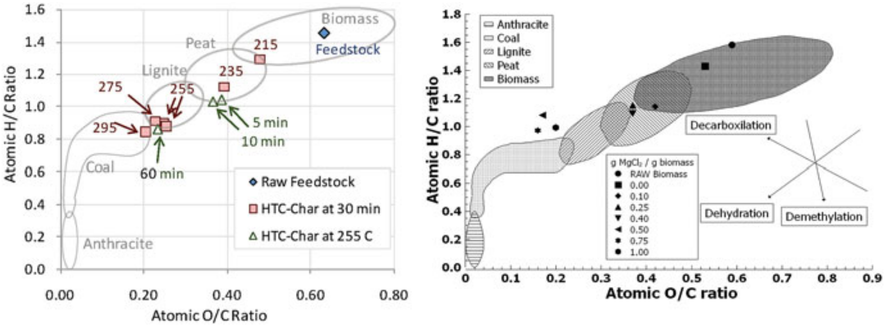

Fig. 27.2 Van Krevelen Diagrams showing (**a**) the effect of residence time and temperature Reprinted (adapted) with permission from (Hoekman et al. 2011). Copyright 2021 American Chemical Society, and (**b**) the effect of catalyst addition Reprinted (adapted) with permission from (Carrasco et al. 2020) on the O/C and H/C ratios in the resulting hydrochars of the respective studies

et al. 2019) or temperature (Jamari and Howse 2012). It is this phenomenon that has been linked to the declining trend of recoverable solids and increasing energy content at higher temperatures (Román et al. 2018).

The results of the elemental analysis can likewise be used to calculate the O/C and H/C atomic ratios for use in a Van Krevelen Diagram (VKD). A VKD is a simple graph with axes representing each ratio for a visual interpretation and comparison of the solid fuel produced to traditional solid fuels. Figure 27.2 shows two Van Krevelen Diagrams; 2A demonstrates the impact that increasing the time and temperature has on the O/C and H/C atomic ratios during the HTC of Jeffery Pine and White Fur (Hoekman et al. 2011), whereas 2B shows the impact of the addition of different quantities of magnesium chloride (MgCl) catalyst has on the fuel properties during the HTC of sawdust (Carrasco et al. 2020). Figure 27.2a produced by Hoekman et al. (2011) shows that when maintaining a residence time of 30 min and the reactor temperature is increased from 215 °C to 295 °C, the atomic O/C and H/C ratios in the hydrochar decrease enough for the sample to be likened to those H/C and O/C atomic ratios typical of coal. Similarly, when maintaining a reaction temperature of 255 °C, an increase in the residence time from 5 to 60 min results in lower O/C and H/C atomic ratios, which can be likened to lignite (Hoekman et al. 2011). Alternatively, Carrasco et al. (2020) demonstrated the effect that the addition of MgCl during the HTC of sawdust had on these ratios and the solid fuel properties of hydrochar when maintaining reaction time and temperature at 1 h and 220 °C, respectively. As shown in Fig. 27.2b, both O/C and H/C ratios decrease with increasing the mass of MgCl per gram biomass, where the O/C ratios eventually decrease to a zone that reflects those typically found in coal (approximately 0.15–0.2). This being said, the H/C ratio is slightly larger (approximately 0.95–1.1 compared with the boundary line at 0.9), yet MgCl behaves as a catalyst in the reduction of oxygen and hydrogen from the sawdust under the HTC process conditions.

Investigations into hydrochar for solid biofuel applications would be incomplete if not characterized by the Higher Heating Value (HHV) or the Lower Heating Value (LHV). The HHV provides a direct measure of the heat released during combustion and the economic potential of a solid fuel. The HHV and LHV are dependent on the feedstock and process conditions, where the HHV of hydrochar has been shown to increase by 36–40% when compared to the feed (Mendoza Martinez et al. 2021). However, the energy content of the hydrochar is typically between 80% and 95% contained in the original feed, and the mass is reduced by 55–90% (Mendoza Martinez et al. 2021). Using the elemental composition, more than a dozen equations have been published for the prediction of the HHV in reference to coal or MSW, as summarized by Friedl et al. (2005). In 1937, Dulong derived the first formula for calculating the HHV of coal as shown in Eq. (27.1) (Demirbaş and Demirbaş 2004) and it is used frequently throughout the literature (Sharma and Dubey 2020). More recently, the HHV for biomass plant material has been proposed to be calculated using Eq. (27.2) (Friedl et al. 2005). Alternatively, the LHV can be calculated using Federal Energy Regulatory Commission (FERCSs) formula, using the HHV as shown in Eq. (27.3) (U.S. Environmental Protection Agency Office of Air and Regulation 2007).

$$\mathrm{HHV} = 0.3383^{*}\%\mathrm{C} + 1.433^{*}(\%\mathrm{H} - \%\mathrm{O}/8) \tag{27.1}$$

$$\mathrm{HHV} = 3.55\mathrm{C}^{2} - 232\mathrm{C} - 2230\mathrm{H} + 51.2\mathrm{C} \times \mathrm{H} + 131\mathrm{N} + 20{,}600 \tag{27.2}$$

$$\mathrm{LHV} = \mathrm{HHV} - 10.55(\mathrm{W} + 9\ \mathrm{H}) \tag{27.3}$$

Where %C, %H and %O are the weight percentages of carbon, hydrogen and oxygen in the solid fuel, and W and H represent the weight % of moisture and hydrogen in the fuel, respectively. It is important to note that Dulong's formula is in MJ kg^{-1}, whereas FERCs formula is calculated using BTU lb^{-1}.

Proximate analysis, to measure the moisture content, ash content and volatile matter of hydrochar is performed using ASTM standard methods ASTM-E871, ASTM-E1755 and ASTM-E872, respectively. From determining the composition of each in the resulting hydrochar, the fixed carbon content can be determined through deduction. Similar to producing a VKD, proximate analysis is experimentally performed in the literature as a means of assessing the applicability of the hydrochar for solid biofuel applications, where knowing the quantities of these contents becomes critical when assessing its feasibility as fuel. To elaborate, the ash content, if too high, can have a negative impact due to slagging and fouling of equipment's (Vardiambasis et al. 2020) as well as a need for the consideration of its disposal. Alternatively, the volatile matter governs the ignition and flammability of a solid fuel, whereas low moisture content in a solid biofuel improves the combustion and reduces the flue gas volume produced per unit of energy (Hajek et al. 2013). This being said, through HTC, the moisture and ash content can be reduced when compared to the raw feedstock, lowering the risk of slagging and fouling (Stirling et al. 2018). Once the proximate analysis has been performed, the fuel ratio, energy densification, energy and ash yield can be calculated (Carrasco et al. 2020; Sharma and Dubey 2020; Wilk and Magdziarz 2017). Beyond these characterizations, the solid hydrochar are most often assessed for hydrophobicity and tensile properties mainly in reference to pellet production, transportability and spoilage assessments. In addition, combustible properties are assessed through thermogravimetric analysis (TGA) (Sharma and Dubey 2020; Wilk and Magdziarz 2017), in order to determine the combustion initialisation and finalization temperature, the maximum reactivity temperature, ash amount and total combustion time.

As described in Sect. 27.2.2, hydrothermal carbonisation has been experimentally performed on a variety of feedstocks to produce the carbon-dense, coal-like solid product. This similarity to coal is what has expedited the research within the field, however, over the past two decades since its rediscovery, the applicability of hydrochar as an alternative to various other products has been assessed, this includes as a soil amendment, as a precursor to activated carbon (or charcoal), as sustainable electrode material and as a catalyst. Extant literature and industrial investigations into the alternative applications for hydrochar are explored in greater detail in Sect. 27.4.

27.2.6 Liquid Product: Process Water

The liquid process water is typically produced at 5–20 wt. % (Bevan et al. 2020) and is rich in organics that are readily extracted from the biomass structure and solubilized under the high reaction temperatures (Reza et al. 2013b). In recent years, research into the liquid-phase resulting from HTC has increased as a means to obtain a more circular approach to the HTC process. For example, studies for the recycling of process water to anaerobic digestion (AD) has been shown to improve methane yields (Danso-Boateng et al. 2015; Ischia and Fiori 2020). Alternatively, the process water that is not recycled (with in the process or to AD) can be sent for additional processing, which, depending on the intended application, location and technology developer, can include purification to produce clean water (Antaco 2019) or for the synthesis of fertilizers (Ingelia SL 2021) or components of which (C-Green 2021; TerraNova Energy LTD 2021).

Of particular interest is the extraction of phosphorus from the process water as it is a non-renewable and ‘critically raw’[1] resource. The demand for phosphorus is in large part caused by the agricultural and chemical industries for crop fertilizer

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[1] Phosphorous was deemed critically raw by the European Commission in 2014 (European Commission 2016). This means that the mineral has growing economic importance as it is in high demand but limited in supply.

production, detergents, animal feed and other chemicals (van Vuuren et al. 2010). There are no substitutes for phosphorus as a plant nutrient in agriculture, and a depletion of 50% (of the lower estimate of phosphorus reserves) by the end of the century could be regarded as a serious threat to the security of phosphorous supply (van Vuuren et al. 2010). However, the extraction of this vital plant nutrient from process water is proving HTC to be a likely part of the solution to this looming problem. To elaborate, Crossley et al. (2020) demonstrated that for the HTC of spent coffee grounds, 82% of the phosphorus can be liberated in the process water, and through nanofiltration and precipitation, 75% of the total phosphorus concentration can be recovered from the process water (Crossley et al. 2020). Not only does this demonstrate how HTC is proving to be a versatile technology, but that its application can provide a holistic solution to the very serious threat imposed by phosphorus depletion.

27.2.7 Gaseous Products

The quantity of gas produced during HTC is typically at 2–5 wt. % of the feedstock (Libra et al. 2011), however, some studies have found the production of gaseous products to be greater, and have been noted to increase with increasing temperature (Hoekman et al. 2011; Reza et al. 2013a). The gaseous stream typically consists in major part of carbon dioxide, typically responsible for 90–95% of the total gas volume. The remaining fraction is majority carbon monoxide, constituting 5–10% of the total gas volume, and trace amounts of hydrogen and methane are likely to be present (Hoekman et al. 2011). Little research has been conducted by way of the separation, sequestration or utilization of the effluent gases resulting from hydrothermal carbonisation, likely due to the small quantities that are produced. This could be inferred as a limiting section of the technology's potential. Therefore, in order to ensure a more circular approach to the use of hydrothermal carbonisation technology, research into the utilization of the gaseous stream is recommended.

27.2.8 Process Limitations and Challenges

In this section, some of the limitations and challenges associated with the hydrothermal carbonisation process are explored along with an evaluation of solutions currently being investigated and/or areas where future research could be directed.

A current limitation of HTC application is the thermal and electrical energy consumption of the process. Although research and process modelling allows for a comprehensive understanding of these quantities, the source and quantity of this energy cannot be overlooked. To elaborate, the process can only be justified as a renewable technology if consuming energy from a renewable source. The process itself could be net positive in energy when utilizing part of the hydrochar for energy, the use of which would lower operating costs. However, the inefficiencies in energy conversion imply that this would not be the most economical use of the hydrochar (Bevan et al. 2020). Alternatively, the external sourcing of renewable energies such as solar or wind energy could supply the plant with its electrical demand, and the use of bio-methane with its thermal demand. However, in utilizing external energy sources to operate the process, the operating costs would be significantly higher, which in turn impacts the profitability and thus feasibility of the plant.

There are several solutions to the imposed energy limitation when not using hydrochar to power the process. One of these is the coupling of the HTC process with an anaerobic digestion plant. In this way, methane from the anaerobic digestion plant can be utilized by the HTC plant, and the HTC process water can be recycled to improve methane yields (Danso-Boateng et al. 2015; Ischia and Fiori 2020). To elaborate, Ferrentino et al. (2020) demonstrated that bio-methane yields could almost be doubled from 55 ± 20 to 102 ± 3 ml CH_4 g^{-1} COD. This coupling method could work for the HTC of a raw feed or when processing the anaerobic digestate. However, it is important the energy and carbon content of the hydrochar would be reduced when using digestate as it is first directed to the production of methane, and therefore the intended application of the hydrochar should be considered when integrating these two technologies.

An alternative solution to the energy limitation could be through integrating hydrothermal carbonisation reactor with a parabolic disc concentrator, creating a 'zero-energy technology'. Ischia et al. (2020) demonstrated that the thermal load of the reactor can be obtained in this way which would favour the deployment of 'standalone' HTC plants for the production of a high-quality hydrochar (as opposed to digestate) as the properties of the resulting 'solar-hydrochar' resemble those of studies performed in traditional HTC systems (Ischia et al. 2020). This could prove to be a likely feature in future HTC reactors, specifically if profitability and/or return on investments are more favourable when compared to HTC processes requiring an external energy supply.

As briefly mentioned in Sect. 27.3.3, a limitation of HTC is the production of a mixture of effluent gases and the minimal research into its utilization, separation or sequestration. Although the typical weight percentage of gases that are produced in HTC equate to 2–5 wt. % of the feedstock (Libra et al. 2011), when produced on a large scale, this has the potential to turn into a very large quantity of effluent gas. Of the gases that are produced, carbon dioxide (CO_2) is the most prominent (Hoekman et al. 2011) with its production being 'carbon neutral' in relation to the carbon cycle. There has been little research into the carbon capture and sequestration (CCS) from the gaseous stream, and efforts could be made to recover or oxidize minor compounds such as carbon monoxide, hydrogen and gaseous hydrocarbons (Child 2014). This remains an area for further study and could be of particular interest as HTC deployment grows, however, its application may only be practical on large-scale HTC processes due to the small production of gases and the greater capital and operating costs likely to be incurred. That is, unless captured CO_2 is turned into a value-added stream through carbon capture and utilization (CCU, e.g., construction materials (Magwood 2019)) or if the integration of CCS/CCU was financially supported.

27.3 Process Conditions and Reaction Mechanisms

27.3.1 Effect of Process Conditions on Hydrochar Properties

As mentioned, the process conditions, namely temperature, time, solid loading and the presence of a catalyst can impact the properties of the resulting hydrochar. In this section, experimental literature on the effects that these conditions can have on properties determined through elemental and proximate analysis are explored. Table 27.2 summarizes the experimental literature referred to in this section. It is important to note that the conclusions drawn in this section are for the relevant data presented in Table 27.2 only, and that although generalizations can be made, the feedstock, type of reactor and processing method can impact the product properties.

27.3.2 Temperature

The reactor temperature during HTC has been shown to influence the properties of the hydrochar, this can be either beneficial or detrimental, depending on the desired end application of hydrochar. To elaborate, more beneficial changes can include the reduction in O/C and H/C ratios (Hoekman et al. 2011; Mohammed et al. 2020) the increase in energy content (Hoekman et al. 2011; Wilk and Magdziarz 2017) and an increase in fixed carbon (Mohammed et al. 2020). Alternatively, detrimental impacts resulting from higher increasing the reaction temperature include a decrease to the solid yield of hydrochar (Zhang et al. 2019) and in most cases, an increase the ash content (Mohammed et al. 2020). In this section, these influences are explored with reference to relevant experimental data extracted from the literature and presented in Table 27.2.

As shown in Fig. 27.2a (described in Sect. 27.3.1), an increase in the reactor temperature leads to a reduction in the O/C and H/C atomic ratios. Similarly, this reverse trend can be seen from the quantification of O/C, and H/C ratios of the miscanthus (Wilk and Magdziarz 2017) and corn stover (Zhang et al. 2019) summarized in Table 27.2. This chemical change to the structure of the feedstock implies a greater energy content of the fuel. This is evidenced by the increasing HHV of the miscanthus feedstock, which increases from 21.2 MJ/kg to 23.9 MJ/kg as the temperature is increased from 180 °C to 220 °C. The influence of temperature to both the O/C and H/C atomic ratios and the HHV of hydrochar can be beneficial where desired application as a solid biofuel is desired. Another beneficial impact from temperature increase can be the increase of fixed carbon (Lucian et al. 2019a; Zhang et al. 2019). Likewise, this trend can be observed for miscanthus (Wilk and

Table 27.2 The effect of process conditions on the hydrochar properties determined through elemental and proximate analyses

	Operating conditions					Elemental analysis		Energy content	Proximate analysis			
Biomass feed	Solid Loading	Temp.	Time	Catalyst	Solid mass yield	O/C	H/C	HHV	Moisture content	Ash content	Volatile matter (VM) content	Fixed carbon
	g/g as %	°C	Min.	g/g	wt %	ratio	ratio	MJ/kg	wt %	wt %	wt %	wt %
Miscanthus	–	–	–	–	–	0.74	1.54	17.5	7.38	1.75	84.1	6.77
Wilk and Magdziarz 2017	10	180	240	–	80	0.55	1.33	21.2	1.48	1.3	81.7	15.52
	10	200	240	–	65	0.48	1.25	21.4	2.37	0.88	75.01	21.74
	10	220	240	–	58	0.36	1.1	23.9	1.36	1.05	73.23	24.34
	10	200	720		65	0.25	1.24	23.4	0.4	0.83	74.95	23.82
Pinus radiata	–	–	–	–	–	0.61	1.58	20.11 ± 0.01	●	0.21 ± 0.01	86.35 ± 0.1	13.44
Carrasco et al. 2020	8.33	220	60	0	66.43	0.53	1.44	22.72	●	0.03 ± 0.01	78.16 ± 0.06	21.83
	8.33	220	60	0.25*	65	0.3	1.16	24	●	1.22 ± 0.01	63.47 ± 0.13	35.31
	8.33	220	60	0.5*	52	0.16	1.1	25.3	●	1.76 ± 0.01	56.43 ± 0.07	41.81
	8.33	220	60	0.75*	50	0.15	0.96	26.7	●	1.18 ± 0.01	51.53 ± 0.35	47.29
	8.33	220	60	1*	49	0.19	0.98	26.5	●	0.73 ± 0.01	50.52 ± 0.32	48.76
Corn stover	–	–	–	–	–	0.75◆	1.51◆	–	●	3.51	79.34	17.15
Zhang et al. 2019	14	180	240	–	67.9	0.69◆	1.32◆	–	●	2.4	78.03	19.57
	14	200	240	–	62.24	0.63◆	1.25◆	–	●	2.38	73.44	24.18
	14	220	240	–	51.22	0.35◆	0.99◆	–	●	2.79	58.46	38.75
	14	240	240	–	46.23	0.30◆	0.90◆	–	●	2.99	51.77	45.24

	14	260	240	–	44.17	0.19◆	0.81◆	–	●	3.07	47.17	49.76
Primary sewage sludge	–	–	–	–	–	1.07◆	1.88◆	–	–	–	–	–
Danso-Boateng et al. 2015	4.3	180	30	–	70.74	1.04◆	1.73◆	17.64	4.81	33.46	63.01	3.53
	4.3	180	60	–	67.18	1.05◆	1.69◆	17.72	4.35	34.05	63.14	2.81
	4.3	180	120	–	64.31	1.06◆	1.66◆	17.88	4.25	37.65	60.44	1.92
	4.3	180	240	–	61.87	1.05◆	1.62◆	18.26	3.7	39.17	57.37	3.46
Agricultural residue digestate	–	–	–	–	–	0.53	1.38	17.8	●	16 ± 0.3	10.2 ± 0.3	13.8 ± 0
Parmar and Ross 2019	10	200	60	–	60.0 ± 2.6	0.33	1.59	21.60	●	14.7 ± 1.4	69.4 ± 1.5	15.9 ± 2.8
	20	200	60	–	67.8 ± 1.5	0.36	1.40	20.70	●	15.3 ± 1.4	67.4 ± 0.5	17.3 ± 1.9
	30	200	60	–	80.1 ± 1.7	0.33	1.42	20.90	●	16.3 ± 1	66.7 ± 0.3	17 ± 1.3
Sewage sludge	–	–	–	–	–	0.44◆	1.76◆	18.84⊙	1.1	18.17	69.96	10.78
Song et al. 2019	1000%	200	120	–	65.76	0.28◆	1.60◆	20.75⊙	0.11	2.6	59.81	12.48
	1000%	200	120	Oxalic◇	54.71	0.37◆	1.51◆	21.97⊙	0.12	17.34	70.31	12.83
	1000%	200	120	Citric◇	51.07	0.30◆	1.51◆	23.81⊙	0.14	13.61	72.06	14.19
	1000%	200	120	Tartaric◇	55.28	0.39◆	1.68◆	21.00⊙	0.13	19.3	67.94	12.63

Notes: *Catalyst used MgCl ●Included in VM ◆ calculated using experimental data available and atomic weights of elements ◇catalyst added as 20 mmoles per 1 g phosphorus in HTC sample (study investigating reduction of phosphorus in hydrochars) ⊙ Converted from kcal/kg to MJ/kg

Magdziarz 2017) and corn stover (Zhang et al. 2019) (Table 27.2). However, this influence enhances the versatility of hydrochar for applications beyond as a solid biofuel, namely as a carbon-rich soil conditioner, as a precursor to activated carbon and as an electrode material, to name a few.

The increase in temperature can be of detrimental consequence to some of the other properties of the hydrochar. Firstly, the increase in HTC temperature has been linked to a decrease in solid yields (Lucian et al. 2019b; Zhang et al. 2019). Evidence of which can be observed by the quantification of the miscanthus and corn stover results presented in Table 27.2. To quantify, when using corn stover as a feedstock, the increase in HTC temperature from 180 °C to 260 °C led to a difference in the solid yield of 23.73 wt. % (Zhang et al. 2019). This represents a major product loss which can in turn impact the economics of the process. However, as the temperature improves the hydrochars energy content and weight percentage of fixed carbon, it is common for literature to refer to the energy yield obtained in the final product (Carrasco et al. 2020; Danso-Boateng et al. 2015) in order to better evaluate the impact and optimize this operating condition.

The transfer of mass from solid-phase to liquid-phase is regarded as occurring from the extent of hydrolysis and dehydration reactions increasing at enhanced temperatures (Román et al. 2018). This being said, the transfer to the liquid-phase does not represent a complete loss to the process as the process water resulting from HTC is becoming of valuable interest (Sect. 27.4.2).

Increasing the temperature is linked to an increase of the ash content in the hydrochar (Mohammed et al. 2020), as shown by the results for corn stover in Table 27.2. This being said, the final ash content is dependent on the precursor ash content, its chemical composition and solubility (Román et al. 2018). For solid biofuel applications, low ash contents are desirable to minimize slagging and fouling behaviour on combustion process equipment (Lucian and Fiori 2017). From this understanding of the influence the reaction temperature can have on some of the hydrochars properties, it becomes clear that optimization for the intended application is needed to ensure process efficiency and economic feasibility.

27.3.3 Time

The residence time for hydrothermal carbonisation is another process condition that can influence the final characteristics and properties of the hydrochar. Studies have shown that the reaction time can influence carbon distribution, the chemical characteristics of the hydrochar and the energy content (Román et al. 2018). These influences can be observed when referring to the HTC results for primary sewage sludge feedstock in Table 27.2 (Danso-Boateng et al. 2015). In which, the increase in reaction time shows a mixed impact on the fixed carbon in the solid product, changes to the chemical content (proximate analysis) through decreasing moisture and volatile matter contents with increasing ash contents. The increase in reaction time slightly increases the energy content of the hydrochar from 17.62 to 18.62 MJ kg^{-1}.

However, the reduction in solid mass yields with time results in lower energy yields overall (Danso-Boateng et al. 2015). For research concerning HTC, the definition of residence time becomes obscured in the literature as some include the time for heating the reactor to the desired temperature, whereas others begin the time from the point at which the set point temperature is reached (Lucian et al. 2019a). This can be a limitation for kinetic modelling progression for the understanding, optimization and predictability of the HTC process.

27.3.4 Initial Solid Biomass to Water Ratio

In addition to time and temperature, the initial dry biomass to water ratio (or solid loading) can influence the characteristics of the hydrochar. In the literature, studies have shown that increasing the initial mass of biomass leads to a higher yield of solid hydrochar, as the greater mass of initial solid lowers the solubility (Parmar and Ross 2019). In addition, higher solids loading have been shown to lead to higher carbon densification within the hydrochar (Aragón-Briceño et al. 2017; Parmar and Ross 2019). Observing the results for the HTC of 'agricultural residue digestate' in Table 27.2, Parmer et al. (Parmar and Ross 2019) show that the increase in solids loading decreased the energy content of the resulting hydrochar; the HHV decreased from 21.60 to 20.90 MJ kg^{-1} as solids loading was increased from 10% to 30%, respectively (Parmar and Ross 2019). Interestingly, the HHV was lowest at 20% (20.70 MJ/kg). This trend is the reverse of that shown when increasing the reactor temperature and time.

In a different study conducted by Lucian and Fiori (2017), a process model for hydrothermal carbonisation was developed and it was determined that as the dry biomass to water ratio decreased, the specific thermal and electrical energy demands (kWh ${kg_{hydrochar}}^{-1}$) increased due to the high water content. Indeed, for a processing temperature >180 °C (independent of reaction time), the hydrochar derived from off-specification compost under a solid loading of 7% could not provide sufficient thermal energy to compensate for the modelled plants thermal energy demand. Alternatively, the hydrochar derived from grape marc under a solid loading of 19% could meet the thermal energy demands of the process for all temperatures and residence times experimentally investigated (180/220/250 °C; 1/3/8 h). Therefore, even though a slightly lower HHV may result from the hydrothermal carbonisation of a greater initial mass of biomass (as demonstrate by Parmar and Ross (2019)) the works of Lucian and Fiori (2017) highlight the importance of consideration for the plants operational energy consumption when decreasing the solid loading. This area of research is of specific importance when aiming to produce a hydrochar for biofuel applications.

27.3.5 Acidic Conditions/Catalyst

The addition of an acidic catalyst -such as acetic, sulphuric and citric acids- have been shown to lead to some favourable properties in the resulting hydrochar (Susanti et al. 2019; Zhao et al. 2013). Reza et al. (2015) found that the use of acetic acid in the HTC of wheat straw led to a maximum increase in the elemental carbon contained in the hydrochar product at pH 2 (Reza et al. 2015). As a greater carbon content is one of the main desirable characteristics of the process, this implies that the use of an acid catalyst can be extremely beneficial, specifically when hydrochar is to be used as a carbon-rich material, for carbon sequestration or soil amendment applications (Rillig et al. 2010; Sevilla and Fuertes 2011). Beyond carbon content, higher yields of hydrochar can be obtained when utilizing an acid catalyst, with a reduction in ash content (Ghanim et al. 2017) and higher specific capacitance (Susanti et al. 2019) also being reported. However, the different acids have been shown to lead to different hydrochar properties being manipulated, and to different extents (Song et al. 2019). Therefore, the optimal acid catalyst and pH level should be determined through experimental research for the specific feed type and desired product property or eventual application of the products.

To quantify, the effects of adding increasing quantities of magnesium chloride (MgCl; slightly acidic) to the mixed reactor feed were investigated by Carrasco et al. (2020). In their study, the temperature, residence time and dry water/biomass ratio were held constant at 220 °C, 1 h and 8.3 %, respectively, whereas the mass of MgCl was increased on a gram per gram of dry feedstock basis. A quantification of these results is shown in Table 27.2, Section 27.3.1. As can be observed, the increasing addition of MgCl dramatically altered the higher heating value and fixed carbon content in the solid, in addition to the O/C and H/C ratios (Fig. 27.2a). In turn, the addition of MgCl could provide an alternative solution for improving the product properties without having negative impacts on the energy balance or process economics, as an increase in reactor temperature or residence time would have.

Alternatively, in the study conducted by Song et al. (2019) the addition of different organic acids, namely oxalic, citric and tartaric were added to a sewage sludge feedstock was investigated when holding constant the HTC temperature, residence time and biomass to water ratio. As shown in Table 27.2, the citric acid resulted in the hydrochar with the greatest HHV (23.81 MJ kg^{-1}) and the highest weight percentage of fixed carbon in the final product (14.9 %), yet the addition of citric acid resulted in the lowest mass yield of hydrochar. In addition to impacting some of the desirable properties of hydrochar, the addition of an acid during HTC can lead to chelation of insoluble phosphate into soluble forms through the addition of organic acids. Song et al. (2019) evaluated the removal of phosphorus by these acids and the quantities added and concluded that phosphorus was most effectively removed by oxalic acid (0.5–1.0 % addition). This highlights the need to investigate and optimize HTC for the desired applications of products or intended process uses.

27.3.6 Reaction Mechanisms

The conversion of biomass during HTC into the carbon-dense hydrochar at elevated temperatures and pressure is a complex network of reactions (Funke and Ziegler 2010). Significant experimental work has been undertaken to identify reaction mechanisms, and the relevant literature is in general agreement of the following reactions occurring under HTC condition: hydrolysis, dehydration, decarboxylation, condensation polymerization and aromatization.

An overview of the some of the reaction mechanisms during HTC are shown in Fig. 27.3 (Kruse et al. 2013), however, the exact details of which remain largely unknown when considering different biomasses due to the complexities and differences in their structures (Funke and Ziegler 2010). Observing Fig. 27.3, the biomass is assumed to be lignocellulosic (plant matter) of origin as it has been broken down into its three main components, which degrade at different temperatures; hemicellulose, which is significantly degraded at 200 °C, cellulose which degrades at 230 °C and lignin which begins to degrade at 260 °C (Jaruwat et al. 2018). As hemicellulose is a semi-crystalline heteropolymer, with a matrix of polysaccharides, and a lack of repeating β-(1–4)-glycosidic bonds (Reza et al. 2013a), it has little resistance to hydrolysis at relatively low reactions temperatures with reports of close to full

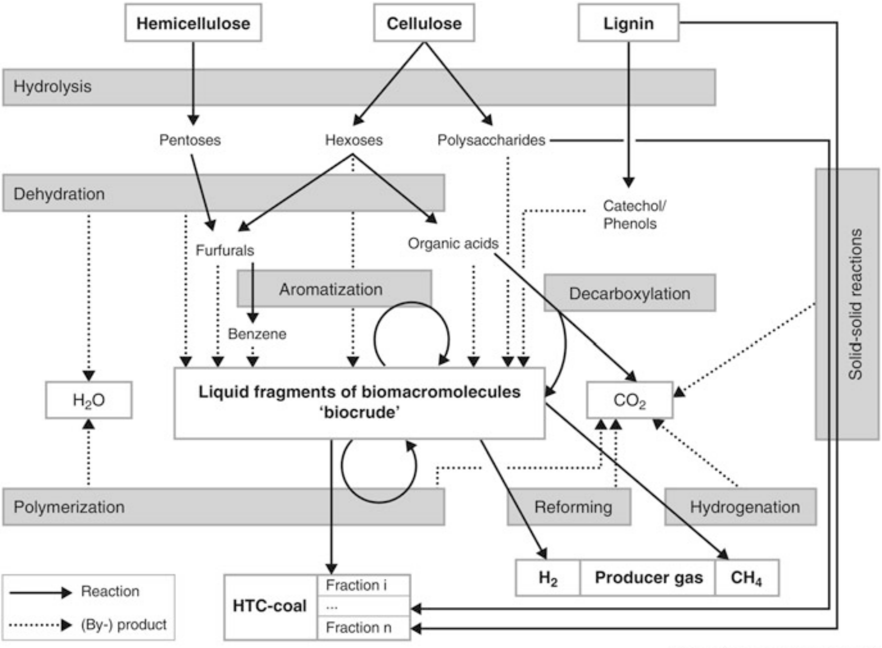

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Fig. 27.3 Principle reaction pathways of hydrothermal carbonisation Reprinted with permission from (Kruse et al. 2013). Copyright 2021 Elsevier degradation at 180 °C during HTC (Funke and Ziegler 2010; Román et al. 2018; Wu et al. 2017). The products from the hydrolysis of hemicellulose are first soluble oligomers before subsequently hydrolyzed into aqueous monomeric sugars (Reza 2011), such as pentose's. Alternatively, cellulose degrades at higher temperatures in a water medium due to its strong crystalline structure from β-(1–4)-glycosidic bonds and hydrogen bonds formed via hydroxyl groups (Paksung et al. 2020). Similarly, the hydrolysis of cellulose leads to soluble oligomers, which are further hydrolyzed into monosaccharides (such as hexoses) (Bevan et al. 2020). The addition of MgCl as a catalyst is thought to promote the acid hydrolysis of hemicellulose and cellulose from the presence of Cl- ions (for *Pinus radiata* (Carrasco et al. 2020)), leading to improved hydrochar properties (Fig. 27.2a).

The aqueous monosaccharides of hemicellulose and cellulose degradation proceed to follow a complex reaction path via dehydration and decarboxylation, referred to as the two major reaction mechanisms of HTC (Fakkaew 2016), which occur simultaneously (Reza et al. 2014). In which, dehydration of hydroxyl groups to form water molecules, furfurals and organic acids (such as lactic, acetic, formic, methane sulfonic, glutaric, succinic, maloic, maleic and oxalic acids (Hoekman et al. 2013)) which can occur at low temperatures of approximately 150–200 °C (Funke and Ziegler 2010). Conversely, this reaction significantly carbonises the biomass, reducing the O/C and H/C ratios to those similar to coal (Reza 2011). Alternatively, decarboxylation of the carbonyl and carboxyl groups existing on organic acids to produce minor concentrations of carbon dioxide and carbon monoxide at temperatures above 150 °C (Reza et al. 2014). Water circulation during HTC has been shown to improve the rate of dehydration and decarboxylation reactions (Lang et al. 2019), suggesting that these reactions are mass transfer limited. Furthermore, agitation has been shown to increase both mass and energy yields (Lang et al. 2019), thus highlighting the importance of agitation for effective large-scale production. The liquid fragments of bio-macromolecules that remain in the HTC reactor at elevated temperatures are very reactive and are believed to undergo a series of condensation polymerization reactions to form a solid residue (Román et al. 2018) forming a part of the HTC coal. This solid formation is been referred to as secondary char in a kinetic model proposed by Lucian et al. (2019a).

Alternatively, lignin is a more complex heterogeneous and aromatic biopolymer with ether bonds (β-O-4', α-O-4') and carbon linkages (β-β', β-5', 5-5') (Bauer et al. 2012). Lignin contains many aromatic rings making it extremely stable under the hot compressed temperature conditions of HTC, where it can be thought of as inert within a temperature range of 200–260 °C (Reza 2011), with structural modifications occurring above 300 °C (Atta-Obeng et al. 2017). Lignin is considered to be the basic building block of the hydrochar (Funke and Ziegler 2010), where during HTC the solid lignin and the solid fraction of cellulose which is not hydrolyzed into aqueous extractives are believed to undergo solid-solid (Kruse et al. 2013), dehydration and decarboxylation reactions to form the primary structure of the biochar (Román et al. 2018).

The composition of hemicellulose, cellulose and lignin varies depending on the type of plant and its cellular structure (Fajardo et al. 2015), thus adding to the complexity for understanding and modelling the reaction mechanisms during HTC. In addition, non-lignocellulosic feedstock's, such as sewage sludge, animal manure, algae and proteins (Li et al. 2020) (in food waste/animal matter) will have very different reaction pathways to those presented in Fig. 27.3. It could be argued that this lack of full understanding of the reaction pathways for different feedstock types could limit the usability of the technology, increasingly so when complexity's such as mass-production, optimization and predictability are desired. However, the growing interest in this field is leading to progressive developments towards the modelling of reaction pathways through kinetic (Keiller et al. 2019; Lucian et al. 2019a; Reza et al. 2013a), statistical (Heilmann et al. 2010; Sabio et al. 2016) and computation modelling. In this way, researchers are attempting to predict the outcomes for the conversion of different types of biomass feedstock and process conditions to propel the usability of the technology across a variety of industries.

27.4 Circular Economy: Products from Waste

27.4.1 Applications of Hydrochar

A biorefinery can be defined as the optimized use of biomass for materials, chemical, fuel and energy applications, where use relates to costs, economics, markets, yield, environment, impact, carbon balance and social aspects (Bridgwater 2013). On the other hand, a circular economy is an economic system aimed at eliminating waste and the continual use of resources. Therefore, by definition, a biorefinery, when reducing any waste biomass for the continual use of resources becomes an enabling factor in the realization of the circular economy. Hydrothermal carbonisation can be utilized as the vector of this realization for the processing of waste biomass into versatile and high-value products. In this section, different applications or upgrading opportunities of the solid hydrochar are explored, with limitations identified in order to reach an optimized circular economy that includes HTC.

27.4.2 Solid Biofuel

Hydrochar can be combusted as a fuel source as it has ideal energy densities and fuel ratios that can be compared to that of lignite or coal (Reza 2011). However, the conversion of (waste) biomass in to this energy-dense solid state results in the production of a *renewable* form of energy when combusted, unlike lignite and coal. Thus, when considering the realization of a circular economy of renewable energy it is unsurprising to learn that academic research papers containing both the terms 'hydrochar' and 'fuel' grew significantly between the years 2014–2019 (Vardiambasis et al. 2020).

As a solid fuel, hydrochar can be supplied for combustion in domestic biomass boilers or alternatively, it can be combusted through a biomass combined heat and power (BCHP) plant or even integrated within an existing combined heat and power (CHP) plants (Medick et al. 2017). This being said (and as can be inferred Table 27.2), the resulting energy content of the hydrochar formed during HTC is highly dependent on the type of feedstock and process conditions. Nevertheless, models have shown that the process can be net positive in energy when considering the energy demands of the plant (Bevan et al. 2020; Child 2014; Lucian and Fiori 2017). Beyond energy contents, there are additional benefits to utilizing hydrochar as a solid fuel, especially when compared to its originating biomass, for example, the uniformity of its structure allows for more efficient combustion with an improved slagging and fouling indices (Reza et al. 2014). In addition, solid fuels are inherently safer to transport than gaseous and liquid fuel mediums. That said, a disadvantage of using a solid biofuel includes the production of ash and the requirement for its logistical disposal. This could be through landfill, but an alternative approach is to utilize the ash as construction material or as a substitute for lime in acidified coal (Mahmoudkhani 2007). The latter options would be more in line with the principles of the circular economy.

Despite the beneficial fuel properties of hydrochar, in 2020, the terms ‘hydrochar’ and ‘fuel’ appearing in papers together decreased from its prior upward trajectory that was previously recorded over 2014–2019 (Vardiambasis et al. 2020). This could be the result from several limitations associated with the use of hydrochar as a solid biofuel. To elaborate, the cost of hydrochar, when sold for solid biofuel applications has been reported as 200 € tonne^{-1} (Ingelia SL 2021; Lucian and Fiori 2017), which is mildly competitive with wood pellets, the cost of which can range between 155–315 € tonne^{-1} (incl. VAT; 2018) depending on the European country and month of purchase (Bioenegry Europe 2019). By comparison, the limitation for hydrochar production is the capital and operating costs associated with its production. Furthermore, both of these renewable pellets are comparatively much more expensive than their fossil counterpart; coals market price valued at 87 € tonne^{-1} (June 2021) (Market Insider 2021). This is a significant increase since 2018 market price of 43 € tonne^{-1} (Volpe et al. 2018), yet the current economic standpoint does not favor the substitution to renewable hydrochar or woodchips, which is effectively limiting the drive towards a circular, net-zero economy.

This being said, an alternative driving force that could lead to an increase in the use of renewable solid fuels could result from the ban on the installation of gas boilers in new builds, which the UK government has set to commence in 2025 (EDF 2021). As renewable wood and hydrochar pellets can be used for low carbon domestic heating purposes within micro-CHP or domestic biomass boilers (Simple Energy Advice 2021), the market demand for these renewable solid-fuel sources may increase from this time in the UK. However, the phasing out of gas boilers in existing dwellings has not been proposed. In addition, alternative technology competitors in the domestic heating market, such as air source and ground source heating and solar panels (Simple Energy Advice 2021) may be more appropriate to implement within new builds, especially city-based apartments.

Alternatively, to using hydrochar for domestic heating, there exists the possibility of integrating the hydrothermal carbonisation process with a CHP plant for the industrial production of electricity and heat. The HTC-CHP integration has been shown to demonstrate several advantages over operating standalone HTC plants, such as increased plant operating times and reduced investment costs (Saari et al. 2016). However, the comprehensive life cycle assessments conducted by Medick et al. (2017) demonstrated that large scale HTC–CHP plant (urban, rural and rural-urban) capable of processing 55,000 tonnes yr.$^{-1}$ of green waste would be economically infeasible when using market prices for electricity and heat as 28 € MWh^{-1} and 30 € MWh^{-1}, respectively (Medick et al. 2017). This being said, hydrothermal carbonisation provides a renewable energy production technology and alternative opportunity for waste disposal, thus fitting holistically with the establishment of a circular economy. However, first to market technologies such as solar and onshore wind power have reached a stage in development where generation costs have fallen between 3 and 16% each year since 2010, with the newest farms undercutting the cheapest and least sustainable existing coal-fired plants (IRENA 2015).

Government support for renewable energy solutions continues to progress, however, at the current time hydrochar pellets for biofuel purposes are limited by their current market price, by its domestic market size and by competing domestic and industrial power generation technologies. Additional government support for domestic or industrial use of HTC or hydrochar pellets could improve the economics around its deployment and thus realization of this application, however, the application of HTC within the energy market may not be the most practical use of this technology and its product. Therefore, alternative applications of hydrochar where profitability is improved may be the answer to ensuring the successful deployment of the HTC technology and the realization of a circular economy.

27.4.3 Soil Amendment

One of the alternative applications of hydrochar could be as a soil conditioner where recent research has shown that hydrochar can provide essential nutrients to crops, where its polyaromatic structure can increase the carbon content of the soil (Busch and Glaser 2015). Soil conditioning is of significant importance due to the increasing depletion of nutrients and vitamins found in today's crops (Jones et al. 2013). What's more, hydrochar is able to act as a medium-term carbon sequestration material; Malghani et al. (2014) determined corn stover-derived hydrochar to have a half-life of 19 years (1 year after application) (Malghani et al. 2014).

Despite its potential to deliver essential nutrients, literature has reported that the application of raw hydrochar to soil can have a negative effect on plant growth due to the presence of phytotoxic substances (Kalderis et al. 2019; Puccini et al. 2018), such as volatile fatty acids (VFAs), polyphenols, sodium and chloride's (van Asselt et al. 2011). This could be indicative of its exclusion from soil standards (UK Soil Association 2021). This being said, Puccini et al. (2018) determined that ageing hydrochar by a year results in lower concentration of phytotoxic polyphenols and

VFAs. In turn, aged hydrochars (derived from municipal woody and herbaceous pruning) lead to improved germination and radical length of lettuce when compared to its raw, non-aged counterpart (Puccini et al. 2018). In an alternative method to remove phytotoxic compounds, Hitzl et al. (2018) determined that seed germination of 130% (representative of phytostimulation) could be achieved when processing food waste-derived hydrochar through a subsequent thermal treatment stage of 275 °C (Hitzl et al. 2018). These works present two beneficial towards the utilization of hydrochar for soil conditioner applications. However, the limitations that become apparent in the techniques established by Puccini et al. (2018) and Hitzl et al. (2018) are the requirements of storage space, or energy consumption and process equipment, respectively, and thus resulting in higher capital and/or operating costs. Another consideration for hydrochars application to agricultural lands is the extensive testing and research that would be required to ensure it does not result in phytotoxic effects on the growth of different crops, nor would it have long-term impacts on the natural ecosystem and cycles.

Alternatively, the main competitor to hydrochar when applied as a soil conditioner is biochar (product of pyrolysis) which is already included in UK standards (UK Soil Association 2021) and certifiable in Europe (European Biochar Certificate 2021). Literature reports that biochar does not have any phytotoxic effects on plant growth and therefore would not require a post-treatment stage, likely as the biomass is already thermal treated during the pyrolysis process. In addition, a 2 year long field study applying both char types determined that biochar would be more suitable as a soil conditioner than hydrochar as it can sequester carbon for longer periods of time (Busch and Glaser 2015). What's more, biochar for soil conditioner application has a current market price of 100 $ tonne^{-1} (Zhengzhou Zhongchuang Water Purification Material Co., Ltd. 2021) this is much lower than the reported 200 $ tonne^{-1} required to achieve a break-even-investment into HTC (Lucian and Fiori 2017). Not to mention, the additional post-treatment stages required for the modification of hydrochar to reduce/eliminate phytotoxic compounds will likely increase this value. This being said, further research within this field could lead to the development of a hydrochar capable of beneficial phytostimulation of crops, and thus improve crop yields and providing a competitive advantage, and higher market price when compared with biochar. Lastly, production costs could be made competitively cheaper over time as the technology matures and research within this area should continue to be supported. However, the carbon sequestration potential of both chars cannot be overlooked for this application given the global incentives. That said, at the present moment, hydrochars most valuable and profitable application maybe elsewhere.

27.4.4 Activation for Adsorption

The high carbon density of hydrochar makes it an ideal precursor material in the production of activated carbon (AC). AC is an extremely porous material that is traditionally manufactured from the activation of charcoal, wood (Danish and Ahmad 2018), bamboo or coconut husk (Jain et al. 2015). The large surface area ($>$1000 m^2 g^{-1}) of the pores makes activated carbon an extremely good adsorbent, with applications spanning both air and water purification methods for the extraction of pollutants and colours across a variety of industries, such as wastewater and pharmaceutical (Tadda et al. 2016). Thus, ACs are usually characterized by several physical parameters such as the surface area and pore volume and the adsorption characteristics such as the capacity and type of pores, such as the methylene blue number for determining mesopores and iodine number for micropores (Shrestha et al. 2021). In turn, these defining characteristics along with AC particle size (powdered or granular), ash content and impurities will determine the quality and overall marketable price of any activated carbon.

Activated carbon derived from hydrochar has been produced in the literature from a range of waste biomass streams, including but not limited to rattan (furniture waste) (Islam et al. 2017), almond shell (Ledesma et al. 2018), hickory and peanut hull (Fang et al. 2017), corn cob residue (Chen et al. 2017a), sucrose (Hao et al. 2016), sewage sludge (Simple Energy Advice 2021), green waste and municipal solid waste (Puccini et al. 2017) to name a few. The activation of hydrochar can be completed through different methods, such as physical activation, chemical activation or a combination of the two. Physical activation is performed by introducing an influx of gas into a pyrolysis chamber (temperature range 400–850 °C (Tadda et al. 2016)) in the absence of oxygen, or presence of gases such as nitrogen (Tasca et al. 2020), carbon dioxide (Miliotti et al. 2020) or steam (Ioannidou et al. 2010). Alternatively, activated hydrochar can be formed through chemical activation by using an acid, such as zinc chloride (Jain et al. 2015) and phosphoric acid (Fang et al. 2017), or a base such as potassium bicarbonate (Sevilla and Fuertes 2011), potassium hydroxide (Fang et al. 2017) or sodium hydroxide (Islam et al. 2017). As the name suggests, physio-chemical activation is the combination of the two methods, physical activation followed by chemical activation.

The production of activated hydrochar presents the opportunity to produce a higher-value end product when compared to biofuel and soil conditioner applications; the market price of activated carbons is 450 to 1786 \$ $tonne^{-1}$ which is highly dependent on the characteristics as outlined above. However, similar to the production of soil conditioner as defined by Hitzl et al. (2018), the production of AC from hydrochar would require an additional thermal treatment stage to reach the desired qualities. This would increase the capital and operational costs associated with an HTC plant, as would the use of chemical activation agent (Tadda et al. 2016). However, the market for AC is growing by 17.5% each year (Grand View Research 2019) and the higher costs could be offset by the greater potential revenues received from upgrading the hydrochar into activated carbon. Alternatively, recent research by Ledesma et al. (2018) into the in situ activation of hydrochar during HTC with air has been shown to improve the micro porosity of the hydrochar and the amount of surface oxides (Ledesma et al. 2018). This method would forego the need for a subsequent stage that requires energy, equipment and chemicals, however, the properties of the resulting hydrochar would need to reflect a profitable activated carbon.

As described, the market price for AC is dependent on the characteristics, which will differ depending on the method of activation, the processing conditions and the initial feedstock used. In turn, the limitation imposed by this application regards the research and knowledge in producing AC from different waste-derived hydrochars, the predictability of the characteristics and how to optimize the process(es) for the production of high-quality activated carbon. Given the higher revenue potential of activated carbon (when compared with soil conditioner, domestic and industrial biofuel applications), the directing of research and support to utilizing HTC as a precursor technology to produce AC from high moisture wastes could lead to an economically viable use of HTC. What's more, the repurposing of a waste stream into a high-value market product in this way would fit well within the circular economy model.

27.4.5 Activation for Electrode Material

A further application of activated hydrochar could be as a precursor for an electrode material, where its carbon structure and porous qualities have been attributed to desirable electrochemical performances (Gao et al. 2015). The use of biomass-based carbon materials in energy storage applications has been attributed to being of a cheap, abundant and sustainable alternative (Gao et al. 2015). However, research into the use of activated hydrochar for this application is comparatively new when compared with adsorption applications and its use for biofuel and soil amendment applications. This being said, early studies suggest that the repurposing of waste material into electrodes could be both possible and successful when using HTC, with waste materials such as orange juice (Veltri et al. 2020), coffee (Jung et al. 2020) and sewage waste (Gao et al. 2015) being previously explored.

Gao et al. (2015) performed chemical activation of glucose-derived hydrochar with potassium hydroxide and showed that the material had outstanding specific capacitance in a basic medium of KOH (Gao et al. 2015). In addition, the calcination (nitrogen enriching method) of the hydrochar prior to activation with KOH was trialled in an acidic medium of H_2SO_4, where it exhibited an even greater specific capacitance of 492 F g^{-1} compared to 279 F g^{-1} for a current density of 0.1 A g^{-1} in the respective mediums. Both types of activated hydrochars in this study demonstrated long-term stability with capacitance retentions of 97–98% over 1000 charge/discharge cycles at current densities of 1 A g^{-1} (Gao et al. 2015).

Alternatively, Fakkaew et al. (Fakkaew 2016) physically activated the hydrochars derived from glucose, rice husk and faecal sludge in an argon atmosphere, under different temperatures (300–1000 °C), for application as the anode in Lithium-Ion batteries. The glucose-derived activated hydrochar had the highest capacitance of 135 mAh g^{-1} when compared to risk husk and faecal sludge, which had capacitances of 100 mAh g^{-1} and 64 mAh g^{-1}, respectively. Fakkaew et al. (Fakkaew 2016) conclude that each material has potential within this application, however, the greater capacitance of physically activated glucose-derived hydrochar was linked to the higher fixed carbon content of the glucose hydrochars (Fakkaew 2016).

As shown, the specific capacitance of physically activated sewage sludge-derived hydrochar is comparatively low when compared with the glucose and rice husk-derived hydrochars trailed in this study (Fakkaew 2016). In turn, physically-activated sewage sludge-derived hydrochar may not make for the best precursor for an electrode material. As this is a relatively new research field for hydrochar application, more research is required in order to determine appropriate feedstock materials that can be used to derive a high-quality activated hydrochar for electrode applications. The same is true for the type of activation method used too; when comparing the physical activation of glucose-derived hydrochar as completed by Fakkaew et al. (Fakkaew 2016) to the chemical activation with KOH as trailed by Gao et al. (2015), the capacitance achieved is a lot lower for physical activation at 135 mAh g^{-1} (F g^{-1}) (Fakkaew 2016) and 492 F g^{-1} (Gao et al. 2015), respectively.

Current limitations to overcome within this application regard the amount of future research that is needed to determine the optimal waste streams to derive the most efficient and appropriate electrode material -in terms of specific capacitance and capacitance retentions- from activated hydrochar. In addition, the optimal activation methods (physical, chemical, physio-chemical) and conditions thereof should likewise be explored. Following which, the use of activated hydrochar as an alternative electrode material should be evaluated on its environmental impact and economic potential, this could be done through life cycle assessment modelling. The economic potential of this application should then be compared to hydrochars use for biofuel, soil conditioner and as a precursor to activated hydrochar for adsorption applications.

27.4.6 Catalyst

An alternative application of hydrochar can be as a catalyst, when activated (Chen et al. 2017b) or modified as a support through metal or metal oxide active sites (Renz 2017). In this way, hydrochar can act as a renewable catalyst for the synthesis of a range of materials and products. For example, Prasannan and Imae (2013) synthesized carbon dots from the orange peel-derived hydrochar and concluded their effective application in the degradation of Naphthol blue black azo dye under UV light radiation (Román et al. 2018).

There exists the opportunity to utilize hydrochar in the production of hydrogen, which would be of particular interest given the plans for the development of a hydrogen-based economy, such as the one proposed for the UK (Hinsen and Adcock 2020; Moreno-Benito et al. 2017). To elaborate, Gai et al. (2019) investigated the use of saw dust-derived hydrochar doped with nickel nanoparticles as a catalyst in the production of a hydrogen-rich syngas when using the gasification of biomass. In their study, the hydrochars were doped with different concentrations of well-dispersed nickel nanoparticles, which were subsequently trailed in a two-stage pyrolysis-gasification reactor system. The biomass used in the reactor system utilized sewage sludge as feedstock. High catalytic activity and selectivity for hydrogen production were found when compared to the baseline addition of non-doped hydrochar, with up to 109.2 g_{H2} $kg^{-1}{}_{sludge}$ and a reduction in tar yields as low as 2.12 mg g^{-1} (Gai et al. 2019). However, as the hydrothermal carbonisation of sewage sludge is more energy efficient than pyrolysis (Xiao et al. 2010), future investigations into an alternative two-stage reactor system consisting of 'hydrothermal carbonisation-gasification' could have an improved energy efficiency and hydrogen yield. It is unclear if this is a future research path of this group, but their research demonstrates the possible role of HTC in the development of a renewable hydrogen economy, be it by producing nickel doped hydrochar as a catalyst in the gasification of biomass, and/or if it can be optimally integrated with gasification. In this way, the use of HTC could lead to successful progressions in the development of a circular hydrogen economy.

The use of hydrochar as a catalyst or support thereof is limited due to it being a relatively new research topic. Therefore, in order to determine the effective use of HTC as a catalyst producer, or indeed within the hydrogen production industry, further research is recommended. In particular, the impact of different feedstock's as catalysts, the optimization of process parameters for desired characteristics of the catalyst, and the integration of HTC with gasification.

27.4.7 Process Water Applications

The process water resulting from the hydrothermal carbonisation of biomass contains a variety of constituents depending upon the feedstock and process parameters. This being said, the process water commonly consists of organic extracts such as acids (acetic, formic, levulinic and glycolic), hydroxyl-methyl-furfural (HMF) and total organic carbon (TOC), which increase in concentrations as reactor temperatures increase (Kambo et al. 2018). Recent research has demonstrated that recirculation of the process water will improve the overall process efficiency (Kambo et al. 2018), in turn this could increase the economic viability of the process whilst contributing in mitigating environmental impacts (Picone et al. 2021). Therefore, recirculation is highly recommended for improving the deployability of HTC. However, there exists a few alternative methods which can be utilized to create valuable product streams from the process water, which may likewise improve the economics and its deployability.

For example, the process water contains a large amount of nitrogen, potassium, organic carbon and small amounts of phosphorus (concentrations dependent on the feedstock and process conditions). In turn, the process water has the potential to be applied as an agronomic fertilizer (Xiong et al. 2019). However, it can contain varied levels of different heavy metals, with some concentrations exceeding the standard emission limits. For example, the process water resulting from the HTC of swine manure was found to contain excessive amount of zinc, lead, chromium and cadmium beyond those permissible by standards in China (Xiong et al. 2019).

This being said, reduction or passivation of heavy metal content in process water and/or dilution to reduce the amount of organic matter and nutrients within the process water (depending on respective levels) could be performed to allow permissible direct application to agricultural lands as a fertilizer.

Alternatively, and as described in Sect. 27.3.4, the use of organic acid catalysts during HTC can lead to the elimination of phosphorus from the solid product as insoluble phosphate is chelated to a solubilized form that remains in situ with the process water (Song et al. 2019). As phosphorus is a valuable resource in the agricultural industry for liquid fertilizer synthesis, the separation of phosphorus from the process water has already moved beyond lab-scale and into the HTC process offered by technology provider TerraNova Energy GmbH. In their process, phosphorus can be separated from sewage sludge into the liquid-phase and can be used for fertilizer applications (TerraNova Energy LTD 2021). As sewage and manure waste are phosphorus-rich biomass waste streams, most HTC studies (Heilmann et al. 2014; Pérez et al. 2021; Song et al. 2019; Xiaoyuan et al. 2020) or industrial applications (TerraNova Energy LTD 2021) concerned with phosphorus extraction are targeted at these waste streams.

As opposed to TerraNova's recovery of phosphorus, the HTC process developed by C-Green GmbH can recover up to 80–90% of the nitrogen in the process water, containing 60% of the total nitrogen content, through ammonia stripping (C-Green 2021). Likewise, to phosphorus, ammonia is a high-demand product within the agricultural industry and HTC provides a renewable alternative for its production and added-value benefit to the HTC process. Other methods of circular use of process water include recirculation to anaerobic digestion to improve methane yields (Danso-Boateng et al. 2015; Shrestha et al. 2021), algal cultivation, bioelectrical system and supercritical water gasification (Usman et al. 2019).

27.5 Limitations in the Field

Although significant advancements have been made in the hydrothermal carbonisation field over the past two decades, there are certain limitations within it that need to be addressed, or at least understood, if deployment is to continue on a mass scale. To summarize, these the are capital and operation costs of the process, the knowledge surrounding the process and the different applications, employing the most practical application of hydrochar at the present moment, and competing with other thermochemical conversion and/or energy-producing processes. Each of these is detailed further in this section, along with potential solutions.

27.5.1 Capital and Operational Costs

The capital costs of an HTC plant, like any process plant, can be expected to be of a significant sum, more so given that it is a new technology. Of course this amount will depend upon the size of the plant and process equipment, but for an example, a total capital investment of £1,773,811 and an annual operating cost of £832,984 has been estimated by Lucian and Fiori (Lucian and Fiori 2017) for a plant capable of producing 5317 tonnes of hydrochar per year. If this capital expenditure is loaned, than additional interest rates will be incurred, typically at 5% (Lucian and Fiori 2017). Alternatively, investment will need to be secured from investors looking to establish—or company's looking to integrate—a HTC plant, which will require a decent return on investment. This being said, as HTC is a new technology, government and institutional support are likely to be required for the deployment of this technology as potential investors could be deterred if perceived as a high financial risk. In this way, a reduction in capital costs as a means to support the carbon abatement associated with HTC would reduce the financial risk for early investors, encouraging deployment and development.

The annual operational costs could also be limiting when it comes to the deployment of this technology. The operational costs mainly consist of power (gas and electricity) if externally sourced (Sect. 27.2.3), labour (Lucian and Fiori 2017) and transportation of waste (Medick et al. 2017). Methods to reduce the operational costs could be through eliminating transport of waste by targeting centralized waste-producing industry's (sewage sludge, paper and pulp, anaerobic digestion, food production plants), through modifications to the underlying technology, such as the incorporation of a solar disc (Ischia et al. 2020) to remove the need for a fuel source and its associated process equipment, the recycling of process equipments or through the automation of labour roles where possible.

To better face this limitation, applications in this early deployment stage would be most suited to those which are most economically viable, to improve the return on investment and reduce financial risk. To elaborate, this would be through integration with centralized, established industries that produce a large mass of wet biomass waste that would be better utilized through HTC compared to current practices. In addition, the production of hydrochar and process water into the most high-value, profitable products would be most appropriate at this time. Alternatively, developing the technology to be cost-effective for smaller scale applications would reduce both operational and capital expenditure but may have different implications on profitability (Tradler et al. 2018). The development of kinetic and process models to predict the feasibility of HTC integration would be extremely beneficial for aiding this technologies deployment within these industries.

27.5.2 Knowledge Surrounding HTC and the Different Applications of Its Products

As detailed in Sect. 27.4, the financial and non-financial support from governments and institutions have led to the expansive knowledge of this technology thus far. With investments from academics and technology developers in the industry, research continues to unearth the potential use of waste-derived hydrochar. However, as HTC is a relatively new technology, the deployment of it could be limited by the lack of full knowledge and understanding of the process regarding the reaction mechanisms and the viability of the different product applications. As HTC can form an integral part of the modern circular economy, research to acquire such knowledge, and support thereof, is required, and the following discussion identified areas for future research.

One such area of research is the mathematical modelling of the HTC process and the reactions that take place in order to establish relationships between a product property and the process conditions (time, temperature, solid loading). This would allow for the optimisation and predictability of the product properties, allowing for the processing of different feedstock's and eventual hydrochar applications to be better understood before investment. This would reduce the risk for investors and allow the economic feasibility to be fully understood.

In terms of alternative product applications, research into the application of thermally treated (Hitzl 2012), aged hydrochar (Puccini et al. 2018) and biochar could be investigated for their comparative growth impact on a range of different crops. In addition, each should be modelled for environmental impacts and economic feasibility, along with carbon sequestration potential in order to determine the most appropriate method to utilize when repurposing waste biomass as a soil conditioner.

Alternatively, research into determining an optimized activation method for the hydrochars derived from different wastes should be continued. In addition, the predictability of the product properties of activated hydrochars would allow for efficient economic evaluation of the HTC–AC process given that the market price of AC is highly dependent upon these. This would similarly be the case for the use of activated hydrochars as a catalyst and as a super electrode material. In addition, deployment of the HTC technology could be improved by supporting research efforts investigating its potential role in a hydrogen economy (Sect. 27.4.5).

Deployment could be supported through conducting large-scale economic and life cycle assessment reports for the different applications of hydrochar and the process water products in order to ensure an efficient use of this technological resource within a circular economy. Lastly, support for research areas that could reduce the capital and operational costs should be continued, such as the integration of a zero-energy solar parabolic dish concentrator as trailled by Ischia et al. (2020), or the in situ activation of hydrochar as investigated by Ledesma et al. (2018).

Furthermore, non-financial support mechanisms such as the creation and dispersing of educational content regarding HTC could be used in order to progress the understanding and abilities of this technology to the wider population. In this way, the alternative applications of HTC and its products can be effectively communicated to a wide range of different investors and/or consumers. To conclude, the solution to this limitation is through continued research and support for research, development and deployment.

27.5.3 Economically Viability of HTC and Hydrochar

In order to ensure that HTC does not become limited by its economic viability in one area or application, and that it is successful in the market, the most economically viable method at the present moment needs to be established. In knowing such, government/institutional support and/or external investors will be more likely to support/invest. This point ties in with Sect. 27.5.2 as economic modelling is required in order to determine the most feasible application.

To elaborate, Fig. 27.4 depicts the past, present and possible future market curve that can be associated with hydrothermal carbonisation[2] over its timeline since modern day rediscovery in 2005 (Nicolae et al. 2020). As depicted, it is likely that in 2021, hydrothermal carbonisation is situated within the trough lying between the ‘facing reality’ and potential future curves. It can be thought that HTC resides somewhere within this trough, given the results of recent studies that demonstrate the economic infeasibility of the technology when used for energy production, mainly as a result of the high capital and operational expenditures (Medick et al. 2017; Saari et al. 2016). As shown, there are three potential trajectories from this point; ‘lift-off’, ‘no market growth’ and ‘failed market growth’. In order to achieve ‘lift-off’ to the ultimate market opportunity of this technology, the most financially feasible application of HTC, its hydrochar and its process water needs to be identified, promoted and encouraged. In this way, HTC technology can be deployed to such applications, whilst overtime demonstrating that it is not a high-risk investment, but a highly profitable one. With this, deployment within the market increases, the technology is continuously developed and improved, the possibility for the costs associated with hydrothermal carbonisation begins to decrease, and full market opportunity can be achieved (‘lift-off’ to other HTC and hydrochar applications).

As described in Sect. 27.5.1, the reduction of capital and operation costs for any HTC application needs to be overcome. In targeting centralized waste-producing plants to integrate HTC, this could allow for improved economic viability, and thus initiate a potential ‘lift-off’. Simultaneously, the most profitable use of the product streams should be determined and pursued at this time, highlighting the importance for research within economic and mathematically modelling of the process to be continually supported (Sect. 27.5.2).

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[2] This has been curated in line with the general market curve trends that can be followed by new technologies (Technology 2012)

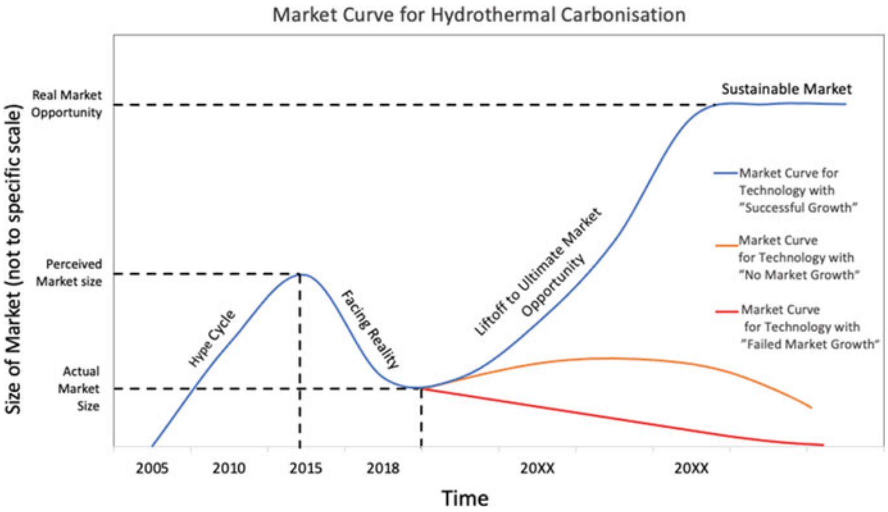

Fig. 27.4 Market curve for new technologies as conveyed by (Technology 2012) applied to hydrothermal carbonisation

A preliminary economic modelling study comparing the revenues generated from different applications of a hydrochar derived from sewage and food waste produced by a small town has been investigated (Bevan et al. 2021). The applications assessed were as a soil conditioner, as a precursor in the production of activated carbon and as a biofuel used in domestic biomass boilers and in a combined heat and power plant. In this study, it was found that hydrochar used to produce activated carbon could generate the highest potential revenue upon activating all (not using any hydrochar for internal energy production) the hydrochar. However, it should be noted that the value of the activated hydrochar would be highly dependent on the characteristics of the final product, with a revenue range of 10,372–41,162 £ year^{-1} being estimated for the 32.01 tonnes year^{-1} of activated hydrochar produced. In addition, a full capital and operational costing methodology was not completed in this study. Future research to into the full economic modelling of this application and its comparison with others is recommended due to the additional process equipment required for activation. Nevertheless, this could provide an indication of the likely most profitable hydrochar application business model to proceed with at this time in order to achieve ‘lift-off’.

Therefore, it is recommended that in order to ensure that HTC is not limited by economic infeasibility in certain applications, further research into the economic potential for a range of industries and product applications ought to be completed in order to propel ‘lift-off’ within the market. It should be noted that although economics plays a large role in the success of new technologies in capitalist societies, it is not the sole driver to its success as the value-added to the specific industry or application of its products will play a huge role in its ‘lift-off’ potential over the coming years.

27.5.4 Competing with Other Technologies and Products

As a waste conversion process, hydrothermal carbonisation is in competition with the other biomass conversion processes mentioned in this book, this includes gasification, torrefaction, liquefaction, pyrolysis and anaerobic digestion. Comparatively, HTC is the newest technology to be established, which can have both beneficial and consequential associations. The consequence of being the newest technology is that the competing technologies are more established and proven, thus swaying potential investment to their deployment. In addition, as the technologies have been around longer, they are likely to have comparatively lower associated costs, again motivating investors towards the competing technologies.

This being said, the beneficial unique selling point that hydrothermal carbonisation has over its competition is its ability to efficiently convert high moisture wastes (up to 70–95% (Libra et al. 2011)). This is because in comparison, dry pyrolysis, gasification and torrefaction are unlikely to be driven economically with feeds that have a moisture content above 50–70% (Libra et al. 2011). Therefore, in order to circumvent the limitation of competing for market share, HTC technology providers would be best to target industries generating large volumes of high moisture wastes as its greater efficiency could lead to greater savings. This includes waste streams such as sewage sludge, paper and pulp sludge, municipal food waste, wet agricultural wastes, etc. In addition, the integration of HTC with gasification (for producing hydrogen (Gai et al. 2019)) or anaerobic digestion to improve methane yields (Danso-Boateng et al. 2015) could progress HTC deployment somewhat synergistically with its competitors. Therefore, techno-economic and life cycle assessment studies are recommended to determine the thermochemical conversion process most in line with the principles of the circular economy when utilizing different biomass wastes.

Another limitation comes forth when considering hydrochar and its competition within each potential application. To elaborate, the application of hydrochar as a solid fuel is limited by its competing renewable energy-producing technologies which are well established in the industry. For large scale energy production in a biomass combined heat and power plant, competing technologies include solar panel and wind turbine farms which, as previously described, have reached a stage in development where generation costs have fallen between 3 and 16% each year since 2010, with the newest farms undercutting the cheapest and least sustainable existing coal-fired plants (IRENA 2015). Alternatively, use in domestic heating would have competition with natural gas boilers and under ground and air heating. In addition, future competition is likely imminent in the form of hydrogen boilers if a hydrogen-based economy with plans for homes integrating such come April 2021 in the UK (Heatable 2021). The solution to using hydrochar for energy would require a significant capital investment which is unlikely given the support for hydrogen. In conclusion, the competition within the energy production industry is limiting the application of hydrothermal carbonisation in this sector.

Alternatively, the application of hydrochar as a precursor to activated carbon will need to compete through having improved or similar adsorption properties and/or product qualities when compared to those when using traditional AC precursor materials, such as charcoal, coconut husk or bamboo. Alternatively, a HTC - AC process could compete with these through offering a lower price per unit mass or identifying its unique application potentials, including as a catalyst or electrode material. Similarly for the application of hydrochar as a soil conditioner, the price must be both non-determental to the environment and competitive with those that already on the market including biochar (product of pyrolysis) in order to compete and be successful. Alternatively, proof of phytostimulation for high-demand crops could indicate a competitive advantage and thus justification of higher market prices.

27.6 Conclusion

Hydrothermal carbonisation can be utilized as the vector towards the realization of a circular economy with its unique ability to efficiently process high moisture waste streams into versatile and high-value products such as activated carbon and phosphorus. It is a unique thermochemical conversion process given its ability to efficiently convert biomass in an aqueous medium, serving as its beneficial unique selling point and competitive advantage. At the current level of technology, the main limitations associated with hydrothermal carbonisation are the high capital and operating costs limiting the deployment potential and economic feasibility of the technology; the knowledge surrounding HTC and the suitability of its products applications; the economic viability of HTC and hydrochar, and; competing with other technologies and products.

To overcome these limitations, hydrothermal carbonisation would be best explored for its application in industries with a centralized plant creating a large volume of wet waste biomass. This could include wastewater treatment, anaerobic digestion plants or the paper and pulp and food manufacturing industries. In doing so, this could improve capital and operational expenditures, improving profitability/economic feasibility, allow for increased deployment and proof of application/project success.

The product streams resulting from hydrothermal carbonisation are proving exceptional versatility across a variety of applications. As a biofuel, hydrochar has improved fuel properties over its originating biomass, such as increased homogeneity, increased friability, higher HHV and reduced slagging potential. However, the competition in the domestic heating (wood chip, coal, solar, air and ground pump) and renewable industrial energy market (solar and wind) suggests the break-even price of hydrochar for use as a solid biofuel (or its derived energy) is less competitive. Likewise, hydrochar as a soil conditioner would need to compete with biochar in terms of environmental impact, crop impact and carbon sequestration. Activation of hydrochar for its application as an adsorbent, catalyst or electrode material could be of greatest economic opportunity at this point and would therefore be more beneficially explored at this time to ensure the successful development and deployment of HTC in the realization of circular economy. In addition, its process water could be extremely beneficial for reclaiming phosphorus, a critically raw material required by the agricultural industry.

Research efforts and support into HTC and its products applications should be continued, specifically into the mathematical modelling of the process for its optimization and predictability of product properties to effectively determine the most feasible feedstocks and product applications.

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Chapter 28
A Comprehensive Outlook to Hydrothermal Liquefaction Technology: Economic and Environmental Benefits

Rogelio Cuevas-García, Isaac Nava-Bravo, and Aline Villarreal

Abstract Production of biomass-based fuels is an urgent research topic due to its value in decreasing our dependence on fossil fuels and, at the same time, diminishing CO_2 emissions. Hydrothermal liquefaction (HTL) can employ various biomass and generate bio-oil (or biocrude) to produce fuels utilizing water as a solvent and reaction medium.

This chapter first provides an overall view of HTL to obtain biocrude focusing on the chemical reactions that occur during HTL for different biochemical compounds and later a view on biomass processing by HTL discussing the effect of pressure, temperature, catalyst, and solvent on the bio-oil yield and products distribution. Also, we included the contribution of HTL processing in the circular economy, presenting its benefits in processing nonconventional feedstocks and using a life cycle analysis approach. Finally, to offer a complete outlook we address the processes needed to convert biocrude from HTL to biofuels such as biodiesel or jet fuel.

28.1 Introduction

Today, human society has become accustomed to a particular lifestyle. Activities like "gourmet" food eating, leisure, and transportation, among others, increase the energy consumption for both industrial production and residential use. Figure 28.1 shows a distribution of the sources of energy that humanity consumes. Nowadays,

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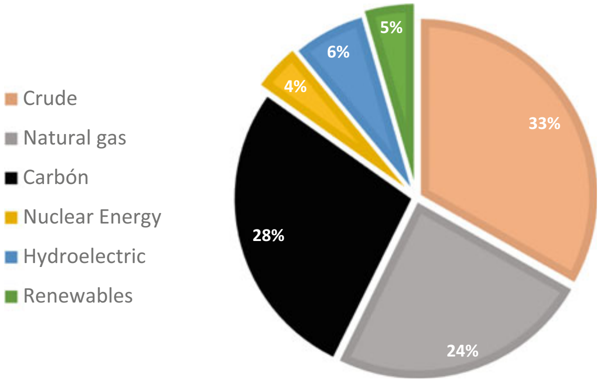
Fig. 28.1 Distribution of energy consumption by source type. Made with data from the international magazine of BP group (BP Group 2020)



the main amount of energy is originated from fossil sources with a contribution of 33% of crude and 24% of natural gas, while renewable sources reach up to 5%.

Energy is realized from fossil fuels through combustion, which emits CO_2 and water. Carbon dioxide is the principal contributor to global warming, increasing the average temperature on the earth's surface. Worldwide governments have tried to limit CO_2 emissions to the atmosphere, signing agreements such as the Kyoto Protocol (United Nations Framework Convention on Climate Change 2008) or the Paris Protocol (United Nations Framework Convention on Climate Change 2015) created with the primary purpose of maintaining the temperature increase below 2 °C, relative to the pre-industrial level.

It is necessary to limit the emissions of CO_2, but to change the actual human lifestyle is challenging. The circular economy has emerged as an alternative to a linear consumption pattern. At its core, the circular economy promotes using renewable and regenerative commodities and tries to maintain the value of final materials. This offers a new framework, in which waste is seen as a resource to be processed in various ways and even as an energy source, replacing fossil fuels, with the aim of decreasing greenhouse gas emissions (Tomić and Schneider 2018).

In this regard, the use of hydrothermal liquefaction (HTL) to obtain biocrudes is in line with the principles of the circular economy. As is displayed in Fig. 28.2, a biomass (e.g., microalgae) can grow in wastewater and sequester carbon dioxide during their photosynthesis process. Since HTL is versatile, it can use many biomass feedstocks. Besides the production of bio-oil, the solid residues after HTL processing can become activated charcoal (biochar), which can be beneficial to soils, and the residual water can be used to grow more algae or as a solvent in the HTL process (Mahima et al. 2021). Thus, HTL is considered a reliable and efficient process to convert biomass into bio-oil (He et al. 2020).

Fig. 28.2 Circular aspects of bio-oil production from microalgae

28.2 Hydrothermal Liquefaction (HTL)

28.2.1 The HTL Process

According to Anastasakis et al. (2018), early reports on HTL were published in the 1970s–1980s, some of them concerning pilot-scale facilities (PERC and Albany facilities). However, in the last ten years HTL investigations have been carried out, mainly, in small-batch reactors. HTL, also called hydrothermal upgrading, hydrothermal processing, and direct liquefaction (Xiu and Shahbazi 2012), is a thermochemical process that allows the conversion of biomass to liquids, generally carried out in the absence of oxygen and in the presence of a solvent, most of the times water. The fact that water is both solvent and reactive gives the HTL an advantage over other processes. As water does not need to be removed from the feed, a previous dehydration step can be avoided decreasing the associated energy costs. Other solvents can be used, for example, methanol, ethanol, propanol, or other organic solvents; if this is the case, then the process is called solvothermal liquefaction.

The biomass conversion starts by breaking the polymeric structures, typical of biological compounds, at temperatures between 520 and 647 K and pressures from 10 to 25 MPa generally autogenerated by the solvent (Garcia Alba et al. 2012; Singh et al. 2015; Tian et al. 2014). The products are gases, solid, a liquid aqueous phase containing some polar organic compounds, and a liquid organic phase. Although the gas and aqueous phases have some intrinsic value, the main product is the organic liquid phase called bio-oil, biocrude, or biocrude oil. Biocrude has various properties similar to fossil crude oil with a slightly lower energy value. Fig. 28.3 shows the comparison between FID chromatograms of fossil crude (Alonso-Ramírez et al. 2019) versus a biocrude obtained when processing microalgae by HTL (Nava Bravo et al. 2019). The so-called fishbone feature corresponding to the saturated alkanes is evident in the fossil crude chromatogram. As can be seen, the bio-oil is a complex

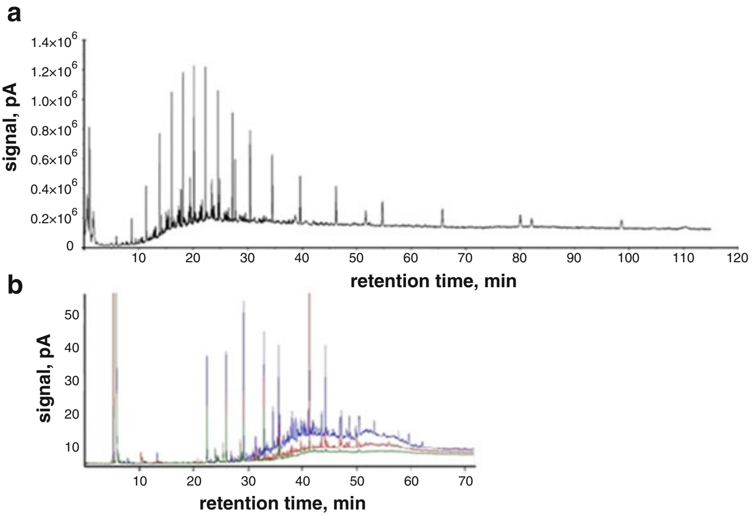


Fig. 28.3 Comparison of chromatograms between fossil crude and bio-oil obtained when processing microalgae

mixture of hundreds of organic compounds; in it can be found alkanes, alkenes, isomers, aromatics, and nitrogenated and sulfurated compounds. Also, the biocrude chromatogram shows the presence of compounds heavier than the fossil crude (longer retention times).

The aqueous phase contains several compounds formed by carbon, nitrogen, and phosphorus. Due to its composition, this aqueous phase is adequate as a growing medium for microalgae. Also, this aqueous phase can be treated anaerobically (preferably if it has a low content of phenol and furfural) or by catalytic gasification to produce synthesis gas (Gollakota et al. 2018).

The solid phase, obtained after HTL, can be seen as renewable carbon material, biochar, with suitable properties for different uses, such as combustion, gasification, electricity generation, water purification, or activated carbon production. This biochar contains residual nutrients and may be used as a soil fertilizer. It has been reported that the use of biochar along with other biomass can increase the methane yield in anaerobic digestion (Ponnusamy et al. 2020).

HTL can process, in principle, any biomass, i.e., microalgae, wood, straw, crops, crop residues, aquatic plants and their wastes, animal or municipal wastes, and even manure. This flexibility in the feedstock has developed high expectations for this process, but, from all these feedstocks, the use of microalgae stands out.

28.2.2 Biochemical Compounds in Biomass

This section describes the biomass composition in terms of the amount of each biochemical compound (lipids, proteins, and carbohydrates) to advance and explain its relation to the different reactions during HTL. Finally, an intent to describe the reaction mechanism is presented.

28.2.2.1 Lipids

Lipids are diverse organic compounds, including fats, oil, and hormones (Thompson 2020). The functions of lipids are energy storage, acting as a structural component in the cell membrane, and signaling. Among the lipid classes are triglycerides, wax esters, phosphoglycerides, sphingolipids, and sterols. Triglycerides are the components of fat. A wax ester is a fatty acid linked through an ester oxygen to a long-chain alcohol; these compounds store energy, especially in plankton. The membranes of cells and organelles are thin structures formed with two layers of phospholipids, sphingolipids, and sterols molecules. In the cellular wall, the most abundant class of compounds are glycerophospholipids. Sphingolipids in the form of glycosphingolipids are found on the external surface of the cell membrane, where their sugar moieties often act as antigens and as receptors for hormones and other signaling molecules. Sterols are a primary constituent of hormones; cholesterol is one of the most recognized sterols. With this information, the chemical atoms in the lipids are, mainly, C, H, O, and in lesser quantities P.

28.2.2.2 Proteins

According to Casem (2016), proteins control every aspect of cellular life. Proteins are polymers of amino acids, and their 3D structure dictated their function, so the dynamic properties are based on protein amino acid sequence. The term amino acid is short for α-amino carboxylic acid (Reddy 2020). An amino acid is constituted by a basic amino group (-NH_2), an acidic carboxyl group (-COOH), and an organic R group (or side chain) that is unique to each amino acid. Proteins provide many of the structural elements of a cell, and they help to bind cells together into tissues. Proteins, in the form of antibodies, protect animals from disease. In addition, proteins act as enzymes to control almost every reaction in a biological cell. From the chemical perspective, proteins are constituted by C, H, O, and N.

28.2.2.3 Carbohydrates

Carbohydrates are compounds that contain C, H, and oxygen. Their general formula is $(C_x(H_2O)_y)_n$ (Davidson 2020). The most important function of carbohydrates is to provide energy to the cell; also they have a structural function. The main classification of carbohydrates is based on the number of molecules in the carbohydrate; thus, five major carbohydrates groups are identified: simple carbohydrates, disaccharides, oligosaccharides, and polysaccharides.

The simplest carbohydrates are monosaccharides or sugars, with a general formula of $C_6H_{12}O_6$, such as glucose, fructose, and galactose. Two molecules of simple sugars produce a disaccharide, for example lactose, saccharose, maltose, and cellobiose.

If a carbohydrate is composed of three to six molecules of simple sugars, it becomes an oligosaccharide. Structural functions are related to the polysaccharide molecules.

The most common polysaccharide in nature is cellulose; it is the main structural component in the cellular wall of plants. Cellulose is a crystalline compound, mechanically robust, and resistant to hydrolysis. Cellulose is a polymer of glucose, formed by β-1,4 glycoside linkage of D-glucopyranose units, and its general formula is $(C_6H_{10}O_5)n$ ($n \sim 100{,}000$) (Cao et al. 2017; Song et al. 2020a). It is a nonpolar compound at room temperature and its solubility increases at higher temperatures (Gollakota et al. 2018). In the plant cell walls, there is also hemicellulose. While cellulose is composed exclusively of glucose, hemicellulose can contain other sugars (5C and 6C) such as xylose, glucose, mannose, and lactose (Cao et al. 2017). Hemicelluloses have a random, amorphous structure with low mechanical strength, and they can be easily hydrolyzed by dilute acid or bases. Glucose-based polysaccharide biomolecules are starch and glycogen. Green plants produce starch, and animals, fungi, and bacteria produce glycogen. Generally, hemicellulose of herbaceous plants is composed by xylan, while woody plants contain mannose, glucose and chitosan, glucan and galactan (Cao et al. 2017; Gollakota et al. 2018; Song et al. 2020b). Finally, lignin is an aromatic biopolymer synthesized using phenylpropanoid precursors (Cao et al. 2017; Saidur et al. 2011). The calorific energy content of the biomass, mainly, is given by the lignin in comparison with the cellulose and hemicellulose (Gollakota et al. 2018).

28.2.3 Reactions on the HTL Process

28.2.3.1 Processes at Meso-Micro Scale

The reaction scheme of HTL is very complex, and several research groups are working in this field. For the description of what happens during HTL or solvolysis, one must be looking at various scales.

Figure 28.4 shows a simplified proposal for the biomass reaction, in this case, oriented to microalgae. As a first step, destruction of the biomass cells occurs at the mesoscale level (mm). On microalgae cells, the solvent or/and temperature causes the rupture of the cell wall liberating the cellular organelles. Cellular walls are a bilayer formed by a fairly regular two-dimensional lattice, but at high temperatures,

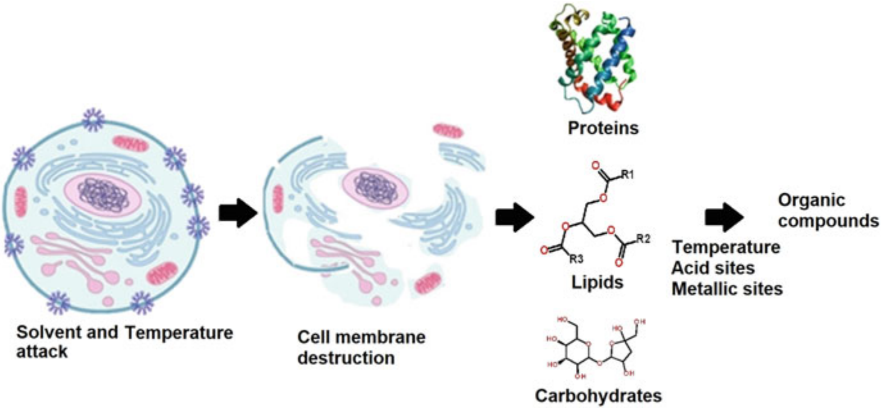


Fig. 28.4 The reaction of HTL from micro to chemical scale

the lipids that constituted the wall are free to rotate about their long axes and slide laterally through the layer. Their acyl chains now undergo considerable motion, leading to transiently kinked conformations. These motions give the bilayer a quasi-liquid behavior (Thompson 2020). At the same time, temperature led to a change in density and generates some pressure inside the cellule. The result is the rupture of the cellular wall. The cellular wall of biomass from plants can also be debilitated by hemicellulose extraction, which can be achieved, for example, with hot water extraction (Tunc and van Heiningen 2008), or with lightly acid or basic solutions.

In the conditions of the HTL process, the next step occurs at microscale. After extraction of the cellular organelles, these are destroyed to liberate proteins, lipids, and carbohydrates. Then at nanoscale, there is denaturing of proteins, depolymerization of carbohydrates, and cracking of lipids. These chemical reactions generate organic compounds. The organic compounds go through many reactions (see next section). All these possibilities give a mixture of chemical compounds that we call bio-oil or biocrude. Another possibility is the generation of biochar. In the end, the quality of the bio-oil depends on the biomass feedstock.

28.2.3.2 Chemical Reactions in the HTL Process

In addition to the complexity of the reactions in the HTL, there is a great variety in the type of biomass used as feedstock and every kind of biomass contains a different bio-compound composition. Another obstacle is the fact that several reactions occur simultaneously, among them cracking, condensation, decarboxylation and decarbonylation, cyclization, for some cases depolymerization, and for other molecules polymerization, and/or carbonization. There is also the possibility of oligomerization of some simple molecules to form compounds with an ample range of molecular weights. In addition, the operation conditions (temperature and pressure) must be considered. So the reaction process is not known in detail, but numerous attempts have been made to describe the whole process. As the first step to comprehend this complicated landscape, the behavior during HTL of each bio-compound has been studied separately.

28.2.3.2.1 Lipids

Lipids are the biochemical compounds in biomass that give a higher yield to bio-oil. Teri et al. (2014) reported that sunflower oil reaches a biocrude yield of 90% and no solid at all. During the HTL process, lipids are hydrolyzed into one glycerol molecule and three fatty acid molecules; then, reactions (e.g., decarboxylation) transform them into alkanes, alkenes, besides, fatty acids, amides, cyclic compounds (Xu et al. 2018), alcohols, as well as aldehydes. Figure 28.5 shows a proposal for the reactions occurring in the HTL of lipids.

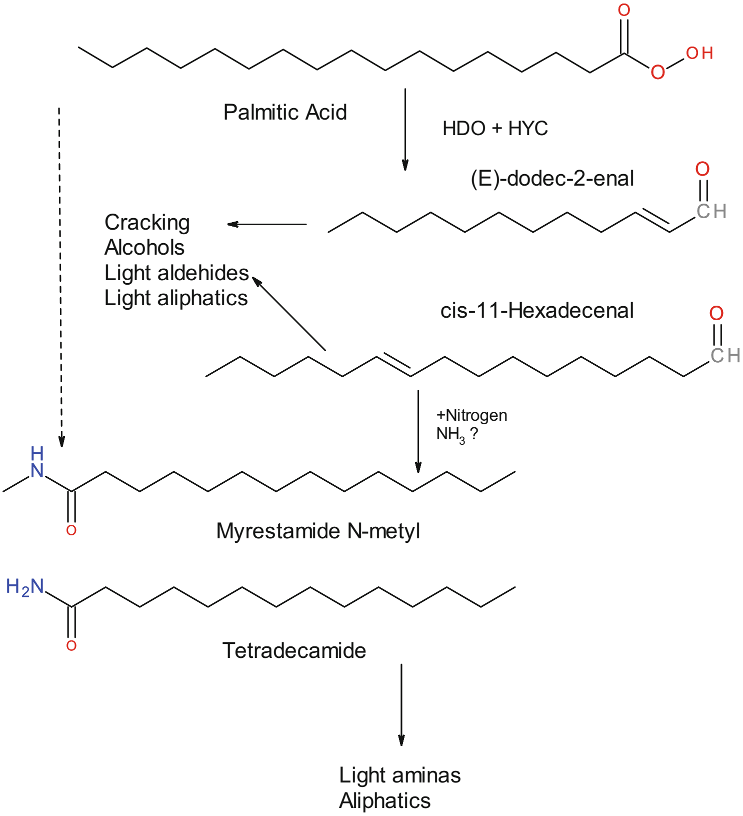


Fig. 28.5 Reaction of the lipids from (González-Gálvez et al. 2020)

28.2.3.2.2 Proteins

Abdelmoez et al. (2010) reported that when HTL is carried out in subcritical conditions, the first step involves the unfolding of proteins, followed by their separation into polypeptides that, in turn, can be broken down into lower molecular weight products. Another part of the proteins forms a solid, non-water-soluble material. The path of decomposing amino acids is very complex, so reactions such as dehydrogenation/cyclization, decarboxylation/deamination, dimerizations, dehydration, dehydration/reduction, and Maillard reactions were reported (Leng et al. 2020). Proteins contribute to the production of biocrude, which increases depending on temperature, at the expense of the waste (Yang et al. 2015). The HTL (300–350 °C, 20 and 60 min) of albumin and soy protein showed a ~ 30% yield of biocrude. Proteins also contribute to the formation of gases (Teri et al. 2014). The final product of the breakdowns is NH_3, nitrites, and nitrates (Arauzo et al. 2019). When NH_3 is released, it can react with fatty acids, which suffered decarboxylation, producing fatty acid amides (Xu et al. 2018). A possible reaction pathway of protein reaction and oriented to the final nitrogen chemical compounds was reported by Leng et al. (2020). Fig. 28.6 shows a very simplified reaction scheme.

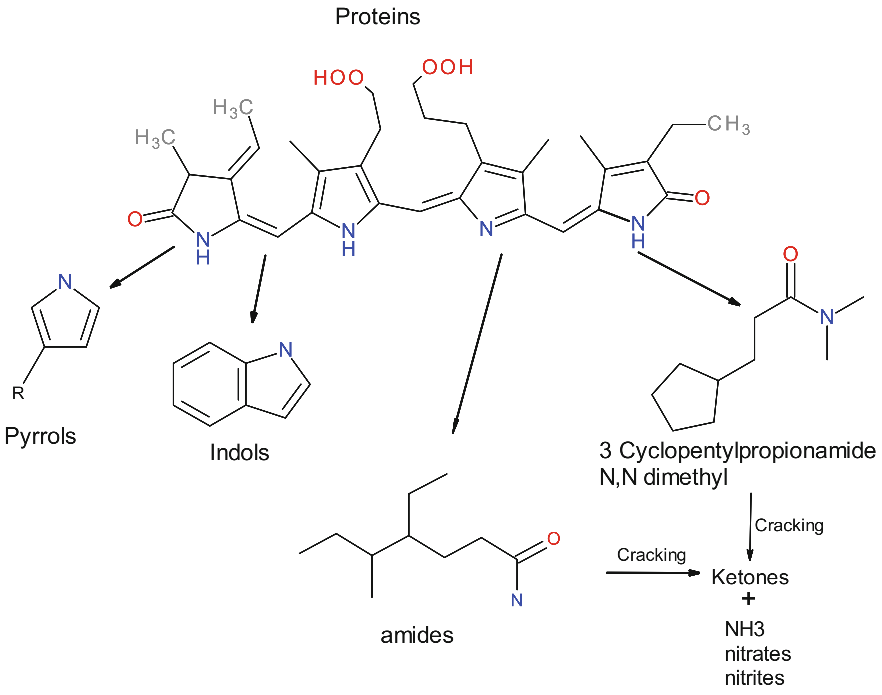


Fig. 28.6 Possible reaction scheme for proteins modified from (González-Gálvez et al. 2020)

28.2.3.2.3 Carbohydrates

Regarding carbohydrates reactivity in HTL, it should be distinguished between simple sugars, mono- and disaccharides, and polysaccharides. In addition, different behavior is observed on hemicellulose and cellulose.

Simple Saccharides

In general, simple saccharides contributed to a high yield of biocrude obtained by HTL. A work with the aim of producing biochar by HTL, and using simple saccharides, such as glucose and lactose (180 °C, 4 h), found that hydroxymethylfurfural (HMF) is the main product of the breakdown of saccharides (Aydincak et al. 2012). Also, phenol aldehyde and some acids are present. Yun et al. (2016) reported a high yield of formic acid by the HTL reaction of mono- and disaccharides at 423–523 K and 3.5–5 MPa; other detected products were acetic acid, lactic acid, and aldehydes, see Fig. 28.7.

Polysaccharides

Polysaccharides are less reactive than simple saccharides in the HTL process. First, they can be depolymerized. Hydrothermal decomposition of cellulose and hemicelluloses leads to the formation of sugars and aqueous decomposition products. But another fraction can be polymerized to produce biochar. According to Scarsella et al. (2020) in HTL, part of the cellulose and hemicellulose gives biochar by a condensation reaction, and water-soluble compounds, such as dihydroxyacetone, hydroxymethylfurfural, and glyceraldehyde. Alcohols and aldehydes also were reported (Mathanker et al. 2020). Significant cellulose degradation products include cellohexaose, cellopentaose, cellotriose, cellobiose, fructose, glucose, erythrose,

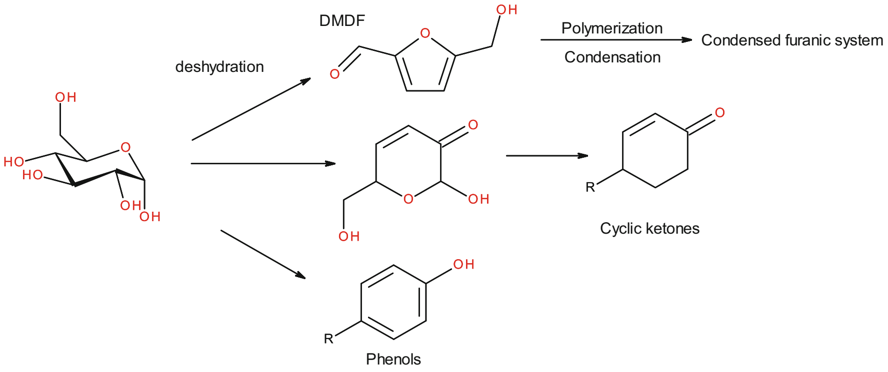


Fig. 28.7 Possible reaction scheme of simple saccharides based on Aydincak et al. (2012) and Yang et al. (2015)

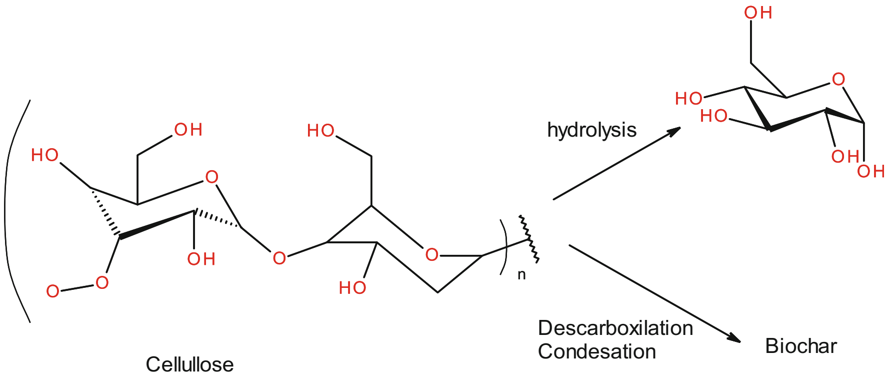


Fig. 28.8 Possible reaction scheme of simple polysaccharides based on Aydincak et al. (2012)

glycolaldehyde, glyceraldehydes, pyruvaldehyde, and furfurals. Wang et al. (2012) report the extraction of sugars by hydrolysis of cellulose at 260 °C and 5.75 MPa in water/alcohol mixtures. In contrast, Yang et al. (2015) described that the contribution of polysaccharides to biocrude is small (<5%). Teri et al. (2014) reported that when cellulose is processed, a biocrude yield of 15% is reached. The reaction of polysaccharides mainly results in carbonaceous residues, and a small part breaks down and results in water-soluble polar molecules; however, these molecules can be repolymerized to give carbonaceous materials.

Regarding lignin, its aromatic structure is a precursor for phenolic and oligomer compounds (Scarsella et al. 2020). The repolymerization of oligomers with alcoholic and aldehydes compounds (formed by hydrolysis of lignin) produces biochar (Mathanker et al. 2020). The reaction path of polysaccharides is shown in Fig. 28.8.

In general, biomass with high carbohydrate content gives a low biocrude yield (Vardon et al. 2011; Huang et al. 2013; Conti et al. 2020). After the analysis in this work, it seems that the behavior is more related to the polysaccharide content. Yang et al. (2018) reported, in terms of residue solid production, the trend: lignin> cellulose> hemicellulose> protein> lipid. The possible reaction scheme for the polysaccharide cellulose is shown in Fig. 28.9.

Starch

According to Nagamori and Funazukuri (2004) when the HTL process (453–513 K, up to 30 min) is applied to starch, the main products are glucose and 5-HMF, along with small amounts of fructose and maltose; i.e., the main reaction of starch is hydrolysis. The obtained solid was about 5%. The behavior in HTL (300 and 350 °C, 86 and 175 bar) for cornstarch was investigated by Teri et al. (2014), the yield to biocrude was 30%, and the rest biochar; the author signaled that the biochar formation is almost complete at 20 min.

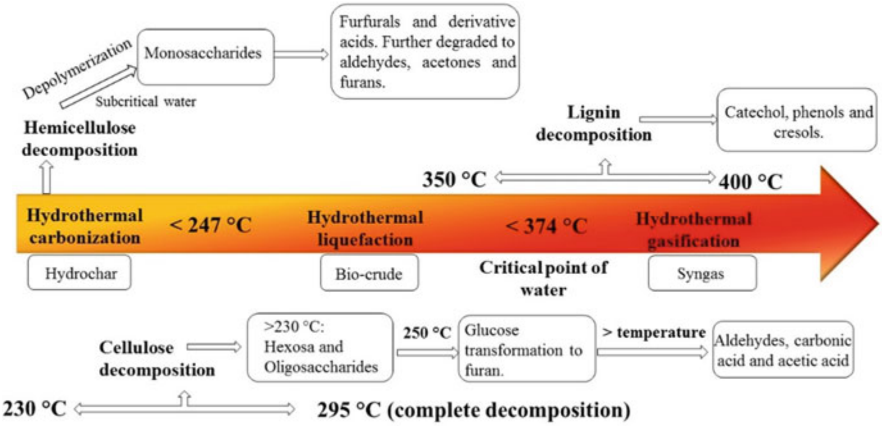


Fig. 28.9 Possible reaction path for hemicellulose, lignin, and cellulose. Based on: Toor et al. (2011), Elliott et al. (2015), Jiang et al. (2018), Guo et al. (2021)

28.2.3.2.4 Bio-Compound Mixtures

The possibility of interaction between different kinds of bio-compounds was covered with mixtures of two of more bio-compounds; the behavior of these mixtures is an additional step on trying to understand the overall behavior when processing different kinds of biomasses. Binary mixtures among proteins, polysaccharides, and triglycerides were tested by Teri et al. (2014). The authors state that polysaccharides-protein and triglyceride-starch mixtures acted as if each of the components reacted individually, while for the triglycerides-proteins mixture, a higher yield of biocrude is obtained, and for the ternary blend (polysaccharides-protein-triglycerides) a yield of approximately 33%, higher than the total lipid content; this value is similar to that obtained when processing microalgae by HTL. This is indicative that other biochemical compounds besides lipids are always processed and that interactions between the different biochemical compounds exist. Similar results are reported by Yang et al. (2015); using a mixture of crude proteins, and polysaccharides, the authors found that there is no linear contribution of each bio-compound in the bio-oil yield signaling and, also, that interactions between biochemical compounds occur. The trend of conversion in HTL process is lipids>proteins, carbohydrates (cellulose> hemicellulose> lignin) (Yang et al. 2018; Ellersdorfer 2020; Skaggs et al. 2018).

28.2.4 *Kinetic Modeling of HTL*

To improve the development of the HTL process at industrial level, information on reaction routes and kinetic data is necessary. To achieve this, comprehensive data of conversion through time are needed. Studies are previously and currently conducted to precisely determine the mechanisms by which HTL occurs. At the moment, it seems that the level of development is the description of the involved reactions, and steps are being taken in order to quantify the effects of the different biochemical compounds and process conditions. Given the complexity of the subject, the models introduced so far are very general and use lumps.

An early point of view was limited to the prediction of biocrude yield using the quantities of each one of the biochemical compounds in the feedstock. Biller and Ross (2011) predict that the contribution of each bio-compound is additive and has a linear behavior (Eq. 28.1).

$$\begin{aligned}\text{Biocrude yield\%} = {} & (\text{protein yield\%})\,(\text{protein content\%}) \\ & + (\text{carbohydrate yield\%})\,(\text{carbohydrate content\%}) \\ & + (\text{lipid yield\%})\,(\text{lipid content\%})\end{aligned} \tag{28.1}$$

The equation fits rightly for *Chlorella sp*. and *Nannochloropsis sp*., but it does not describe the case for cyanobacteria. Teri et al. (2014) described the possibility of including interactions between different biochemical compounds. In their experiments, the authors used pure compounds and different binary mixtures (Eq. 28.2).

$$\text{yield (wt\%)} = a\text{X}_\text{L} + b\text{X}_\text{C} + c\text{X}_\text{P} + d\text{X}_\text{L}\text{X}_\text{C} + e\text{X}_\text{L}\text{X}_\text{P} + f\text{X}_\text{C}\text{X}_\text{P} \tag{28.2}$$

where the X_i terms are the mass fractions of lipid (L), carbohydrate (C), and protein (P) in the mixture and *a, b, c, d, e*, and *f* are adjustable parameters.

Reaction schemes have also been proposed where lumps are based on the obtained product (Valdez and Savage 2013); see Fig. 28.10. Hietala et al. (2016) made a study that includes the temperature effect and points out that the gas generation is not only from feedstock, but gas can also generate biochemical compounds.

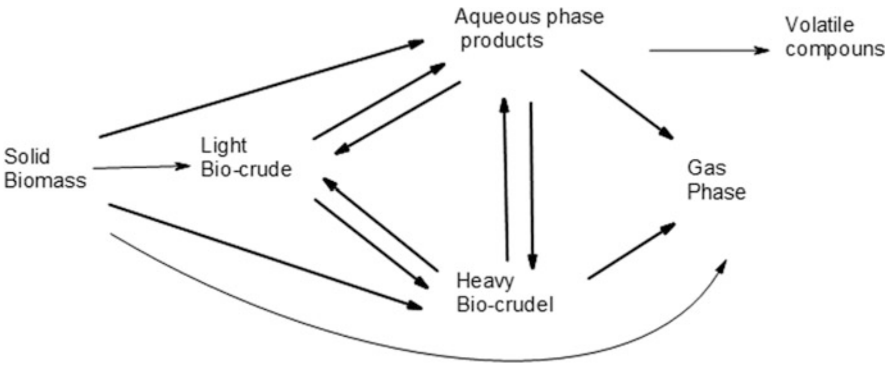


Fig. 28.10 Reaction scheme for lumps based on the kind of products, based on Hietala et al. (2016); Valdez and Savage (2013)

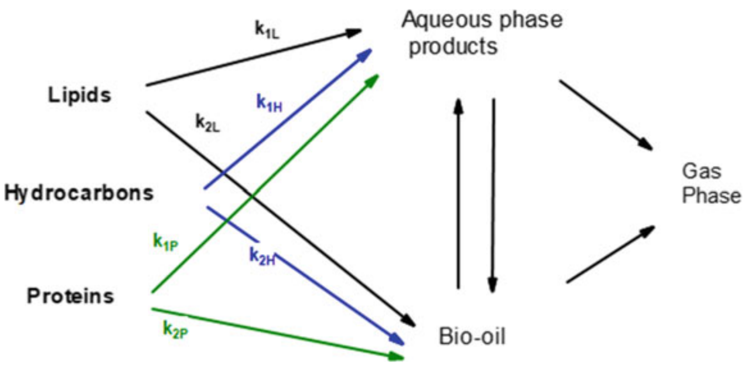


Fig. 28.11 Kinetic modeling of biomass HTL processing based on bio-compound lumps

However, according to the discussion in Sect. 28.2.2, lipids, carbohydrates, and proteins react differently and produce different kinds of products. Moreover, sometimes there are interactions between them that change the final bio-oil yield. Therefore, most recent reaction models use a lumped approach based on the type of biochemical compounds, for example, those shown in Fig. 28.11 (Valdez et al. 2014). Due to the variety of chemical compounds and the complexity of the reaction, for the moment, the kinetic fit is achieved using first-order equations.

28.3 Effect of the Feedstock on the Production of Bio-Oil

Now we focus on the effect of different kinds of feedstock on the biocrude production by the HTL processes.

28.3.1 Advantages of Microalgae for Biofuel Production

The major quantity of the published works about the production of bio-oil by HTL refers to microalgae. In this section, we will discuss the generation of biocrude directly from microalgal biomass. Microalgae have been described as a heterogeneous set of prokaryote (cyanobacteria) and eukaryotic autotrophic (photosynthetic) microorganisms with simple nutrition requirements. Microalgae play a major role in maintaining the terrestrial ecological system, including controlling the environmental pollution and renewal of atmospheric oxygen.

In the production of biofuels, it has been concluded that a major part of the costs is related to the production of feedstock. For example, it is estimated that up to 88% of the cost of biodiesel corresponds to the production of vegetable oil or fat used as feedstock (Haas et al. 2006). Then there is a lot of pressure for a decrement in the

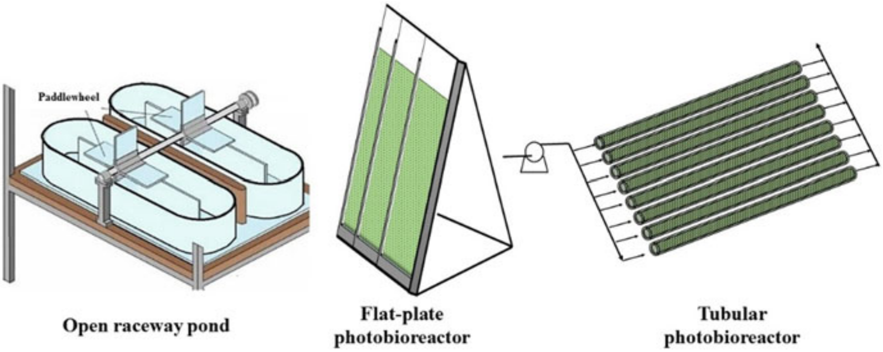


Fig. 28.12 Biological reactors for microalgae production

cost of raw materials as well as process costs. So, it is no surprise that the way to reduce these costs has been studied in terms of cheaper feedstock; in this issue, the use of microalgae is remarkable.

Although this chapter is dedicated to the description of HTL, to make a self-contained document and facilitate reading a brief description about microalgae grow is included in the next paragraphs. About the production (of biofuels), the advantages of microalgae are the following:

1. If they are grown in open ponds or closed systems (Fig. 28.12), it can be thought that they do not incite new demands for arable land.
2. They are relatively easy to grow, with little or no attention, so it is possible to grow microalgae in saltwater or wastewater. In water treatment processes, they are a by-product that has been proven to produce biocrude (Nava Bravo et al. 2019).
3. The level of reproduction and growth is very high. It is estimated that the mass of microalgae in a crop is doubled every 24 h.
4. With the above facts, microalgae can be harvested more than once per year.
5. If the right culture water is used, they are a relatively inexpensive source of nutrients even for humans.
6. It has a production potential of up to 100 times greater than the yield of seeds per kilogram, and the oil yield is estimated to be 30–300 times relative to the seeds when compared by production area.
7. In microalgae, lipid content can be found between 40 and 80% by weight on a dry base, and it is possible to adjust the lipid content of microalgae by changing growing conditions.

28.3.1.1 Microalgae Cultivation

Paddock (2019) refers that in the 1940s, microalgae production began to be investigated as a food source: because of the advantages of these microrganisms: fast growth, high protein content, and ability to use non-arable resources compared to traditional crops. In the 1950s the first microalgae production systems were developed: photobioreactor and open ponds. Carbon dioxide, sunlight, and water are the main inputs for the cultivation of microalgae. Among others, microalgae have been used in the following circumstances:

1. To remove CO_2 generated in industrial facilities (Wang et al. 2008). No high purity CO_2 is required to grow microalgae (Brennan and Owende 2010).
2. In water treatment, in fact, common water pollutants such as NH_4^+, NO_3^-, and PO_4^{3-} can be used effectively as nutrients for microalgae growth.
3. Microalgae compounds such as carbohydrates, lipids, and proteins can be used to produce ethanol, biodiesel, bio-jet fuel, green diesel, methane, or simply burn biomass for energy cogeneration (electricity and heat).

Additionally, it should be remembered that microalgae are a relatively poorly studied biological group, from the point of view of their biochemistry, so it is quite possible that they are the source of some rare lipids or other types of fine chemistry inputs.

In general, the biochemical compounds that can be found in microalgae are lipids (9%), fatty acids (10–38 mg/g microalgae), polyunsaturated fatty acids (PUFA), proteins (20–40%), and carbohydrates (Ahlgren et al. 1992).

28.3.2 Influence of the Operation Variables in the HTL Process

28.3.2.1 Temperature Effect

Li et al. (2014) worked at temperatures of 220–300 °C and reaction times of 30, 60, and 90 min and tested two types of microalgae, *Chlorella* sp. with high lipid content (38.0% - 63.4%) and one with high protein content (*Nannochloropsis* sp.). Higher heat value (HHV) and higher bio-oil yield were achieved for microalgae with high lipid content. In the case of *Nannochloropsis*, the main product was terpineol. Temperature is the main factor that determines the distribution of products; in principle, the increase on temperature causes:

1. An increment in the value of the kinetic coefficient, i.e., an increase in activity.
2. Initially, biomass depolymerization is facilitated, probably by increasing the hydrolysis reaction.
3. At intermediate temperatures, bio-oil performance is favored.
4. At medium-higher temperatures, breakup of bonds increases, and this increases the presence of free radicals. These can increase depolymerization of some molecules and increase oligomerization and other molecules initiate condensation and polymerization to produce coke.

5. At higher temperatures emerges the repolymerization reaction that would lead to the formation of coke.

The bio-compounds follow these general rules; for example, increasing temperature decreases the final content of fatty acids; these kinds of compounds can participate in reactions like cracking, transesterification, or combination with nitrogen compounds. In contrast, with temperature increment the nitrogen content in the bio-oil and aqueous phase increases, caused by protein rupture into amino acid and carbonitride (Li et al. 2014), as shown in Fig. 28.9 (above, Sect. 28.2.3.2.3). At temperatures greater than 220 °C, the biochar formation begins, a further increase in temperature leads to thermal cracking, $>$ 375 °C, and gasification reactions take place (Cheng et al. 2017); thus, very high temperatures are not good from the point of view of costs and bio-oil generation. According to Akhtar and Amin (2011) and other references, the recommended temperature range of operation for high bio-oil yield was 300–350 °C.

28.3.2.2 Pressure Effect

The thermodynamic effect of pressure is related to the gas–liquid phase equilibrium. At high pressures, the predominant phase is liquid under the subcritical conditions or one phase under supercritical conditions. Pressure also raises the density of the solvent. According to Akhtar and Amin (2011), above the critical pressure of the medium the rate of hydrolysis and biomass dissolution is controlled.

28.3.2.3 Solvent Effect

In the HTL process, reactions can occur at temperature and pressure when water is at subcritical or supercritical conditions. Research suggests that the dissociation of water catalyzes several of the reactions in HTL in H^+ and OH^- generated at high temperatures (Cheng et al. 2017). Both ions can catalyze the hydrolysis of complex bio-compounds; that is, the acid–base properties of water are used. Marshall and Franck (1983) studied the ionic product of water ($Kw = [H+] [OH-]$) and signaled that it increases near the critical point (374 °C, 22.1 MPa). The solvent is also a heat transfer medium.

In addition to biocrude, other by-products are gases and solid residues, along with water from the nutrient-rich reaction medium. Song et al. (Song et al. 2020a; b) investigated the effect of aprotic (g-valerolactone, acetone, tetrahydrofuran) and protic (methanol, ethanol) solvents on the HTL of glucose and fructose. There is a higher conversion for the aprotic solvent, but the aprotic ones are more selective and inhibit isomerization.

28.3.2.4 Effect of the Solvent/Biomass Ratio

From an economic point of view, it is better to process more biomass with/or low solvent quantity. However, and in general, a high amount of water produces more liquid and gas yields. Jena et al. (2011), using *Spirulina platensis*, tested the effect of various quantities of feedstock (10, 20, 30, 40, and 50 wt %) and different reaction times and temperatures. They found that the yield of bio-oil (~39%) remains constant after a load of 20 wt %.

28.3.2.5 Use of Catalysts in HTL

The use of catalysts has the objective of increasing biocrude yield performance; also, the quality of biocrude can be improved by various catalyzed reactions, such as denitrogenation, deoxygenation, desulfurization, and decarboxylation reactions. These reactions allow to obtain a biocrude low in nitrogen, oxygen, and sulfur and improve the production of aliphatic compounds, respectively. Studies carried out in this context used pretreatment with homogeneous additives or heterogeneous catalysts.

28.3.2.5.1 Homogeneous Catalysts

Acid or basic compounds are essential to break bonds and produce bio-oil. The homogeneous catalysts used in HTL must be soluble in water at room temperature. Ross et al. (2010) used alkaline salts Na_2CO_3 and KOH and organic acids CH_3COOH and HCOO. In the same work, the authors determined that catalysts allow increasing the biocrude yield from 20.1% to 51.6% under the reaction conditions: 280 °C–360 °C. Catalyst performance presented the following order $Na_2CO_3 > CH_3COOH > KOH > HCOOH$. A point to take into account is that basic catalysts can induce lipid saponification and increasing solid production. One disadvantage of homogeneous catalysts is the negative effect on the pH of liquid products that can cause strong corrosion in reaction equipment (Xu et al. 2018). Besides, the need for an additional neutralization step increases energy use.

28.3.2.5.2 Heterogeneous Catalysts

Heterogeneous catalysts in HTL have a competitive advantage over homogeneous catalysts because they can be recovered and reused. Catalysts with different properties have been evaluated in recent years. For the moment, three kinds of catalytic functions have been studied, as shown in Table 28.1.

Catalysts with acidic properties, for example zeolites, have also been tested, and in this case the gas exhibited significant amounts of $N_{2,}$ showing that zeolite is

Table 28.1 Catalytic functionalities used in HTL

Catalytic functionality	General purpose	Examples
Acidity	Bond cracking in polymeric or simple biochemical compounds. Denitrogenation	Acid support: Like zeolites, Basic compounds: Na_2CO_3, MgO, ZnO
Hydrogenation	Improvement of the quality of the bio-oil, hydrogenation of double bonds, decarboxylation	Noble metals/C
Hydrolysis	Bond cracking of the heteroatoms compounds. Elimination of N, S	Sulfided CoMo, NiMo; metal nitrides MoN

effective for denitrogenation reactions; at the moment it is not clear if the reaction can be considered an acid–basic reaction (N: in the organic molecule reacts with the catalysts acid site). If this is the case, then a deactivation of the catalysts is expected. Generally, tests in hydrogen presence (3550 kPa H_2) show that heteroatom content in biocrude was insensitive to pressure.

Acid catalysts are active for improving the bio-oil. It has been reported that the use of HZSM-5 reduces the final content of sulfur and nitrogen in the biocrude, even if microalgae with a high protein content are used, if both HTL (Nava Bravo et al. 2019) and solvolysis (González-Gálvez et al. 2020) are used. Other works report the use of modified ZSM-5. Xu et al. (2014) worked with Ce/HZSM-5 and HZSM-5 and showed that the catalyst with Ce (Ce/HZSM-5) had a superior effect of catalytic microalgae cracking, achieving a biocrude yield up to 49.87% higher than HZSM-5 catalysts, 34.02%. In addition, the use of catalysts showed a more significant effect on the breakdown of cellulose, hemicellulose, and proteins from microalgae. A later work pointed out that the Ce/HZSM-5 catalyst is also capable of carrying out denitrogenation reactions (Xu et al. 2018).

Catalysts with basic properties like Na_2CO_3 were used with *Chlorella* microalgae, producing low aromatic content at high temperatures (from 300 to 450 °C), and higher biocrude quality compared to a non-catalytic process (Azizi et al. 2018; Babich et al. 2011). In addition, oxides (MgO, ZrO_2, and the zeolitic catalysts NaY-Zr and HY-Zr) increased the obtention of long-chain ketones while Zr-HY promoted the formation of aromatic hydrocarbons and nitriles from *Schizochytrium limacinum* microalgae (Anand et al. 2017; Azizi et al. 2018).

HTL by catalysts with hydrogenating properties has also been reported; for example, Duan and Savage (2011) tested Pd/C, Pt/C, Ru/C, Ni/SiO_2-Al_2O_3, CoMo/γ-Al_2O_3 (sulfided catalysts), and zeolite, with microalgae *Nannochloropsis* sp. The yields obtained to bio-oil were up to 57% with the Pd/C catalyst. In general, the authors observed that the gas phase consisted of H_2, CO_2, CH_4, and in a lower proportion C_2H_4 and C_2H_6. In contrast, with Ni and Ru, the produced gas reached high yields of methane.

28.4 The HTL Process in the Circular Economy

At its core, circular economy promotes the use of renewable and regenerative goods and tries to maintain the value of materials (George et al. 2015; Tomić and Schneider 2018). This offers a new framework, in which waste is a resource that can be processed by various ways to use it as an energy source, replacing fossil fuels, which in turn decreases greenhouse gas emissions (Tomić and Schneider 2018). Energy from waste ensures the use of local resources, helps to reduce dependence on fossil fuel, promotes energy security, saves millions of tons of CO_2, and provides sustainable, local, low-carbon, cost-effective, and reliable energy (Malinauskaite et al. 2017).

Regarding biofuels, and in particular bio-oil, two main factors must be taken into account: the cost of the process and the ecological benefits. Chisti (2007) considers that the economic condition for replacing fossil crude as a source of hydrocarbons will be presented when the cost of seaweed oil relative to the price per barrel of fossil crude oil is:

$$\text{Cost}\ (\text{seaweed oil/L}) = 6.9 \times 10^{-3}\ \text{Cost}\ (\text{USD crude barrel}) \tag{28.3}$$

In a way to reduce costs, the use of microalgae grown in wastewater fulfills the aim of the circular economy, because a material that is currently classified as a sub-product of a necessary process can be used to produce bio-oils or other fuels. In addition, HTL can be performed from feedstock like:

1. Algae growth in the natural environment
2. Microalgae used for water treatment
3. Lignocellulosic materials
4. Other waste biomass

28.4.1 HTL of Microalgae Used for Water Treatment

28.4.1.1 Use of Microalgae for Water Treatment

Water is a vital element to humanity. Its availability has been reduced due to the increasing contamination by the different human activities: domestic, agricultural, and industrial. Abdel-Raouf et al. (2012) reported that three-quarters of organic carbon in wastewater is present as carbohydrates, fats, proteins, amino acids, and volatile acids. There are, also, inorganic compounds with calcium, sodium, potassium, magnesium, chlorine, sulfur, phosphate, bicarbonate, ammonium salts, and heavy metals. In addition, protozoa, viruses, and pathogenic microorganisms are present. Thus, different stages are involved in a conventional wastewater treatment plant (WWTP) (Fig. 28.13): starting with the removal plants, leaves, garbage by screening, until the oxidation of organic material to biosolids, $CO_{2,}$ and water by

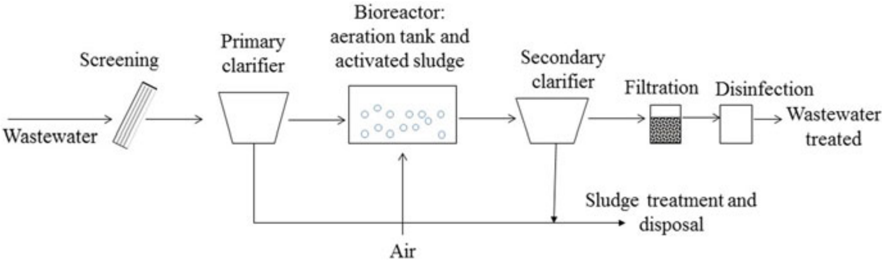


Fig. 28.13 Simplified representation of conventional wastewater treatment train

aerobic microorganism (secondary treatment) (Abdel-Raouf et al. 2012; Ghernaout and Elboughdiri 2019).

Nitrogen and phosphorus removal is also one of the aims of a WWTP because those nutrients can lead to eutrophication of the water bodies, but the presence of these compounds stimulates algae, microalgae, and aquatic macrophytes flourish. So, microalgae are an attractive solution to remove coliform bacteria, BOD, nitrogen organic, urea, inorganic (ammonium, ammonia, nitrates, and nitrites) and phosphorus compounds, and heavy metals (Abdel-Raouf et al. 2012). Microalgae can avoid the transition between process (N and P removal in WWTP) and saving energy (Mohsenpour et al. 2021). In the 1960s Oswald and Goulueke proposed microalgae for biofuel production, suggesting its production using existing wastewater treatment ponds for municipal, industrial, and agricultural wastewater (Kadir et al. 2018; Mehrabadi et al. 2015). Komolafe et al. (2014) isolated microalgae from an artificial lake. Microalgae not only removed nutrients from a defoamed raw wastewater influent but increased its biomass concentration reaching up to 0.58 g/L. These results were obtained with *Desmodesmus* sp., and also on a mixed culture dominated by *Oscillatoria* and *Arthrospira,* respectively. Moreover, lipid production was in the range of 14–20% by weight of dry biomass. Some examples of different wastewater treatment by microalgae are shown in Table 28.2.

28.4.1.2 HTL Process with Microalgae Used in Water Treatment

Nava Bravo et al. (2019) used a microalgae consortium from an artificial lake (Nabor Carrillo lake) to produce bio-oil. The lake is fed with wastewaters (from Mexico City) treated by facultative lagoons. The microalgae consortium consists of cyanobacteria (*Arthrospira* sp., *Oscillatoria* sp.) and green algae (*Desmodesmus* sp. and *Scenedesmus* sp.) as the most abundant genera among other microalgal species; two methods of harvesting were used: ozone flotation and centrifugation. An HZSM-5 zeolite (0, 5, and 7 wt% loading with respect to dry biomass) was used. The products were characterized by gas chromatography and mass spectroscopy. The authors reported that the best quality of biocrude oil (lower nitrogen (3.2%), oxygen (4.8%), and sulfur (0.7%) content) was produced from microalgae harvested

Table 28.2 Microalgae used in wastewater treatment

Microalgae	Results	Reference
Chlorella pyrenoidosa (**Cp**) and *Scenedesmus* sp. (**Sd**)	**Sd** removed 98.1% of NH_4-N from settled wastewater (primary sedimentation), while **Cp**, 75.3% from an effluent treated by secondary processes (activated sludge with nitrification/denitrification). Phosphorus was removed 70–80% in all treatments	Tam and Wong (1989)
Chlorella vulgaris (**cv**)	**Cv** was acclimatized in primary settled wastewater. Inorganic N and P were removed (in 2 days) at 70% and 86%, respectively. Without acclimation, only 50 and 54% removal, respectively, was achieved	Lau et al. (1996)
Chlorella sp.	Different wastewater samples were tested: Before and after primary settling (#1 and #2), after activated sludge tank (#3), and centrate from sludge centrifuge (#4). NH_4-N was removed in 82.4% (#1), 74.7% (#2), and 78.3% (#4). Same order for phosphorus (83.2%, 90.6%, and 85.6%) and COD (50.9%, 56.5%, and 83.0%). Sample #3, removal of phosphorus (4.7%) and COD increased slightly. Al, Fe, mg, Mn, and Zn were removed in the range of 56.5–100%	Wang et al. (2010)
Chlorella pyrenoidosa	Dairy wastewater industry treated by an oxidation pond (influent and effluent) was used. Nitrate (60.54%), nitrite (42.1%), fluoride (87.14%), and chloride (58.3%) in influent were removed, while nitrate (49.09%), nitrite (70.06%), phosphate (49.09%), and fluoride (60.50%) in effluent were obtained	Kothari et al. (2012)

and pretreated by ozone flotation using 7 wt% of HZSM-5. Authors probed that HTL can be used to process a consortium of wild microalgae to obtain biocrude. The use of tetralin as a solvent in the same consortium was tested by the same group (González-Gálvez et al. 2020). A high yield of bio-oil (53%) with an estimated HHV (32–33 MJ/kg) was reported. Despite the high protein content in the feedstock, the resulting bio-oil shows a relatively low nitrogen content of 1.2–1.5 wt.%.

28.4.2 Other Feedstocks to the HTL Process

In this section, we briefly address the use of other raw materials as a feedstock to the HTL process. This is particularly important for HTL taking into consideration circular economy criteria. Since HTL is very flexible as far as feedstocks are concerned; several materials such as woody biomass, industrial waste, food waste, swine manure, and herbaceous plants have been tested. Among them, using waste as feedstock material could be the best option because this could help solving the disposal problems of waste, and at the same time, it produces energy and other valorizable chemical products. Further advantages can be envisioned, for example, sewage sludge needs to be stabilized before their final disposal in order not to be an extra contaminating material or an infection vector. In sewage sludge up to 90% DNA of viruses like adenovirus, herpesvirus, papillomavirus, coronavirus, rotavirus, etc., has been found (Chen et al. 2020). To manage this material safely, some treatments, commonly incineration, landfill, and composting, must have been used (Badrolnizam et al. 2019). Swine manure from agricultural livestock is a waste linked to the spread of hormones, pathogens, and nutrients runoff (Vardon et al. 2012). The use of HTL can avoid these pollution sources.

Table 28.3 shows the results on applying the HTL to some conventional and nonconventional feedstock. The advantages of the HTL process, for example, energy content (HHV, MJ/kg) of biocrude, increased in the range of 1.1 to 4.0 times than the original feedstock; there is an oxygen removal, and the associated improvement in the energy content (HHV).

28.4.2.1 Processing of Sludge from Wastewater Treatment by HTL

Sludge obtained from urban wastewater treatment plants (WWTP) is cheap and available in large quantities, especially in large cities. Moreover, the use of wastewater sludge represents savings since its disposal must be covered as part of the WWTP.

Although HTL sludge has not been systematically studied, early research has shown that biocrude produced from HTL of sludge and swine manure is very viscous (843 cP at 50 °C); thus, it cannot be used as naphtha directly and it must be distilled (Dimitriadis and Bezergianni 2017; Xiu et al. 2010).

Vardon et al. (2011) utilized digested anaerobic sludge (solids content of 26%), swine manure, and *Spirulina* to produce a biocrude oil by HTL. By using simulated distillation (SimDis), the author argues that the produced biocrude may be suited for uses like bunker crude (residual fuel oil), boiler, or asphalt applications, and the produced biocrude is similar to vacuum gas oil or vacuum residua fractions produced from fossil petroleum. Thus, a biocrude upgrading is needed. From the used feedstocks, *Spirulina* biocrude had 30% of low boiling point (bp) compounds (bp $<$ 343 °C, heavy naphtha, kerosene, and gas oil fractions). Sludge biocrude had 21% of high boiling point compounds (bp $>$ 538 °C: classified as vacuum residue). Swine manure biocrude presented 69% of mid-boiling point compounds (342–538 °C) and the lowest percentage to the other two bp fractions. Huang et al. (2013) reported a comparison between the HTL biocrude from sewage sludge (SS) and *Spirulina* microalgae (Sp). The volatility distribution of hydrocarbons in the biocrude was similar: 22.04% and 21.20% from SS and Sp*;* for example, C_5 and C_9 were 17.73% and 3.04% (C_{18}) for Sp biocrude, while sewage sludge biocrude contains 7.0% and 9.31%, respectively. Compounds in the diesel range, mainly C_{17} (22.0 (SS) and 21.2 (Sp)%) and C_{20}, were also found (18.64% (SS) and 16.25%, (Sp)). Anastasakis et al. (2018) reported that the production of biocrude from sewage sludge was composed of fatty acids ranging from C10 to C20 (myristic, palmitic,

Table 28.3 HTL process on some nonconventional feedstocks

Feedstock	Reactor and process condition	Feedstock composition (wt.%) and HHV (MJ/kg)	Biocrude: yield (wt.%), composition (wt.%), and HHV (MJ/kg)	Reference
Spirulina microalgae (**SM**), swine manure (**SM**), and digested sludge (**DS**)	Reactor 2 L. 300 °C, 10–12 MPa, 30 min reaction time. 800 g of slurry (20% w/w solid content).	Not specified	**SM**: (32.6%), C (68.9), H (8.9), N (6.5), O (14.9), S (0.86), and HHV (33.2) **SM**: (30.2%), C(71.2), H (9.5), N(3.7), O (15.6), S (0.12), and HHV (34.7). **DS**: (9.4), C(66.6), H(9.2), N (4.3), O (18.9), S(0.97). HHV (32.0)*	Vardon et al. (2011)
Rice straw (**RS**), *Spirulina* microalgae (**SM**), and sewage sludge (**SS**)	Reactor 500 ml. 350 °C, 9.4–10.1 MPa, 20 min reaction time. 7.9 g of biomass in 100 ml of ethanol.	**RS**, C(45.04), H(5.05), N (1.06), O(48.85), and HHV (13.71) **SM**, C(43.17), H(8.53), N (8.91), O(39.39), and HHV (19.80). **SS,** C (43.38%), H (5.91%), N(3.18%), O (47.53%), and HHV (14.63)*	**RS**: (21.14%), C(73.06), H (8.38), N(2.46), O(16.1), and HHV (33.90) **SM**: (34.51%), C(70.31), H (8.72), N(9.7), O(11.27), HHV (34.33) **SS:** (39.46%), C(72.51), H (9.44), N(6.96), O(11.09), and HHV (36.14)	Huang et al. (2013)
Grass *Miscanthus* (**GM**), Spirulina microalgae (**SM**), and sewage sludge (**SS**) from primary treatment	Pilot-scale HTL-continuous, capacity 100 L/h, 20 L. 350 °C, 6 h total run. Slurry dry matter: 15.0 wt. % **GM**, 16.4 wt. % **SM,** and 4 wt.% **SS** of dry mass content. **GM** mixed with catalyst (KOH 1.4 wt.%) and carboxymethyl cellulose (CMC 0.25 wt. %) as thickener	**GM**: C(49.1), H(3.8), N (0.7), S(0.2), O(43.5), and HHV (17.2) **SM**: C(50.6), H(7), N (11.8), S(0.8), O(23.3), and HHV (23.3) **SS**: C(46.5), H(6.1), N (3.3), S(0.4), O (31.2), and HHV (19.8).*	**GM**: (26%), C(68.5), H (7.3), N(1.2), S(0.19), O (17.7), and HHV (30.7) **SM**: (32.9%), C(69.1), H (8.6), N(6.6), S(1.12), O (9.5), and HHV (33.2) **SS**: (24.5%), C(58.2), H (6.5), N(2.4), S(0.47), O (5.9), and HHV (26.9)*	Anastasakis et al. (2018)

Swine manure (**SwM**), dairy cow manure (**CM**), fish sludge (**FS**), secondary sewage sludge (**SS**).	Reactor 10 cm^3, 350 °C and 400 °C, with and without catalyst (K2CO3, 2.5 wt.% of water–biomass mixture) 7 g of slurry (20 wt.% concentration) Pressurized with N2 (1.5–2.0 MPa). 15 min reaction time	**SwM**: C(44.89), H(5.91), N (2.39), O(46.81), and HHV (19.68) **CM**: C(49.63), H(6.55), N (1.68), O(42.14), and HHV (19.10) **FS**: C(53.49), H(8.05), N (7.55), O(30.91), and HHV (23.30) **SS**: C(46.43), H(7.62), N (7.37), O(38.58), and HHV (21.93)*	Only results at 400 °C with catalyst: **SwM**: (34.7), C(75.56), H (9.14), N(2.99), O(12.31), and HHV(35.83) **CM**: (32.29), C(76.02), H (8.90), N(2.61), O(12.47), and HHV(35.70) **FS**: (47.17), C(73.94), H (10.18), N (7.22), O (8.66), and HHV (36.80) **SS**: (35.7), C (73.10), H (10.85), N (5.45), O (10.60), and HHV (37.13)*	Conti et al. (2020)
Sewage sludge (**SS** from WWTP), green waste (**GW),** food waste (**FW),** grease residue (**GR**), and *Chlorella vulgaris* (**CV**)	Batch-autoclave system (600 cm^3). 350 °C, 16–18 MPa, 15 min time reaction. Dry biomass in 200 cm^3 distilled water (10 wt.%). Mix biogenic waste biomass with *chlorella*: 50:50	**SS**: C(29.7), O(61.3), H (4.3), N(3.7), S(1.1), and HHV(12.1) **GW**: C(22.2), O(73.8), H (2.6), N(1.2), S(0.2), and HHV(8.1) **FW**: C(48.1%), O(42.0), H (7.0), N(2.7), S(0.2), and HHV(19.8) **GR**: C(65.2), O(23.0), H (10.1), N(1.6), S(0.2), and HHV(30.5) **CV**: C(32.6), O(57.1), H (4.9), N(4.9), S(0.5), and HHV(14)	**SS**: (12.0), C(71.3), O(14.7), H(3.8), N(8.4), S(1.7), and HHV(32.1) **GW**: (4.4), C(76.6), O (12.8), H(3.1), N(7.4), S (0.1), and HHV(32.5) **FW**: (18.2), C(71.3), O (15.9), H(3.9), N(8.7), S (0.2), and HHV(32.1) **GR**: (76.3), C(61.5), O (28.3), H(0.2), N(9.8), S (0.2), and HHV(34.9) **CV**: (18.3), C(66.2), O (20.1), H(8.1), N(5.0), S (0.7), and HHV(31.9)	Ellersdorfer (2020)

linoleic, oleic, and stearic acids) and long straight chain alcohols (C_{10}, C_{12}, C_{14}, C_{16}, and C_{18}) with a lower content of alkylated phenols. The fatty acids observed were almost those found by Huang et al. (2013). In the case that ethanol was used as solvent reaction medium (Table 28.3), a production of ethyl ester of tetradecanoic acid, hexadecanoic acid, pentadecanoic acid, (E)-9-octadecanoic acid, etc. which can be used as biodiesel, was reported.

28.4.2.2 Woody Biomass

Woody biomass can come from post-consumed furniture, sawdust, urban pruning waste, and some herbaceous plants, for example grass. Its composition can include pinewood, beech wood, cypress, and poplar wood. In general, woody biomass can be effectively converted into bio-oil by HTL and test has been performed at different reaction temperatures, residence times, water amounts, and initial N_2 pressure. Results showed that the higher reaction temperature, longer residence time, and larger mass ratio of water to sawdust decreased the bio-oil yield as part of the bio-oil was converted to solid residue and gases under these conditions. The formation of small molecular compounds was the dominant process at lower temperature, and secondary polymerization became predominant above 280 °C (Jindal and Jha 2016). The poor liquid yield of woody biomass can be explained taking into consideration that lignin, the main component, is stable in nature, and its molecular chains are relatively difficult to break, but they can be easily coked during the liquefaction process (Cantero-Tubilla et al. 2018). On the other hand, the physical structure of cellulose and hemicellulose, also contained in woody biomass, is relatively simple with relatively weak hydrogen bonding and stacking interactions, showing poor thermal stability and thus higher degradability in HTL (Cantero-Tubilla et al. 2018).

28.5 Biocrude Processing

Fuels from biomass can be used to mitigate the greenhouse effect by the substitution of fossil fuels. However, biocrude has a high content of nitrogenous and oxygen compounds. In general, if you plan to use the bio-oil for fuel applications, the following undesirable characteristics arise due to the chemical composition: 1) high oxygen content and consequently low heating value, 2) high viscosity, related to the high molecular weight of the constituent molecules, 3) high content of water—this and the first point confers to the biocrude a polar quality, 3) high corrosiveness because its acidity is high (Oasmaa et al. 2010), 4) high nitrogen and possibly sulfur content, and 5) thermal and chemical instability during storage (Saber et al. 2016). Also, it would be desirable that this fuel can be used in already existing engines. This means that the post-processing has as one of its objectives to transform the biocrude into a product chemically like fuels obtained from fossil crude.

28.5.1 General Aspects

In general, biocrude obtained by HTL has much lower content of oxygen and nitrogen compared with the one from pyrolysis. Nonetheless, the important challenges for converting biocrude to fuels were maintained since up to 8–12% of N content has been reported in biocrude oil from HTL (J. Zhang and Zhang 2014), which is much higher than what is found in the fossil crude, up to 2.4% (Boduszynski 1987). This situation is similar for oxygen up to 10.4% in biocrude (Yu et al. 2017) versus 1.62% (Gaweł et al. 2014). In biocrude from HTL, several compounds are identified like nitrogen compounds (pyrrole, pyridine, indol, quinoline etc.), nitrogen-oxygenated compounds (derived from pyrrolidone, piperidone, etc.), oxygenated compounds (phenol, fatty acids, fatty acid esters, alcohols, etc.), cyclic hydrocarbons (cyclohexane, cyclopentane, etc.), aliphatic (hexadecene, heptadecane, pentadecene, etc.), or even sulfur compounds (González-Gálvez et al. 2020; Nava Bravo et al. 2019). Two strategies have been implemented to reduce N and O: (a) the production of the biocrude, which was briefly discussed in the use of catalysts in the HTL section, and (b) the processing of the biocrude oil. For the processing of the biocrude oil two main reactions can be implemented, “direct” deoxygenation (DDO) and hydrotreatment process (HDT). DDO does not require hydrogen and is carried out over an acidic support like HZSM-5 (Guo et al. 2004).

The issue of decreasing nitrogen, oxygen, and sulfur from fossil crude has been addressed before in the refinery industry with the hydrotreatment (HDT) process. This process is versatile, and it is adapted to all types of refinery cuts from light cuts such as naphtha to heavy ones such as vacuum residue (VR), but H_2 is needed at high pressures, since its presence reduces coke formation (Gholizadeh et al. 2016). One advantage of HDT is that the existing infrastructure in refineries can be implemented for HDT of biocrude. In the HDT of VR also, a functionality for improvement of the cut is reached through the hydrocracking reaction (HYC); this reaction can also be used to improve biocrude quality. Commercial catalysts used in the refinery industry are CoMo and NiMo catalysts supported on γ-alumina. Also, in research work the use of noble metals was reported for example (Duan and Savage 2011). The cracking function was implemented with support acidity by modification of alumina (F, Cl, B, etc.) or the use of more acidic support, for example, zeolites.

Bai et al. (2014) conducted a screening study about the performance of 5% Pt/C, 5% Pd/C, 5% Ru/C, 5% Pt/C (sulfided), Mo_2C, MoS_2, alumina, Ni/SiO_2–Al_2O_3, and HZSM-5 active carbon and Ni Raney catalysts. All the metal catalysts produced a freely flowing bio-oil with high yields. Metal and sulfide catalysts reduced N and O content and the sulfide NiMo and CoMo catalysts produced less coke. Using a Pt/C catalysts, Duan and Savage (2011) reported the production of low viscosity product with an HHV of 44 MJ/kg (similar to diesel 44.4 MJ/Kg), where H/C ratio increases, and the O/C and N/C ratios decreases. Formation of coke increases along the catalysts content and time on stream. In the same type of catalysts, Gunawan et al. (2013) reported the hydrotreatment of raw biocrude from fast pyrolysis, where hydrogenation of light oxygenated compounds like furfural produced cyclopentanone, while the evolution of propyl, ethyl, and methyl-guaiacol and syringol confirmed the depolymerization of lignin-derived oligomers.

Yu et al. (2017) examined the performance of commercial (Haldor Tøpsoe) NiMo catalysts with low (TK 951) and high (TK 341) nickel content on the HDT of biocrude oil from aspen wood. A reduction from 10.7% to 0.7% was reached at 350 °C for 4 h. A study about the use of a continuous reactor and possible arrangement of reactor beds was reported by Horáček and Kubička (2017). The authors worked with NiMo and CoMo catalysts and recommended a three-bed reactor to process biocrude. The first bed operated at low temperature to reduce coke formation, but high enough to transform some compounds with oxygen. Second and third beds operated at 350–400 °C to increase the breakage of C–C bonds. Castello et al. (2019) upgraded biocrude, which was produced from miscanthus, an herbaceous plant with high lignocellulose content, biomass primary sewage sludge, and *Spirulina* microalgae: the operation conditions were 350–400 °C, 4.0–8.0 MPa initial pressures of H_2, and 9.9–16.9 MPa of total pressure; a $NiMo/Al_2O_3$ catalyst was used. As a result, the upgraded biocrude from sewage sludge contains n-paraffins in a ~ 85% chromatographic area, while naphthenes, aromatics, and O-containing are contained in the upgraded miscanthus biocrude. The N and O can be better removed as pressure and temperature increased. At 8 MPa, from 350 °C to 400 °C, sewage sludge biocrude upgraded from 2.5 to 0.9 (nitrogen content) and 0.0 (oxygen). Miscanthus biocrude upgraded shows a decrease for oxygen from 4.3 to 0.0 and a slight increase of nitrogen from 0.8 to 1.5. As a consequence, the HHV of the upgraded biocrudes was in the range of 41.1–46.1 MJ/kg (the highest values were for sewage sludge biocrude upgraded). Furthermore, the C contents were in the range of 83.7–87.4% and H, 12.1–13.8%, more than the reported cases of raw biocrude; the increment in the H/C ratios was present except for biocrude upgraded from miscanthus, where the hydrogen content decreased slightly when temperature increased. Also, Castello et al. (2019) concluded that high pressure H_2 is crucial to avoid reactions as decarboxylation and coking which can reduce yield; besides, it may potentially cause problems during operation in continuous plants.

28.5.2 Transformation from Bio-Oil to Bio-jet Fuel

The biocrude, produced either by pyrolysis or by hydrothermal liquefaction, can be used as a raw material for obtaining bio-jet fuel. Zhang et al. (2015) used biomass (Douglas pine) and pyrolysis to obtain a biocrude and then performed the improvement of it by hydrotreating; ZSM-5 catalysts were used during biomass pyrolysis, and Raney nickel for hydrotreating. The production of paraffins and aromatics in the jet-fuel ebullition temperature range was reported. In the hydrotreating stage of bio-oil, paraffin selectivity (C_8-C_{15}) of 12.6% and 19.4% for aromatics was obtained. Hydrotreatment of lignocellulosic biomass and a mixture with a proportion of plastic to lignocellulosic materials of 0.75 has also been tested, and in this case, the production of cycloalkanes and alkanes in the jet fuel range (Zhang et al. 2016). Bio-oil was first obtained from pyrolysis with zeolite ZSM-5; subsequently, it was hydrogenated to obtain the desired products (selectivity of 84.6%) with Raney nickel at 200 °C and 2 hours of reaction at 500 H_2 psi. Another catalyst that has been used for pyrolytic biocrude hydrogenation has been Ni-Mo at 450 °C. Pyrolytic bio-oil was obtained at 850 °C from a mixture of eucalyptus dry saw with waste soybean oil and CaO. After the hydrotreating process, more than 60% of oxygenated and nitrogenous compounds were converted to hydrocarbons with properties similar to aviation kerosene, including freezing point, flash point, density, viscosity, and combustion heat (Shah et al. 2019).

28.5.3 Co-Processing of Biocrude with Fossil Crude in a Refinery

There is also a proposal that biocrude can be processed as a part of the feedstock to refineries. The advantages are (a) provide a renewable content to the production of fuels, thus improving the CO_2 atmospheric balance. (b) Low capital requirements because of the use of existing infrastructure. However, the chemical differences have to be acknowledged, and this creates a new scenery. The ability of processing bio-oil has been tested at the laboratory level on an FCC reactor (Corma and Sauvanaud 2013). de Pinho et al. (2015) analyzed the feasibility of processing simultaneously raw biocrude (from pyrolysis) and vacuum gasoil (VGO), by ^{14}C isotopic studies; the renewable carbon content in gasoline cuts varied in the range of 3%–5% when 20% biocrude was co-processed. When 10% of biocrude was used, then the total liquid product contained 2% of renewable carbon. Ibarra et al. (2016) analyzed the products of the mixture 20% of py-oil with VGO. Bhatt et al. (2020) evaluated the changes in air pollutant emissions and regulatory implication when biocrude is co-processed in a refinery and estimated that environmental objectives can be achieved with this action.

28.6 Life Cycle Assessment of HTL

To know the feasibility of a process to produce an item, different types of studies can be carried out. One of them is the life cycle assessment (LCA). According to ISO 14040, LCA is a methodology tool for assessing the potential environmental impacts generated throughout at product’s life cycle, from raw material acquisition to waste management (called “cradle to-grave” perspective) (García-Sánchez and Güereca 2019). LCA can also determine if the biofuel produces less greenhouse gas

(LC-GHG) than conventional fuel, besides identifying the processes that require more development to improve the sustainability of these fuels (Fortier et al. 2014). Another metric parameter used in this analysis is the net energy ratio (NER: ratio of energy consumed to energy generated); less than 1 is an economically viable process (Ponnusamy et al. 2020). Results from the literature show that GHG for biofuels is favorable, but NER values are not compared to conventional fuel. Bennion et al. (2015) studied the biofuels production using HTL and pyrolysis process of microalgae. Large environmental impacts from pyrolysis (290 g CO_2 eq/MJ diesel) were attributed to feedstock drying requirements and co-product combustion, compared to results obtained with HTL process (-11.37 g CO_2 eq/MJ diesel). Both scenarios considered the CO_2 absorbed by microalgae (assumed algae carbon composition of 50%). However, NER value, at industrial scale model, for HTL and pyrolysis process was 1.24 and 2.28, respectively, while NERs for conventional diesel, corn ethanol, and soy biodiesel are 0.18, 1.07, and 0.80, respectively (Bennion et al. 2015). For bio-jet fuel produced by HTL of microalgae cultivated in wastewater showed an LC-GHG of 35.2 Kg CO_2 eq/GJ (refinery plant located at the WWTP), while a jet fuel conventional production is 88.1 Kg CO_2 eq/GJ (Fortier et al. 2014). However, NER value is not reported in this work. Conversion agricultural waste (delactosed permeated whey) for yeast fermentation and its HTL processed to produce renewable diesel produced 30.0 g CO_2-eq/MJ and net energy ratio of 0.81 (conventional diesel: 0.19) (Summer et al. 2015).

Some studies have suggested to take into account all products from HTL process, for example, biochar and aqueous water. Nie and Bi (2018) studied the LCA for three scenarios: collected bulky forest residues are transported to the central integrated refinery (Fr-CIR), forest residues are first converted to bio-oil and transported to be upgraded in a major oil refinery (Bo-DBR), and in another option, forest residues are first densified to wood pellet and then transported to central integrated refinery for conversion (Wp-CIR). Results showed a GHG of 20.5, 17.0, and 19.5 g CO_2 eq/MJ, respectively (78–82% reduction with respect to petroleum fuels). From the same author, using the biochar as credit (applied as soil amendment), the GHGs is reduced by 6.8 g CO_2 eq/MJ (there was a reduction of 85%, 89%, and 86%, respectively, compared with petroleum fuels). There are some LCA studies on biofuel production using different technological routes. However, results vary from study to study because different parameters exist: functional unit, boundary system, scope of the study, geographic location, feedstock, treatment of the by-products or waste, assumptions, differences in the process pathway, etc. (Bennion et al. 2015; Nie and Bi 2018). Some studies show poor compliance with ISO 14040-44; others omitted sensitive analyses, or a comprehensive assessment of all impact categories (Mayer et al. 2019). However, thanks to the variety of these studies, some results can provide preliminary vision for more research and improve decision-making for future technologies selection and biofuels pathways production.

28.7 Conclusions

HTL is a versatile process able to obtain biocrude from a wide variety of biomass feedstocks. However, the composition and yield of biocrude will depend on the feedstock structure and the process variables, temperature, pressure, and catalyst nature.

One of the challenges in HTL is to notice that several processes are happening at various scales, starting with the rupture of the cellular wall and the release of cellular structures. Then the cell organelles are destroyed, and their molecular constituents are left in the reactor (proteins, lipids, and carbohydrates). These biomolecules are transformed by various parallel reactions that include cracking, condensation, cyclization, (de)polymerization, and carbonization.

One crucial step to improve the HTL process is to understand the reaction routes and their kinetics. Several approaches have been used, such as studying the effect of process conditions independently for each biomolecule or using a “lump” approach based on the compositions in terms of bio-compounds.

Microalgae are a valuable feedstock since they can be grown using wastewater and solar energy, thus complying with circular economy principles. Their processing also depends on their composition and the process parameters. Generally, high yields are obtained from algae with a high lipid content, such as *Chlorella* sp.

Regarding temperature, above 220 °C biochar formation begins, and above 375 °C gasification reactions occur. Since we aim to obtain liquid products, gasification reactions are not desirable. For its part, pressure increments the density of the solvent. The solvent also plays an important role. From an economic point of view, the ratio solvent/biomass must be kept at a minimum, while from a chemical perspective, high amounts of water produce more liquid and gas and less solid.

Another strategy to increase biocrude production is to use a catalyst that can be homogeneous or heterogeneous. Homogeneous catalysts are acid or basic molecules that enhance bond breaking, such as Na_2CO_3, CH_3COOH, or KOH. Basic and acidic catalysts can produce corrosion and thus require more expensive equipment. Three alternatives have been explored so far regarding heterogeneous catalysts: zeolites, noble metal-based, and Ni(or Co)-Mo sulfided catalysts. All of them contribute to increment the yield of biocrude and decrease the number of heteroatoms (N, O, and S) in the product.

Biocrude has undesirable characteristics that must be eliminated during post-processing, such as high water, nitrogen, and oxygen content, high viscosity, corrosiveness (acidity), and thermal and chemical instability. The elimination of these detrimental characteristics is one of the goals of biocrude post-processing, which currently constitutes up to 70% of biofuel’s cost. In this way, biofuels can comply and even surpass the environmental requirements for fuels. Post-processing of biofuels mainly uses hydrotreating, with zeolites or Raney nickel to obtain hydrocarbons in the range of C8-C15.

Another alternative for biocrude post-processing is co-processing with fossil feedstocks in existing refineries. This approach allows using existing infrastructure in biocrude post-processing, thus decreasing the net CO_2 balance in the obtention of fuels and eliminating the cost of new refineries.

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Chapter 29
Landfill Gas Utilization

Abhishek N. Srivastava and Sumedha Chakma

Abstract Municipal solid waste (MSW) landfills are one of the largest anthropogenic sources of greenhouse gas (GHG) emission. Landfill gas (LFG) emitted from landfills or MSW dumps significantly contains methane (CH_4) and carbon dioxide (CO_2) as major GHGs. Un-engineered way of dumping MSW in landfills and release of LFG poses fire hazards, particulate matter pollution, and GHG emission risks. However, LFG utilization through engineered gas collection system could prove its value as new renewable source for electricity generation. Being methane as one of the major constituents, LFG possesses extraordinary heating value as well. This chapter reveals the aspects, opportunities, and challenges associated with LFG utilization along with its economic and environmental paybacks. Attempts for enhancing LFG recovery from landfill system were also covered, thoroughly.

29.1 Introduction

Municipal solid waste (MSW) contributes more than half of the total 4 billion tons of generated solid waste every year, globally (Gutberlet 2015). In recent years, MSW generation has increased rapidly owing to advanced lifestyle and extreme consumerism. Moreover, MSW generation has been receiving substantial attention in the recent past owing to momentous amount of its generation volume (Cheng et al. 2020). Based on lifestyle and corresponding per capita generation rate of different income group countries, MSW composition also varies. The commingled nature of MSW across the world possesses varying physicochemical properties. In general, the lower middle-income countries possess high fractions of organic content (~ 65%) unlike developed and high-income countries, which contain mostly combustible fractions (Chakma et al. 2014). The MSW in capped landfill system undergoes anaerobic digestion until stabilization. As soon as MSW is disposed in landfills, the biochemical reactions occur (Srivastava and Chakma 2021). Owing to the

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presence of atmospheric air near the cover surface of landfill, aerobic decomposition takes place for natural organic compounds. Reactions prevailing in this section are similar to combustion reactions because of its end products in the form of carbon dioxide (CO_2) and water vapor. In the remaining parts of the landfills, mostly anerobic digestion reactions take place in the four stages, namely, hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Srivastava and Chakma 2020). The complex organic matter was fragmented by hydrolytic fermentative bacteria in the first phase. In the second phase, hydrolyzed molecules were converted to simple organic acids including acetic acid, propionic acid, butyric acid, CO_2, hydrogen, and ethanol (Cesaro and Belgiorno 2014). These acids are converted to acetates, which further get converted into methane by methanogenic bacteria. Following prime reactions take place during anerobic digestion in landfill.

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \text{ [Acetogenesis]}$$

$$CH_3COOH \rightarrow CH_4 + CO$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \text{ [Methanogenesis]}$$

The quantum of natural gas produced from the landfills could be estimated by the following equation:

$$C_6H_{10}O_4 + 1.5H_2O = 3.25CH_4 + 2.75CO_2$$

The reaction signifies emission of very less amount of heat with almost 54% methane (CH_4) and 46% CO_2. The landfill gas (LFG) is flammable and a potentially harmful mixture of gases, which contains more than 99% (v/v) volume of biogas apart from water vapors, and non-methane organic compounds (NMOCs) (Krause et al. 2016). Besides volumetric contribution of NMOCs less than 1% in LFG, they possess serious adverse health impacts. However, biogas being the major constituent contributes substantial energy generation potential for LFG. LFG utilization for heat and electricity generation is promising option for preserving energy and dropping air pollution. LFG could be stable and potential source of energy as 300 m^3 of LFG can be produced from a ton of landfilled MSW (Chakma and Mathur 2017). Trace gases and halogenated and organosulfur compounds are also present in LFG in large quantity, which hampers the energy generation potential (Manasaki and Gikas 2014). However, during the consumption of LFG for energy generation, such harmful compounds are often removed with advanced LFG clean-up technology (Srivastava and Sumedha 2020). Without treatment LFG could create greenhouse gas (GHG) emission on its open release.

29.2 Impurities Removal Methods for Improved LFG Utilization

Treatment of LFG is necessary for its volumetric enhancement and thereby increasing energy recovery potential of landfill system. Apart from methane and carbon dioxide, LFG contains various poisonous compounds that hinder the heating value of overall LFG (Themelis and Ulloa 2007). Sometimes, CO_2 is also considered as unwanted element for CH_4 augmentation in LFG. Physical adsorption, chemical adsorption, and membrane separation are appropriate methods for CO_2 removal from LFG (Gaur et al. 2011; Gong et al. 2019). Various simulation and full-scale studies are available for CO_2, N_2, H_2S, and other VOCs removal from LFG (Cavenati et al. 2005; Chakma and Mathur 2017; Chetri et al. 2020; Divsalar et al. 2019; Gaur et al. 2011). Apart from these, adsorption of toxic elements such as aromatic substances, trichloroethylene, carbon tetrachloride, chloroform, etc. is also performed for improvement of LFG energy content (Baytar et al. 2020; Gong et al. 2019; Narros et al. 2009).

29.3 LFG to Energy Technologies

There are numerous technologies available for the production of electricity from LFG. Internal combustion engines (ICEs), gas oxidizers (GOs), microturbines, and turbines are the frequent ones for this purpose (Tozlu et al. 2016). The most used appliance for electricity generation from LFG is ICE as it contains the advantages of relatively low capital cost, quick startup, and raging to full load. Nevertheless, ICEs have comparatively lower operational availability with respect to other technologies (Manasaki and Gikas 2014). It can accomplish electricity yield with 40% efficiency and operational availability of ~85% and can function at methane concentration of 40% in LFG (Tozlu et al. 2016). The electricity produced through reciprocating ICE as an appropriate system with satisfactory economic income is in the range of 1–3 MW with reasonable investment cost (Bove and Lunghi 2006).

Gas turbines (GTs) have been very effective to recover heat from waste. The GT is like ICE in as much as it is not usually a “heat engine.” They work based on the principle of Brayton cycle (Ziółkowski et al. 2019). In general, the GTs are used for large-scale production of electricity from LFG, specifically more than 1 MW (Tozlu et al. 2016). Microturbines (MTs) are operated at comparatively lower temperatures and lesser compression ratios and are appropriate for minor applications (Medeiros et al. 2017). MTs can utilize methane concentration above 35% in LFG and produce electrical yield ~30% and operational availability till 95% (Tozlu et al. 2016). Both GTs and MTs require extensive maintenance cost and major service after 8 years of continuous functioning (Medeiros et al. 2017).

Gas oxidizers are comparatively latest technologies, which operate at lower temperatures. They can be operated at methane concentration as low as 1.5% in

LFG with operational availability of ~95% (Tozlu et al. 2016). Moreover, efficiency obtained could be near about 29% after such operation. Oxidizers are susceptible to major service and cost-intensive maintenance at the interval of 9 years of continuous operation (Hansen and Ringler 2013). It is notable that oxidizers are used where LFG contains very low methane content and it cannot be utilized by conventional technologies. Nevertheless, it is required to have significant flow rate of poor LFG as minimum prescribed energy production for market scenario is 250 kW.

29.4 Conclusion

Thus, by the theme of this chapter, it can be concluded that LFG could act as renewable energy source with significant energy generation capacity. Although newer technological advancements are desirable to uplift the recovery potential of LFG, conventional technologies of purifying LFG are cost intensive, less efficient, and time-taking. Besides new developments in purification of LFG there is a certain need of developing cost-effective technologies with zero-waste discharge generation. Adsorbents made from waste sludges could exemplify the cost-effective scenario in case of impurities removal from LFG.

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Chapter 30
Plasma Technology in Waste-to-Energy Valorization: Fundamentals, Current Status, and Future Directions

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Mohd Fadthul Ikmal Misnal, and Muhamad Nor Firdaus Zainal**

Abstract Plasma is a biorefinery technology that has gained popularity in the twenty-first century for waste-to-energy conversion. This advanced biorefinery offers improved energy capture efficiency, better emission control, and the ability to generate fuels or synthetic precursors from waste instead of energy. However, there are a number of issues that must be addressed in order for plasma gasification to be successful. The fundamentals of plasma gasification in waste-to-energy processing were discussed in this chapter, as well as the plasma gasification mechanism and processing. The efficiency, ability, and energy savings generated by plasma gasification can be used to make biorefinery plasma a successful technology in waste to energy-food-feed-chemical-material technology. A circular economy approach, which employs all aspects of waste throughout the production chain, is an alternative that can be used to achieve economic success.

30.1 Introduction

Intense proliferation of waste today is a result of rapidly growing population, consumerism, and industrial progress. By 2030, it is estimated that there will be 10 billion people on the planet. By 2025, it is expected that the world's population will have increased to the point where municipal solid waste (MSW) will amount up to almost 2.5 billion metric tonnes annually (Munir et al. 2019). 33.3% of world food supply has been squandered or lost based on research by the United Nations Food and Agriculture Organization, resulting in an annual waste of 1.6 billion tons of food (Talan et al. 2021). Lack of infrastructure and maintenance facilities, as well as limited resources in most underdeveloped countries causes the sustainable garbage disposal is still in the introduction phase. The significant rate of living excess production and disposal to an undeveloped landfill or contaminated disposal site is

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wreaking havoc on the environment, economy, and society. The unplanned growth of new cities in poor areas is exacerbating the problem (Nizami et al. 2017). Food waste decomposes quickly, posing serious environmental and ecological concerns, as well as the risk of humans becoming unsteady in natural surroundings. Besides, it also affects flora and fauna ecology and behavior due to consumption of food waste. This in turn impacts other biological mechanisms (Talan et al. 2021). The long-term strategy of trash management aims to improve waste treatment in order to avoid landfill dumping and its environmental consequences (Fabry et al. 2013). In addition, landfilling can have a considerable negative impact on the circular economy. Waste must be transformed into valuable resources such as "energy" by means of efficient waste treatment in order to support the radial economic expansion, manage rising energy demand, and counterbalance energy costs of waste-to-value processes (Munir et al. 2019).

Biorefineries are vital on a global scale. The International Energy Agency defined biorefining as the process of converting biomass into a variety of organic products and bio-energy sources in a sustainable manner. The food, feed, chemicals, and materials are types of organic products while the biofuel, energy, and/or heat are examples of the bio-energy sources. Organic resources, such as farming and timberland leftovers, meals, and other industrial waste, can be separated into a variety of elements and products through a series of reactive stages. A biorefinery can take advantage of the value associated with biomass feedstocks from a financial, social, or environmental standpoint (Liu et al. 2021; Nizami et al. 2017). The biorefinery concept strives to increase the economic potential of bioproduct manufacturing by looking for ways to reuse by-products through the use of various production technologies (Ubando et al. 2021). The notion of waste biorefineries is relevant and imperative in most of developing countries. This has to do with the current unwanted dumping practices imposing an environmental and economic burden, as well as for convention rising energy demands. Other than that, it also contributed to the creation of new businesses, job markets, and improvements in public health and local environment (Nizami et al. 2017).

A number of thermal processes and techniques, like combustion, pyrolysis, or gasification, have been set up for handling wastes and disposal with the goal of making progress energy from the biological fraction and landfilling (Fabry et al. 2013). Waste is also disposed and processed using biological, hydrothermal, and thermochemical techniques. These processes and techniques have their pros and cons (Munir et al. 2019). As a consequence, technology of plasma is meant to reduce or disregard this concern by extinguishing all hazardous wastelands (Paulino et al. 2020). Plasma gasification is a high-temperature waste-to-fuel gas conversion method. The plasma delivers the energy required to maintain the reactor's temperature at levels that can cause the gas molecules generated by material decomposition to dissociate. The use of plasma arc gasification for MSW is particularly common in nations where landfill space is limited, such as Japan. This technology is only used on a small basis in Europe. The units are capable of processing up to 130 tonnes of MSW per day (Ouda et al. 2016).

The improvement for waste treatment is that all the potentially harmless compounds in the waste are devastated (Breeze 2018). Other advantages of using plasma include the elimination of landfills, the disposal of hazardous waste, the replacement of crude oil, and the use of vitrified material (Fabry et al. 2013). Thus, the development and potential of plasma gasification technology on treated waste with the goal of converting waste to energy were reviewed in this study. The plasma technology is explained in detail for a better understanding, and the plasma parameters are also explained so that the elements associated with plasma technology can be recognized. It is also important to understand the fundamental and mechanism of the gasification and processing in converting waste into energy as well as for better public health and the environment.

30.2 Definition of Plasma

In 1923, Irving Langmuir was first in line to implement the "Plasma" term. Irving Langmuir defined plasma as a jelly-like behaviour in which an electrical transmit can exhibit a routine mobilization of charged particles (Zainal et al. 2015). Plasma is the fourth state of matter and it is made up of positive and negative ions, neutral electrons, and molecules. Generally, plasma can be emitted once the voltage is applied on the electrode with the assistance of carrier gas such as nitrogen, helium, and air. It generates excited species and ions that further combine to garner ultraviolet (UV) light (Tendero et al. 2006). Some plasma is derived from natural sources, also including lighting, northern light, solar wind, and the Earth's ionosphere (Keidar and Beilis 2013), while some other plasmas can be formed by human; for example, lamp and plasma television. In other words, plasma is a chemically active medium whose working power is determined by how plasma was activated. Plasma can be created at either low temperature (cold plasma) or an extremely high temperature (thermal (hot) plasma). Figure 30.1 depicts the properties of cold and thermal plasma. Thermal plasma can be produced at high pressure (>10 kPa) by using direct current (DC) or alternating current (AC), radio frequency (RF), and microwave sources. Thermal plasma is created between two electrodes in the presence of a high-temperature gas flow and plasma density. Thermal plasma is created by being sandwiched between two electrodes in the existence of a high-temperature gas flow and plasma density. The temperatures of electrons (T_e) and ions (T_h) produced by thermal plasma are comparable (Tendero et al. 2006; Von Woedtke et al. 2013). Furthermore, thermal plasma, also known as plasma jet, can be generated beyond the electrodes (Bonizzoni and Vassallo 2002).

Direct current (DC) and alternating current (AC) torches can be separated into transmitted and non-transmitted arc. The categories and details of the plasma system can be referred to Samal's 2017 review. Classic illustrations of thermal plasma involve DC transferred arcs, plasma torches, and RF inductively coupled discharges. Over the past decades, most research in thermal plasma technology have emphasized that this technology has a wide range of applications in the industry. This technology

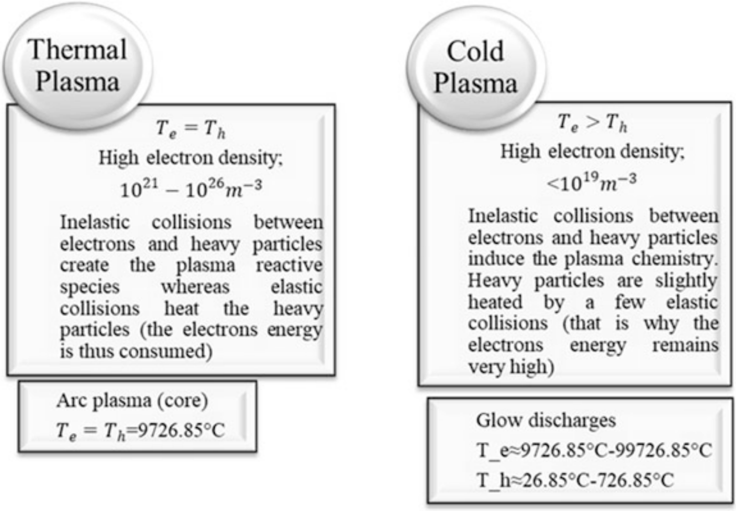

Fig. 30.1 The properties of cold and hot plasma (Tendero et al. 2006)

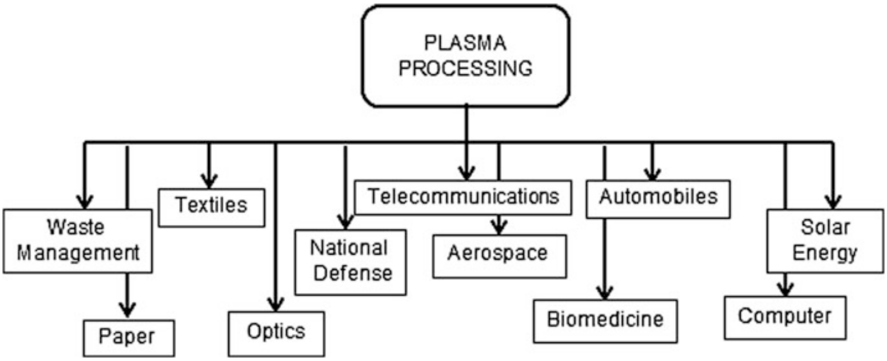

Fig. 30.2 Illustration of thermal plasma application. Source: (Samal 2017)

is commonly used for destruction of waste materials. Other areas include thermal plasma processing capable of extractive metallurgy for metal value recovery from granulated blast furnace and production of areas of oxide nanoparticles such as AlN, SiC, Si_3N_4 and processing metal nano powder formation, refractory, and refining (Samal 2017).

Besides, it is also used in deposition areas in layers for oxidation and decay shield (with red mud as coating on metal to prevent oxidization), thin film installation, nanoparticles constituents, metallic/porcelain sequence supplies, and oxide superconducting dealing out (Samal 2017). Each application provides a distinct benefit to humanity and the environment. The application of the thermal plasma can be clearly seen in Fig. 30.2. A plasma torch generates heat via the passage of an electric current through a gas flow. To date, plasma torches and plasma arc technology have been used in a variety of industrial, military, space, and other applications such as space program, waste disposal on Navy ship, and remediation of radioactive waste. Other applications of plasma arc technology include medical waste destruction, asbestos destruction, PCB destruction, melting incinerator ash, cutting heavy metals as well as melting scrap metals (Pourali 2010).

30.3 Thermal Plasma: Fundamentals, Concept, and Mechanism of Gasification

The biorefinery concept was developed to provide an alternative in the direction of promptly run-down carbon intensive, as well as pollution from oil and gas production sites. The major specific goals are to: (a) increase the demand for agricultural, nature reserve, urban, as well as commercial biodegradable (biomass) waste products while lessening environmental damage (greenhouse gas (GHG) emissions), (b) maintain a persistent fuel stockpile to encounter the aggregate population's energy essentials, (c) bring alternative chemical building blocks that can be employed resourcefully to encounter human chemical, medical, and pharmaceutical demands; and (d) focus on job creation locally, nationally, and internationally (Kumar and Verma 2021).

Physicochemical (esterification), biochemical (anaerobic digestion and fermentation), and thermochemical (pyrolysis, gasification, and combustion) procedures are the three types of biomass to energy conversion methods. The thermochemical conversion is perhaps the most advantageous and appreciated of these processes since it may reduce waste and toxicity while also producing several products that can be reused. Thermochemical is extensively employed in biorefineries to disassemble solid bio-polymeric structures into specific parts (Zhou et al. 2019). Plasma gasification is a thermochemical technique that may convert a wide range of biomass resources into useful energy and biochemicals (Inayat et al. 2020). Plasma gasification transforms biomass into syngas, which contains several gases; for example, hydrogen (H_2), carbon monoxide (CO), methane (CH_4), and carbon dioxide (CO_2). These gases can be utilized to produce vapour or heat, fuel cell feed, hydrogen, gas (natural), and some artificial compounds after the gasification process (Qin et al. 2021). Plasma gasification consumes external power heating (all thermal) as well as maintains the high temperature in order to decompose the desired waste in an oxidant starved medium. The plasma is created with high-temperatures ranging from 2000 °C to 14,000 °C. All materials with higher conversion efficiency are significantly broken down and at the same time, products like ash, slug, and syngas are released (Gray 2014; Sanlisoy and Carpinlioglu 2017). Plasmas' high temperatures can manufacture or destroy chemical species under conditions that traditional combustion cannot reach and they can greatly speed up chemical reactions.

Biological modules are oxidized and compounds are dissociated, while inorganic components of treated materials melt. After the synthesis of metallic nanoparticles cast is withdrawn from the reactor, a similar lava substance is formed after cooling and solidification.The organic components are degraded into syngas, which can be utilized as a high-quality fuel or in the chemical synthesis sector (Paulino et al. 2020). The proportion of responses in the reforming process is also accelerated by high temperatures. Compactness, rapid reaction quality, low building costs, besides the capacity to reform a comprehensive range of materials with a high proportion of bio-hydrogen production are all advantages of this method (Inayat et al. 2020). As plasma technology causes ionization and destroys toxins properly, it has also been investigated as a pyrolysis treatment for hazardous waste contaminants (Sanito et al. 2021). Ionization processes are defined as plasma-chemical processes. When it comes to waste treatment, plasma ionization is crucial. As soon as the temperature upswings rapidly and electrons are mislaid, ionization occurs, resulting in a great attentiveness of energetic and chemically active species.

The waste plasma gasification exploits the thermochemical properties. According to thermogravimetric analysis, the volatile content of both organic municipal solid waste and refuse derived fuel begins to release at 200 °C, and volatiles are totally eliminated at 500 °C and 700 °C, respectively (Bhatt et al. 2021). Due to their low mass and great movement, electrons are the first one to gain energy from magnetic charges throughout the waste treatment process. It serves as an energy source for a variety of plasma–chemical interactions. Electrons are positively charged elementary particles with bulk three to four orders significantly lower than that of neutral particles and ions.

Furthermore, the procedure must be completed with a sufficient quantity of electrons with suitable energy. The energy is then transferred to other plasma components, allowing ionization, excitation, dissociation, and other plasma-chemical reactions to occur. An energetic diffusion function of electrons is the name given to this process (EEDF). Direct ionization by electron influence, stepwise ionization by electron influence, ionization by large particle collision, photo-ionization, and external ionization are the five types of ionization (Sanito et al. 2021). Figure 30.3 illustrates an example of a plasma gasification reactor schematic which involves multiple processes of waste sorting, processes of plasma gasifier, gas purification, and conversion unit (Munir et al. 2019).

30.4 Plasma Operating Parameters

Waste materials have a variable composition and may contain impurities or other undesirable fractions that are difficult to remove. Besides, it is a permanently and extensively available source generated by the society (Inayat et al. 2020). Ancient biorefinery technological and cultural views do not directly correspond to debris biorefineries (Alibardi et al. 2020). Plasma is an appropriate technology to assess the overall environmental profile and economic sustainability of the whole process to be adopted to evaluate and compare different value recovery options. Plasma is the compelling biorefinery technique to deliver powers from wastes such as municipal

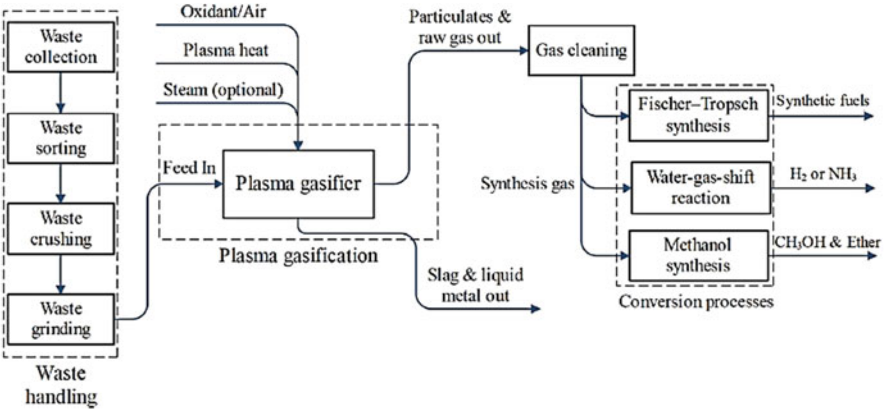

Fig. 30.3 Schematic diagram of plasma gasification reactor (Munir et al. 2019)

solid waste, animal waste, agriculture waste, industrial waste, forestry waste, and industrial waste (Kumar et al. 2019). The information about plasma gasification operating parameters on waste material must be understood to attain optimum and sustainable bio-mass and waste conversion. Input power, plasma flame length and electric field strength, experimental setup, and the effect of reactive species generated during treatment are all examples of factors that directly affect expected outcomes. The plasma flame dimensions are inversely proportional to the plasma carrier gas flow rate (Inayat et al. 2020; Đukić-Vuković et al. 2017).

30.4.1 Plasma Reactor

Technically, plasma gasification reactor can be generated using direct current (DC), microwave, and radio frequency (RF) (Tang et al. 2013). Sanlisoy and Carpinlioglu elaborated three main techniques of plasma generation. For the case of plasma generation using DC, high voltage was applied to the main energy source which eventually leads to plasma formation between the electrodes through the ionization process. Meanwhile, the plasma formation through the microwave requires lower applied voltage in comparison with DC and RF. Without any electrode design arrangement requirement, its main energy source of plasma generation depends on microwave signal created by magnetron which travels through a so-called waveguide. On the other hand, plasma generation using RF requires the electrode design arrangement, as it will act as anode and cathode according to the cycle operated by alternative current (AC) source. The intensity of applied power from AC source leads to gases ionization which contributes to the plasma formation inside the reactor (Sanlisoy and Carpinlioglu 2017). According to Sanito et al. (2021), thermal plasma and atmospheric-pressure microwave plasma can be considered as proper methods to deal with contaminants in electronic waste treatment (Sanito et al. 2021).

30.4.2 Reactor Design

Reactor design is among the most crucial plasma gasification system characteristics in order to ensure highest possible treatment effectiveness and efficiency. In chemical engineering perspective, the appropriate design selection consideration influences the desired gasification reaction kinetics. There are three categories of plasma gasifiers; plasma fixed-bed, plasma entrained-bed as well as plasma moving-bed. For the case of plasma fixed-bed, plasma is channelled into the fixed-bed (or batch mode) as slag is collected from the bottom (Zhang et al. 2011). Meanwhile, plasma gas becomes the input stream as feed is channeled into the gasifier with slag, and syngas becomes the output stream for the working operation of plasma entrained-bed (Sanlisoy and Carpinlioglu 2017). Plasma moving-bed is operated with plasma injection into continuous moving feed. Since there are a variety of reactor designs, appropriate selection in terms of feeding mechanism, gasifier configuration and specification, as well as slag and syngas collection techniques are essential (Salaudeen et al. 2019).

30.4.3 Gasifier Reaction Temperature and Residence Time

The effectiveness of plasma gasification is also influenced by gasifier reaction temperature and its residence time. Higher gasifier reaction temperature increases the gasification of MSW, net energy content, and combustion enthalpy, and at the same time generates lower tar content in syngas (lower than 10 mg/Nm^3) which eventually requires smaller reactor volume. Meanwhile, shorter residence time is preferable in order to yield simpler and stable syngas contents (Salaudeen et al. 2019).

30.4.4 Gas, Oxidant, and Steam Streams Requirements

Plasma process permits the easiest enthalpy governor by fine-tuning the electrical power. The reactive species; for example, radicals of atomic oxygen and hydrogen or hydroxyl radicals formed by the plasma are a further improvement for the practice of plasma. In plasma gasification, the generation of plasma is driven via the utilization of gases such as argon, nitrogen, helium, carbon dioxide, and carbon monoxide (Ar, N_2, H_2, CO_2, and CO). The conversion of raw syngas into alcohols, hydrogen, and synthetic fuels necessitates the cooling, cleaning, and conversion processes. In general, the success of the implementation of plasma gasification reactor design is influenced by the gas selection as well as the effectiveness of the plasma gasifier itself in order to efficiently carry out those processes in decomposing the industrial or municipal solid waste (Munir et al. 2019). Appropriate gas selection should be taken into crucial consideration which determines the composition amount of syngas. For example, more hydrogen was produced when utilizing nitrogen gas as the selected plasma gas. On the other hand, lower flow rate may be suitable to achieve a certain level of plasma gasification (Hlina et al. 2014; Tang and Huang 2007). According to Mazzoni and Janajreh (2017), the 0.7 MSW is the optimum feedstock combinations, moreover, producing the much more effective plant outcomes of 38% once pure oxygen is utilized by way of plasma gas. As vapour is introduced to airflow to generate the plasma gas, a final best vapour proportion exists for each of the waste mixes, and a maximum plant efficiency of 21.7% is achieved for the 0.5 MSW mixtures at a 34% vapour proportion in the plasma gas. For a given waste composition, a high or low vapour proportion in the plasma gas leads to a consistent decrease in process efficiency. When a high percentage of hydrogen is desired in the syngas, adding vapour to the plasma gas results in the highest percentage of hydrogen in the syngas (Mazzoni and Janajreh 2017). Meanwhile, the existence of oxidizing agents eventually influenced higher carbon conversion into syngas. Simultaneously, the importance of steam should not be overlooked, as increased steam has a huge impact on increase in the heating value of product gas, char conversion, syngas yield, and liquid fuels (Rutberg et al. 2013; Zhang et al. 2012).

30.5 Municipal Solid Waste Treatments and Value Added by Plasma Technology

Plasma techniques have been used in the metalworking industry since the eighteenth century, when plasma was created and used to supply increased temperatures in furnaces. Chemical sector employs plasma to produce acetylene using natural gas as a feedstock. Industries used plasma to make acetylene using natural gas as a feedstock in the early twentieth century. Since the early 1980s, plasma has been used to process MSW, and its performance in digesting challenging wastes reflects the technology's maturity (Sikarwar et al. 2020). MSW is challenging to employ directly in any waste-to-energy process due to its high heterogeneity in composition (Inayat et al. 2020). The MSW is made up of a variety of materials that are used on a regular basis. As indicated in Fig. 30.4, MSW includes electronic wastes such as televisions, computers, printers, cell phones, and refrigerators, as well as building and devastation garbage, healthcare waste, as well as excess waste generated in homes, businesses, enterprises, education, as well as agricultural and manufacturing operations (UNEP 2011). Around 38% of total waste is comprised of paper, cardboard, plastics, metal, and glass (Bhatt et al. 2021). Green and food waste account for 44% waste globally (Inayat et al. 2020). Worldwide, by 2025, the demand for waste-to-energy technological innovations is projected to grow by 6.45% (Sharma et al. 2021). Converting biomass and waste materials into energy, heat, and value-added petroleum goods is a viable option since these resources can produce energy, heat, and value-added petroleum products while lowering CO2 emissions to zero.

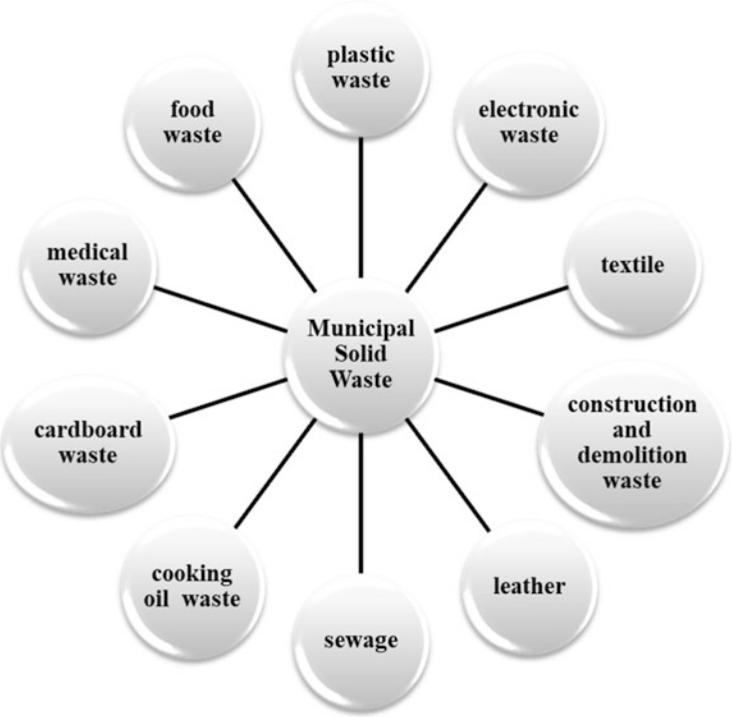

Fig. 30.4 The types of municipal solid waste for waste biorefineries (UNEP 2011)

Electricity and chemical compounds, particularly hydrogen fuel, are the principal results of biomass thermochemical transformation (Inayat et al. 2020).

Although most gasification projects are now focused on producing heat and energy, certain businesses, such as Enerkem (https://enerkem.com/) in Canada, are incorporating gasification into biorefinery systems. The Enerkem MSW gasification chemical recycling plant turns 350 thousand tonnes of trash hooked on 0.27 billion litres of methanol each year (Khan et al. 2020). Plasma torches located at the bottom of the gasifier are used by Hitachi Metals Env. Syst. Co. and Alter NG to melt inorganics and form glass aggregate and metal nodules. Plasma torches are also used in this technique to produce synthesis gas with high sensitivity and low tar concentration. Figure 30.5 depicts the outline of the gasification plant.

Organic waste in MSW includes farming and natural resources debris, effluents and waste from the food processing industry, waste-waters, yard garbage, and residential organic matter. Proteins, carbohydrates, fats, fibres, vitamins, and bioactive agents (antioxidants and antibacterial agents, enzymes) are all valuable components of these materials and they should be recovered. Pigments, pharmaceuticals, flavours, organic acids, biopolymers, biofuels and soil improvers can be extracted or manufactured using a mix of treatments followed by adequate separation and purification techniques. The vitrification of incinerator ash; a hazardous leftover

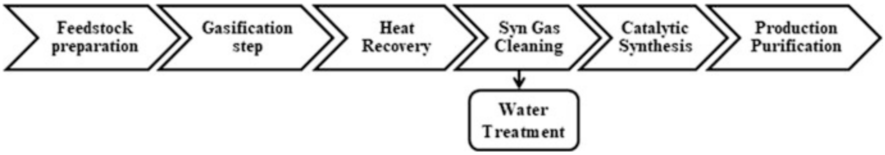

Fig. 30.5 The outline of gasification plant (Khan et al. 2020)

that is possibly immobilized with a plasma treatment, is the most commonly acknowledged use of plasmas for waste management. Several existing installations use plasmas for concentration of nuclear material from low level nuclear wastes. The application of plasma is expected to expand as it has been proven to be highly reliable (Heberlein and Murphy 2008).

According to Nizami et al. (2017), plasma arc gasification has the potential to gasify both organic and inorganic waste. The advantages of using plasma for this waste include no greenhouse gas emissions, ability to treat all waste types, and easily expandable technology with 32% of efficiency. Electricity costs can be reduced by generating electricity from exhaust fumes (Nizami et al. 2017). The capacity to provide higher temperature with high intensity concentration, autonomy from waste type, the potential to garner marketable co-products while achieving high chaos performance, processing facility regulation, environmental friendliness, and waste to energy have all stimulated support in the use of sophisticated thermal plasma technology for waste treatment.

The thermal plasma pathway has been utilized to heal a number of pollutants and release fuel gas, which has been used in a range of applications. Surprisingly, the inert glassy slag produced as a byproduct of waste treatment boosted by plasma can be improved into value-added products such as glass, ceramics, material for road filling and concrete industry resources, among other elements. In real-world applications, plasma can be used to recover prized elements and eliminate pollutants from e-waste. The air was heated to 6000 °C by plasma torches located near the air nozzles, melting and trapping the undesired inorganic components in MSW as a vitrified slag (Sikarwar et al. 2020; Sanito et al. 2021; Nanda and Berruti 2021).

30.5.1 Plastic Waste

Plastic waste is a dangerous global problem that has negative socioeconomic and environmental consequences. The rapid growth of the world's population, along with the desire for improving the living standards, has resulted in an increase in the demand for energy resources and the rate at which they are consumed per capita. It currently weighs 8–12 million tonnes globally and is expected to grow fast.

The improper disposal of solid plastic trash has harmed the environment and made it harder for countries to achieve their sustainability aims and ambitions. Only 15–20% of plastic waste can be recycled using traditional recycling procedures such as sorting, washing, grinding, and extrusion. As a result, regulations for the management and dumping of malleable trash are becoming increasingly important around the world. By 2025, the market for waste-to-energy technology is expected to grow by 6.4% globally (Sharma et al. 2021). Mazzoni and Janajreh (2017) constructed the plant to see if plasma gasification could be used to make progress energy from MSW once plastic solid waste was incorporated. The consumption of oxygen-enriched air by way of a plasma creating gas in the co-gasification of plastic solid waste and MSW can increase plant efficiency. These make it worthwhile to invest in an air separation unit (ASU) for additional oxygen. The most effective presentation of traditional combustion-based waste-to-energy innovations as a guideline is the plant efficiencies, which reach well beyond 26%. In the process of plasma processing waste plastics, Mączka et al. (2013) developed a method for obtaining liquid fuels and fuel gas. The liquid products of plasma processing of polyethylene contained almost only homologues of aliphatic carbohydrates and lack of contaminants should make further processing and application easier. Their study proves that the plasma is able to generate large amounts of hydrogen (also called the fuel of the future). The plasma method is more environmentally friendly than traditional method of combusting plastics.

30.5.2 Food Wastes

Food wastes are the total amount of wastage generated within different stages of food supply chain (Vilariño et al. 2017). Food wastes had been rated at the uppermost and third place in the entire amount of domestic waste in the waste disposal (Ma et al. 2020). There are approximately 1.3×10^9 tons (t) of food waste created annually due to urban migration and explosive growth of human population (FAO 2017). Integrated biorefinery solutions are large enough to make fuel production from underutilized seaweeds economically viable.

The biorefinery concept for seaweed has been presented in order to use all useful seaweed ingredients in an economically possible cascading process while limiting climate change impact. When 4% seaweed was treated with a product, plasma progesterone levels jumped by 158% compared to the study's starting point. Seaweed supplementation had no effect on milk output or composition, and triiodothyronine and thyroxine levels were also greater (Torres et al. 2019). Zhou et al. (2019) has demonstrated that pulsed energy from low-temperature plasma transforms both dry and wet algal biomass into value-added compounds and solid carbon fast and efficiently. The catalyst employed in plasma catalytic liquefaction (PCL) is critical for reducing liquefaction time, boosting liquefaction yield, and improving biocrude yield and quality. The chemical examination of the resultant liquid product also revealed that plasma-enabled liquefaction is possibly more successful than other traditional methods in transforming the protein components of biomass. In order to assist PCL gain momentum in new applications, more attention should be made into power station and strategy and optimization, solvent exchange for directly bio crude split-up and refining, and high achievement catalysts for improving product selectivity (Zhou et al. 2019). Qin looked at a variety of fruit trashes and wood leftovers, including apple debris also apple twigs, to see if they could produce hydrogen-rich syngas via plasma gasification processes. Syngas production yields were measured at 850 °C response temperature, 0.25 g/min flow of the water, and particle sizes of 1.0–2.8 mm. Food wastes like apple pomace generated a H_2-rich syngas resulting in gasification process alternatively produced methane (CH_4) by methanogenic bacteria (Qin et al. 2021). Contreras et al. (2019) in his study also showed the effectiveness of high voltage electric discharge through plasma technology to extract proteins from seeds.

30.5.3 Electronic Waste

Electronic waste, also known as e-waste, is made up of a variety of circuit boards that are generated from various electronic wastes made up of engineering plastics. Engineering plastics make up the majority of the garbage, which contains large amounts of heavy metals. Large household utilizations, IT (information technology) also telecom devices, consumption facilities, lighting systems, electronic components, toys, recreational and recreation equipment, healthcare products, instantaneous dispenser, computer monitor, and governor devices are among the categories of e-waste applications (Nanda and Berruti 2021; Sikarwar et al. 2020).

According to Sanito et al. (2021), the overall load of worldwide electrical and electronic equipment (EEE) increased by 0.0025 billion metric tonnes (Mt) in 2019, with the overall load of monitors reaching 53.6 Mt. of e-waste (average 7.3 kg per capita). Developing technology and electronic gadgets are leading to increased e-waste volumes, which are growing at a quicker rate than other types of wastes. According to Rath et al. (2012), treatment of e-waste to recover metal values using thermal arc plasma reactor coupled with acid leaching showed a good efficiency of metal recovery in solid form. Hence, the leaching process resulted in two products for subsequent hydro and electrometallurgical operations to recover pure metal values (Rath et al. 2012). Breeze (2018) stated that various types of plasma such as thermal plasma and atmospheric-pressure microwave plasma have been employed to deal with pollutants from e-waste in the recent decade. Plasma gasification, according to Chanthakett et al. (2021), offers the best performance in treating diverse forms of waste with low emissions. As a result, plasma technology can be used to treat e-waste, making it a suitable approach for biorefinery waste.

30.6 Plasma Gasification Technology Challenges

30.6.1 Fundamental Process Understanding

One of the main challenges in plasma gasification technology implementation is the lack of fundamental process understanding especially involving the chemical engineering perspective of operations in thermodynamics, which consists of mass transfer and reaction kinetics knowledge. The lack of expertise in integrating this theoretical knowledge into real industrial scale reactor plants contributed to low understanding of its engineering system process, thus making the proposed plasma gasification technology difficult to be evaluated in terms of its industrial readiness. In addition, lack of understanding can lead to major industrial disaster since the technology involves the utilization of high degree thermal plasma processing. It is therefore crucial for all scientists and engineers to sit down together and work on details in fundamental thermodynamics, especially in terms of mass transfer and reaction kinetics in order to gain a better understanding of its engineering system process, thus achieving more effective and efficient reactor plant design for this relatively new technology (Munir et al. 2019).

30.6.2 Operational Cost

In comparison with other waste-to-energy processing technologies, plasma gasification can be considered as relatively costly in terms of its implementation. Several considerations such as advanced plant automation, material selection to withstand its extreme thermal condition, and the need of appropriate waste sorting should be taken into consideration, making the implementation of plasma gasification reactor in industrial or community scale rather expensive. According to various data on plasma gasification reactor construction costs, constructing a power station with a daily capacity of 0.5 thousand tonnes MSW will cost between USD 65 and 200 million (Young 2010; Clark and Rogoff 2010). Apart from plant design consideration, the cost increment is also contributed by the plasma source assemblage itself which can be even more costly than USD 50 thousand, not including the operational maintenance of the plant itself (Young 2010; Wilson et al. 2013). Specific mobile plasma waste processing plants are available to be appealing because they eliminate waste shipping costs plus lower asset expenses, employment charges raise the cost of this sort of treatment (Heberlein and Murphy 2008).

30.6.3 Commercialization

One of the indicators that show the readiness level of a technology is the commercialization factor. For plasma gasification technology, the commercialization factor remains the obstacle that needs to be resolved, which is why there are only five commercialized plasma gasification plants worldwide. Despite its potential for waste-to-energy application, other external factors such as safety concerns (due to extreme operating thermal condition) and high labour costs need to be seriously considered as this technology is still in the early phase of implementation especially at the community level (Byun et al. 2012). This limitation is the primary reason why the government and industry players are still hesitant to invest in large-scale implementation (Gomez et al. 2009; Asadullah 2014). Despite a number of technical challenges in its implementation, this technology is still preferred for the purpose of waste disposal, especially with the establishment of several plasma gasification reactor plants in Japan (Mihama-Mikata) and China (Wuhan Kaidi/Alter NRG) (Byun et al. 2012; Fabry et al. 2013).

30.6.4 Community Readiness Level

The issue with implementing new technology is usually how to get it from a pilot scale study to a community (or industrial) scale practice. Due to limited technical knowledge (especially in operational mechanism understanding and safety concern due to its higher thermal operation process), plasma gasification technology is still considered to be at moderate community readiness level (CRL). Therefore, it is crucial to educate the public as well as industrial players in terms of its practicality for the waste-to-energy processing management, in order to gain their approval and support to implement this relatively new technology (Munir et al. 2019).

30.6.5 Energy Intensive Process

Technically, the process of plasma gasification itself involves high intensity of plasma energy in order to heat and melt as well as vaporize the feed wastes. High intensity of plasma energy is required to break down the molecular bonds in gaseous phase, which is the main reason why this process requires a costly DC power source. Since this technology is considered as highly-energy-intensive process, the concern arises on several aspects such as high power consumption as well as significant amount of greenhouse gas (GHG) release to the surrounding environment (Fischedick et al. 2014; Munir et al. 2019).

30.6.6 Waste Sorting Difficulties

When dealing with MSW, there will be a serious challenge for differentiating and sorting of wastes based on its types, since there are different categories such as metal, glass, inorganic, organic as well as wet wastes. Ineffective waste sorting affects the synthesis of gas production which eventually deteriorates the plasma gasifier refractory linings. Despite proof of concept demonstrations on a pilot scale, the waste sorting system has yet to be implemented in industrial scale reactor plants for plasma gasification technology. In addition, some types of wastes will influence the efficiency of waste-to-energy processing; for example, wet wastes which require higher energy in the gas synthesis process, in comparison with dry wastes (Munir et al. 2019).

30.7 Conclusion

Plasma gasification is a potential biorefinery technology, for instance, in waste–to-energy conversion. The benefits of plasma gasification in the treatment of municipal solid wastes (MSW) were placed as a value added when looking at the overall economics. Even though the costing of the plasma technology is expensive, this problem can be overcome by (1) lowering gaseous flow rate and (2) using low-temperature plasma for waste treatment for low power operation. Scaling up existing plants should be investigated, as should the use of new technologies in conjunction with government incentives and initiatives. Perhaps in the coming years, the plasma technology poised to be shown in genuine applications. Future research should look into the quality of the products after plasma treatment, the budget concern, the appropriate stability proxy to exclusively present, and other harsh environment in plasma technology's essential features for the plasma e-waste application technology in the trade.

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Part IV

Criteria for Policy, Environmental, Social, Intellectual Property, Economic Aspects, and Scalability

Chapter 31
Strategy and Design of Innovation Policy Road Mapping for Waste Biorefineries

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Abstract The trend to move toward utilization of renewable feedstocks has gained momentum over the past decade due to the increasing understanding of climate change consequences. Every country across the globe now aims to keep itself self-sustainable in terms of energy requirements, reducing the import dependence to the maximum extent possible. This calls for the effective utilization of domestically available carbon resources for the production of fuel, materials, and energy. With the increasing awareness of the benefits of bio-based feedstocks conversion/utilization, many countries have come up with their own policies for incentivizing biomass utilization and its products. Residues or waste processing biorefineries best work in decentralized model to meet the local requirements due to the feedstock supply chain/scale of requirement, energy optimization, and net carbon emissions. This chapter aims to provide a holistic view on the different policies adopted across the globe on circular economy with respect to biotic materials and the current status of biomass utilization to help understand the differences and similarities among them. This will help researchers to get a view on the innovations required to strategically map the feedstocks available to the suitable processes and make biorefinery concept a reality in the days to come.

31.1 Introduction

Humankind has used fossil fuels to produce various forms of energy without considering its environmental implications. It has not only led to massive damage of the planet but also reduced the share of renewable sources of energy due to its ease of utilization and high energy density (Rama Mohan 2016). The so-called developed and developing societies are generating huge amount of agricultural and industrial waste in addition to household waste that gets accumulated as municipal solid waste.

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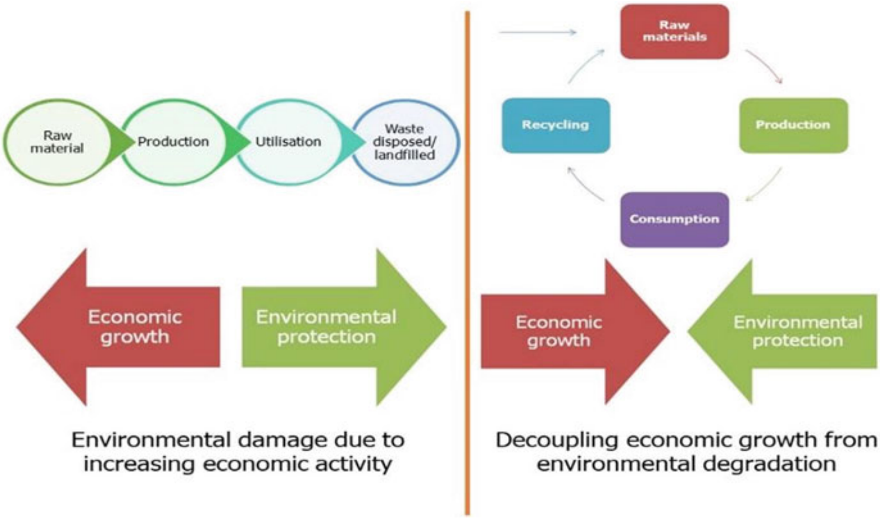


Fig. 31.1 Linear vs. circular economy

Treatment and management of construction debris has been quite a challenging task as millions of tons of waste are generated every year worldwide. All these problems have led to a plethora of adverse climatic changes ranging from forest fires, droughts to polar ice caps melting, cloud bursts, and floods. The Paris Agreement requires mankind to limit global warming to well below 2 °C, preferably to 1.5 °C as compared to pre-industrial levels. The Intergovernmental Panel on Climate Change (IPCC) suggests that to retain warming to well within 1.5 °C, CO_2 emissions should decline by 25% by 2030 and by 100% by 2070 ("IPCC — Intergovernmental Panel on Climate Change," n.d.).

The COVID-19 pandemic is an eye-opener for the humankind to take urgent steps to reduce the environmental damage caused globally that could lead to several other dangers in the future. To tackle such issues, environment-friendly renewable resources have attracted attention to meet the energy demand.

In the past, materials were mined or manufactured from scratch, used once, and thrown as waste. There has been an increased awareness recently on the concept of reuse and recycle. This has led to the rise of service economy as compared to manufacturing/mining industries. This linear economy concept created an image that economic development is always associated with environmental damage. Researchers are working relentlessly on developing waste remediation/conversion processes to meet the energy demands and produce useful products maximizing the value of the available resources. Such a transition from a linear to circular economy will lead to economic development without causing environmental degradation (Fig. 31.1). They will also help in meeting several of the sustainable development goals as put forth by the United Nations.

Biorefineries are units where processing of biomass into biofuels, bioenergy, and bio-based products is carried out. These are integrated networks of facilities that cover a wide range of processes targeted at the sustainable transformation of biomass into fuels, energy, chemicals, and/or materials. Unfortunately, factors such as policy framework, governmental actions, industrial cooperation, etc., have so far resulted in limited implementation and commercialization of these biorefineries. Yet this is an important area of research that still requires continual attention to develop/improvise processes that can target the future requirements in an environment-friendly manner (Rama Mohan 2016).

Innovation is a systematic approach that comprises a variety of actions by the innovator and innovating organization (Smits and Kuhlmann 2004). Systematicity is a massive challenge for policymaking itself and requires the inputs of researchers, developers, and policymakers. Over the last few years, road mapping of the innovations carried out in different areas has been substantially compiled for making a strategic policy formulation. Innovation policy road mapping (IPRM) has emerged as a new methodological framework linking R&D results to policymaking (Ahlqvist 2012).

In this scenario, it is extremely important to understand the different policies adopted by the different governments across the globe with respect to biomass conversion, waste utilization, and residue management. These areas require a top-down approach where the decision-makers present their long-term vision for its utilization. This will then provide cues to the researchers working in these areas to choose gaps that need to be filled to ensure that the target is reached with combined efforts. The current status of deployment of biorefineries will help in understanding the different policies that have helped in their growth and shaped their sustenance. With an overview of the trends for future requirements, it is possible to learn from the past and devise better strategies for the future with respect to biomass conversion. This chapter aims to provide a holistic view of the policies adopted by major players/governments with respect to biomass conversion. It also aims to make the readers aware of the current biomass conversion processes that are at present on field and the policies that were supportive of its deployment.

31.2 Effect of COVID-19 on Global Projections

The demand for crude oil had fallen considerably since the COVID-19 pandemic. Globally, it created ripples in all areas of economic development, transport, manufacturing, import and export of different countries, etc. With respect to crude oil usage, there was a drop in fuel requirement due to reduced land and air traffic caused by several lockdowns. Similar pandemics may reoccur and is difficult to predict its far-flung effects in different sectors in various countries.

As a positive side effect of lockdown, carbon dioxide (CO_2) emissions reduced and there was a worldwide reduction in pollution till the governments were back on track for increased economic development.

The pandemic has caused several countries to rethink their strategies and has led to course correction to meet their commitments (Flach et al. 2020). Most countries are aggressively targeting the use of renewable resources as soon as possible so that their net emissions are reduced. In this scenario, biomass is given preference by the harder-to-abate sectors which require organic carbon.

31.3 Biomass Usage in History

Prior to the futuristic utilization of biomass, it is necessary to understand the role of biomass in the past. It has been used by mankind since time immemorial, initially, to provide heat from cold weather, act as a fire source to save themselves from wild animals or for cooking purposes, etc. Over the course of years, humans learnt to make charcoal that could be used in household and industrial applications. Biomass-based stoves were slowly introduced into the civilization for household cooking. Industrial revolution in terms of using furnaces also started with the ability to reach high temperatures using charcoal that led to the growth of metals (Metal Age). Worldwide biomass consumption increased from 700 Mt. in 1700 to 2.5 Gt in 2000 which is less than 4 times increase. In the same period, fossil fuel extraction increased from less than 10Mt to 8.1 Gt in terms of oil equivalent that is a huge 800-fold expansion. In gross energy terms, global supply of biofuels and fossil fuels was the same in 1900 (~ 22EJ), and by 1950, the fossil fuel usage was 3 times that of biomass which later became eight-fold by 2000. When this is adjusted to actually deliverable useful energy, the rise in fossil fuel usage is 20-fold. Biomass dependence slowly reduced in Western Europe by 1850 due to coal usage. The situation was similar in the USA as well where coal and oil were used. Elsewhere, the dependence on biomass existed till twentieth century like in the most populous nations of Asia where biomass was significantly used till the 1970s. It is still the single largest primary source of energy in sub-Saharan Africa (Smil 2017).

31.4 Biomass Composition

Terrestrial civilization is a solar energy dependant one, be it direct or indirect manner for all possible needs. Biomass is an organic material that is formed through the process of photosynthesis. As an energy source, biomass has many advantages mainly due to its renewable nature. It is believed that green energy consists solely of wind, solar, and geothermal energy. However, biomass has the potential to provide nations with the most required renewable organic carbon. It can be used to produce bio-based materials, chemicals, fuels, and even energy/electricity (Hayes 2013).

First-generation biofuels are produced using edible feedstocks causing the food vs. fuel issue. Second-generation biofuels are produced from lignocellulosic biomass that are usually residues or process wastes. They can be crop residues, forestry wastes, defatted cakes, invasive terrestrial species, etc. The main natural polymers in lignocellulosic biomass are cellulose, hemicellulose, and lignin. In addition, it also consists of minor amounts of extractives, pectins, proteins, and minerals. The abundance of individual components varies between different biomass and also within its parts. In general, cellulose comprises of 35–55% of lignocellulosic biomass and is the most prevalent natural polymer. Cellulose is a homogeneous, linear polysaccharide with a well-defined structure, consisting entirely of a 4 C1 conformation of β-1,4-linked D glucopyranose units (Hayes 2013). Hemicellulose is the second most prevalent natural polymer, accounting for 20–35% of lignocellulosic biomass, followed by lignin, which accounts for 10–30%. 4-O-methylglucoronoxylans, arabinoxylans, galactoglucomannans, xyloglucan, and -1,3;1,4-glucan are all major hemicellulose polysaccharides. Lignin is a three-dimensional polymer with phenylpropane units with a complex structure. The chemical composition of lignin reveals that it is largely aromatic in nature. Its simple molecular units are often bound by ether bonds, but there are also carbon-to-carbon linkages. Different functional side groups such as hydroxyl, methoxyl, and carbonyl groups may be distinguished. Both hemicelluloses and cellulose have covalent bonds giving the plant greater mechanical ability. The holocellulose part of biomass is majorly used by the pulp and paper industry leaving behind lignin as a by-product. The latest contender for the cellulose and hemicellulose fractions is the 2G ethanol industry which will also end up producing huge quantities of lignin as by-product. As of now, lignin is mostly used for producing process heat by burning, but it can be a good source of high-value chemicals like vanillin and phenol (Vassilev et al. 2010; Kohli et al. 2019). Third-generation biofuels are produced from aquatic biomass. Algal feedstocks such as microalgae and macroalgae are used to produce several high-value products.

Researchers all over the globe are working on various conversion methods to valorize different types of biomasses (Fig. 31.2). They are in various stages of development: lab scale, pilot scale, demo scale, and commercially viable on field. The following sections will discuss the processes/units that are either in demo or commercial scale as the chapter aims to provide views on strategic policymaking in biomass area. Unless proven to be viable on larger scales, R&D may not be able to influence decision-makers immediately and hence the decision to restrict in this chapter.

31.5 Biochemicals and Biomaterials

The amount of biomass available at a particular location is usually restricted, but there are several competing applications for the same. Usually, processes are developed considering the complete availability of resource at a particular location ignoring its competing uses. This leads to issues in on-field deployment of the process due to lack of feedstock availability. Hence, to tackle this it is important to

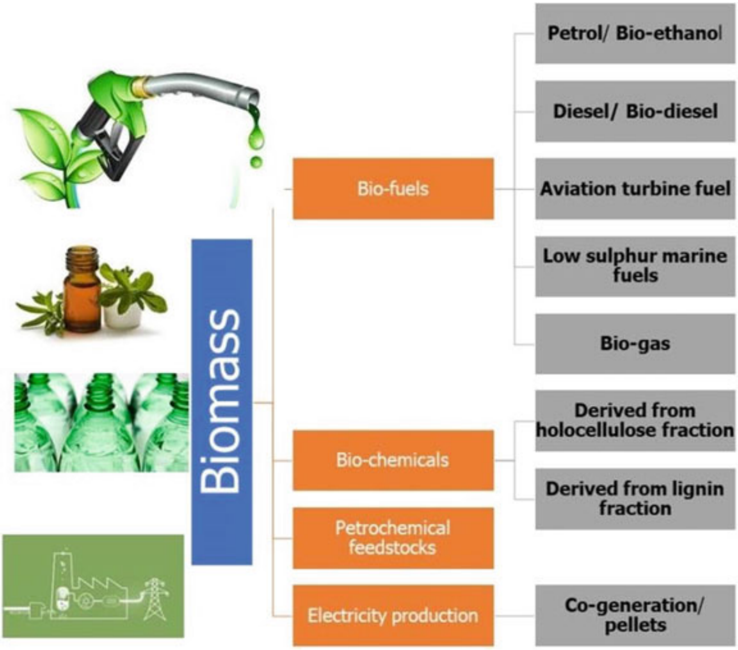


Fig. 31.2 Different biomass conversion methods

prioritize the feedstock usage to processes that help in retaining the organic carbon on the earth's surface rather than emitting it into the atmosphere in the form of CO_2 as shown in Fig. 31.3 (Müller et al. 2015). The first preference should be provided to the production of biomaterials followed by biochemicals. These two areas require the presence of organic carbon and hence the usage of biomass to produce materials/ chemicals is justified. This is followed by biofuels production that can be used for harder-to-abate sectors like in shipping or aviation till long-range EVs or hydrogen fueled vehicles are well established. In cases where biomass availability is less than that required for an optimal scale or in cases where end-of-life wastes are available, production of bioenergy is favored. This will help in retaining the renewable, sustainable nature of biomass through a circular economy.

31.5.1 Biomaterials

Numerous types of biomaterials can be generated from different biomass that has applications in various fields. Some of the biomaterials being produced so far are bioplastics made from plant oils and sugars; biofoams and biorubber made from plant oils and latex; and biocomposites made from agricultural and forestry biofibers used to make car door panels and components (Popa 2018).

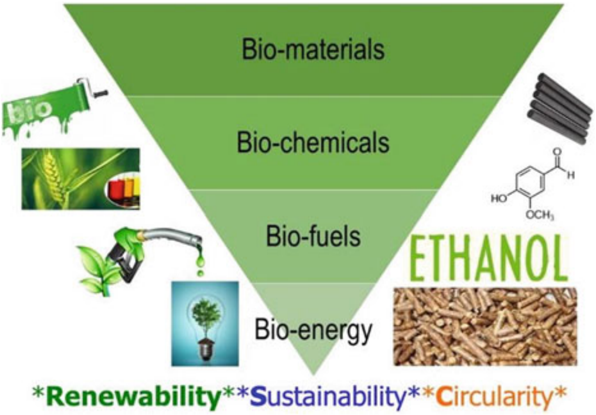


Fig. 31.3 Prioritization of biomass feedstocks for utilization

31.5.1.1 Biofibers and Biocomposites

Biofibers are biodegradable materials that have a wide range of applications in paper making, textiles, structural parts, architecture, and furniture industries. They can be mixed with oil-based polymers and resins for use in cars, aerospace, and other industries where robust materials are required. Depending on the matrix used, they can be biodegradable or recyclable. As a consequence, according to some reports, the use of bioderived polymers with natural fiber reinforcement may result in a whole new generation of biodegradable goods suitable for packaging and disposable applications. Difference in properties of biomaterials can be attributed to the feedstock used and its characteristics which in turn depend on the soil and other conditions of its growth. The rapidly expanding bio-derived polymer market has resulted in extensive research on natural fibers in a variety of matrices (Popa 2018; Zhou et al. 2016). Biofibers act as insulation in biocomposites adding resilience and stiffness to the resulting composite. Low cost, low density, high hardness, acceptable basic strength properties, reduced tool wear, reduced dermal and respiratory discomfort, ease of separation, increased energy, and biodegradability are some of its benefits. The biggest disadvantage of biofibers is that they are hydrophilic in nature.

31.5.1.2 Bioplastics

Bioplastics are gaining importance due to the increased use of single-time plastic derived from fossil resources. At present, polymers are being made from starch crops and vegetable oils rather than waste biomass. Polyhydroxyalkanoates (PHA), polylactic acid (PLA), polybutylene succinate (PBS), and polycaprolactone (PCL) are the primary bioplastic segments ("Biodegradable Plastic Market Research Report: Market size, Industry outlook, Market Forecast, Demand Analysis, Market Share, Market Report 2021–2026," n.d.).

Lignin is a very good source of aromatic compounds which can be used as petrochemical feedstocks for the production of many polymers (Yang et al. 2019). As of now, processes are under development and also deployed in some locations for the utilization of waste lignin available for the production of biopolymers. This area still has a lot of scope for R&D and further commercialization (Ashter 2016; Coppola et al. 2021).

31.5.2 Biochemicals

The integrated biorefineries generally use the same or different biomass feedstocks and a variety of conversion processes to produce targeted products. Highly efficient conversion processes are required to produce high-value chemicals from an industrial standpoint (Kohli et al. 2019). Alcohols, organic acids such as formic acid and levulinic acid, and furanics such as 5-hydroxymethylfurfural (5-HMF) and furfurals are among the chemicals targeted. These chemicals can then be processed into various derivatives as they have potential applications in polymers, solvent, and other industries (Werpy and Petersen 2004). Processes for lignin-derived chemicals are still in the lab and pilot scale of development and requires more optimization before it can see the dawn of deployment (Program et al. 2004).

31.5.2.1 5-Hydroxymethylfurfural (5-HMF)

AVA Biochem BSL AG, headquartered in Switzerland, announced the world's first industrial plant startup for manufacturing 5-hydroxymethylfurfural (5-HMF) at Muttenz in Clariant's Infrapark near Basel. The plant has been designed to produce 20 tons per year of 5-HMF with a purity of up to 99.9% using woody feedstock. A modified version of the hydrothermal carbonization (HTC) process is being used to make the platform chemical in industrial quantities and consistent quality (Hoydonckx et al. 2007). Fructose is usually the sugar feedstock used in the production of 5-HMF, but since fructose is costly, some studies have been conducted using glucose instead. 5-HMF was used to create derivatives such as levulinic acid, 2,5-bis(hydroxymethyl)furan (2,5-BHF), 2,5-dimethylfuran (2,5-DMF), and 2,5-diformylfuran (2,5-DFF). These derivatives are used as precursors in the synthesis of products such as polyesters, polyamides, and polyurethane (Werpy and Petersen 2004) ("World's first 5-HMF industrial facility | Green Chemicals Blog," n.d.).

31.5.2.2 Levulinic Acid

In 2004, the US Department of Energy's Biomass Program identified levulinic acid as one of the most potential value-added bio-derived compounds. Bioactive textiles, batteries, and electronics are among the many uses for this compound (Werpy and Petersen 2004). Lignocellulosic biomass was converted to LA on a commercial scale in Caserta, Italy. As a result of a modification, the facility now has two reactors. Upon switching to locally available tobacco chops or paper mill waste as feedstocks, salt and humin deposition clogged the first reactor (Galletti et al. 2012). For the recovery and purification of levulinic acid, GFBiochemicals has developed a novel process that uses a combination of chemical and physical methods. The formic acid and char produced by the continuous process are recovered. High product yields and productivity, focused process streams, and fast recovery are the results of this approach. Levulinic acid derivatives (gamma-valerolactone, methyltetrahydrofuran, 1,4-pentadiol, diphenolic acid) are some of the targeted products ("Caserta Levulinic Acid Plant," n.d.).

31.5.2.3 Furfural

Furfural is another critical chemical formed during lignocellulosic biomass conversion processes (Verevkin et al. 2009). Hemicellulose is composed of C5 sugars such as xylose and arabinose that can be used to make furfural. Furfural is as an intermediate in the processing of chemicals such as furan, furfuryl alcohol, and tetrahydrofuran (THF). The Quaker Oats Company manufactured furfural for the first time in 1921 using oat hulls. The firm faced several drawbacks such as minimal demand, high maintenance costs, and poor yields, yet the manufacturing processes have not dramatically changed since 1980 (Werpy and Petersen 2004). Some of the raw materials include corn cobs, rice husk, sugarcane bagasse, etc. and the targeted end products/applications are furfuryl alcohol, solvent, etc. Their end users are petroleum refineries, agricultural formulations, paints and coatings, pharmaceuticals, and others ("World's first 5-HMF industrial facility | Green Chemicals Blog," n.d.).

Furfuryl alcohol (FA) is the most significant chemical derived from furfural and accounts for around 65% of its utilization. Currently, FA is generated industrially by hydrogenating furfural in the gas or liquid phase over Cu-Cr catalysts. Chromium in these catalysts poses significant environmental issues due to its toxicity. As a result, current research is focused on developing more environmentally friendly catalysts capable of selectively hydrogenating the carbonyl group while retaining the C=C bonds (Kobayashi et al. 2014; Verevkin et al. 2009).

31.5.2.4 Succinic Acid

Succinic acid is another high-value bio-based chemical with the potential to increase biorefinery viability and productivity. It is used to make chemicals such as 1,4-butanediol (BDO), −butyrolactone (GBL), N-methyl-2-pyrrolidone, tetrahydrofuran (THF), and succinic acid esters (Werpy and Petersen 2004). BioAmber, Myraint, DSM, Mitsui & Co, Mitsubishi, BASF, Roquette Frerse S.A, Purac, and Reverdia are some of the major companies profiled in the bio-succinic acid industry.

Cassava bagasse, sugarcane bagasse, agave, cheese whey, and sake lees are the feedstocks currently used. The dry yield of succinic acid ranges from 0.4 to 0.8 g per gram of biomass when various pretreatment, hydrolysis, and fermentation microorganisms are used ("Bio Succinic Acid Market (Applications and Geography) - Size, Share, Trends, Analysis, Research, Future Demand, Scope and Forecast, 2013–2020," n.d.).

31.5.2.5 Lactic Acid

Lactic acid (also known as 2-hydroxypropanoic acid) is a vital chemical and can be used to make alkyl lactates, propylene glycol, propylene oxide, acrylic acid, and polyethylene glycol. Several industries including cooking, pharmaceuticals, and cosmetics require this chemical (Sun et al. 2011). It is usually produced after a series of complex reactions that include aldol condensation, retro-aldol condensation, dehydration, and 1,2-hydride changes (Datta and Henry 2006). Lactic acid and formic acid were historically produced by fermentation, but advancements in biotechnology and chemical synthesis have replaced the earlier fermentation technique. Various agro-industrial residues such as cassava bagasse, coffee husk, apple pomace, soybean, sugarcane, corn cobs, press-mud, citric pulps, wheat bran, and kiwi fruit peel are at present being used to produce organic acids (Hayashi and Sasaki 2005).

31.6 Biorefinery Concept Gone Wrong: Case Study

Some of the major players in the area of biomass conversion to valuable products are BASF SE, UOP Honeywell, Royal Dutch Shell, Cargill Inc., The Dow Chemical Company, Eastman Chemical Company, Du Pont. Carbion, BioAmber, Genomatica, Senvia Chemicals, Nature Works LLC, SIM Chemicals, Discovery Fine Chemicals, Synbra Technology, and Galactic are among the other players in the value chain (Bird 2011). However, in the recent past we have also noticed some plants that were built and operated for a very brief period of time and were later shut down due to both technical and non-technical reasons. Some of the issues that have plagued the biorefinery industry are the continuous availability of feedstock, consistent quality of feedstock, reactor clogging, catalyst sintering, varying market demand of product, etc. We have therefore discussed one particular case of a biorefinery concept failure in the recent past but also wish to put on record that this is not the only case of shutdown in recent times.

KiOR began as a collaboration between Khosla Ventures and BIOeCON which is a small Dutch startup that had created a groundbreaking "Biomass Catalytic Cracking Process" (BCC). Through this technology, biomass such as grass and wood could be converted into bio-oil which would then be upgraded to transportation fuels. Though the first manufacturing plant opened in May 2011, the first batch of fuel was not produced until November 2012 due to various manufacturing problems at the plant. Technical operational issues cropped up at the woodchip conveyor system and the cleaning system being clogged with a tar-like material. Even with an increase in the operating costs, the issues could not be solved to achieve a stable production rate ("Kior Falls as Biofuel Production Misses Forecast by 75% - Bloomberg," n.d.). The design was to produce 72 gallons of diesel from one ton of biomass, but the process was far from successful. The corporation was subsequently forced to file for bankruptcy with the SEC ("A Biofuel Dream Gone Bad | Fortune," n.d.).

Similarly, several biofuel startups seeking to generate next-generation fuels from plant waste (rather than corn and soybeans) have found it very difficult to scale up. They face enormous difficulties to make it through the so-called valley of death transition from small-scale development to large-scale commercialization at the low price point needed to compete with fossil-derived hydrocarbons ("RIP KiOR: The Khosla-backed biofuel company finally files for bankruptcy – Gigaom," n.d.). This calls for the need of a supportive policy and incentivization mechanism in place. The processes which use waste feedstock may be given the benefit in terms of carbon credits or viability gap funding to compete with products derived from fossil resources.

31.7 Bioenergy and Biofuel Policies across the Globe

31.7.1 Germany

Agriculture is the primary source of biomass production in Germany followed by wood supply. Primary source of biomass is rapeseed oil, which is used to make biodiesel and substrates for biogas processing. With the Biofuels Quota Act, Germany had agreed to mix 6.25% biofuels into petroleum in 2014. Beyond 2020, the German government intends to raise renewables' share to 30% by 2030, 45% by 2040, and 60% by 2050 ("Germany 2020- Analysis, https://www.iea.org/reports/germany-2020 - Google Search," n.d.). The aim of Germany's integrated policy framework for biomass is to "improve social acceptance for biomass to energy and fuels by directing attention to the use of untapped waste and residual biomass streams in biomass power plants (existing and new ones); facilitate the use of perennial crops; reinforce cogeneration and heat uptake; and ensure a clear plan for biofuels in transportation is in place." Biomass is used in household heating applications widely with wood/wood pellets being the primary biomass feedstock. The Clean Energies Heat Act of 2009 has mandated owners of newly constructed buildings to use green energy to meet a portion of their heat demand. Growing wood prices and falling fossil fuel prices have reduced the potential for private households to switch from fossil to biomass fuels. Biomass-based power plants are steadily increasing along with efforts to enhance the performance of biomass boilers and stoves to reduce particulate matter pollution. There is an emerging rivalry between biomass for heat applications and biomass for material use. This has led to an increase in the cascading use of timber, thereby increasing resource quality and utilization of non-woody biomass for different applications. This also necessitates legislative changes and technological advancements for the use of biomass. The availability of biomass feedstocks such as manure and energy plants sparked a biogas boom as well. The latest amendment with respect to electricity production (2014) led to significant reduction of biomass feed-in tariffs, providing only limited incentives for the construction of new biomass power plants. With respect to the transportation sector, most vehicle owners chose gasoline with a maximum bio-ethanol content of only 5%. The target for GHG reduction capacity of biofuels has increased from 4% to 6% in 2020. Future policy framework for biomass seeks to provide equitable opportunities for resource and energy quality development across industries, technology, and applications in Germany. However, there are a number of concerns that could obstruct the country's achievement of its goals and potential business growth which is expected to be addressed in future policy formulations (Energy Agency n.d.)

Germany's national climate change policy is described in the Climate Action Plan 2050, which lays out a longer-term road map for sector-specific emissions reductions. The main objectives are to reduce greenhouse gas (GHG) emissions by at least 40% by 2020, 55% by 2030, 70% by 2040, and 80–95% by 2050, when the world plans to be largely GHG neutral. Short- and medium-term expectations for electricity demand and production, as well as sustainable energy availability, are added to these goals (Energy Agency n.d.)

31.7.2 USA

Biomass has accounted for almost half of all renewable resources used in the USA. It is plentifully available and often a low-cost source of electricity in rural areas. Currently, the majority of biomass-based transportation fuel is made from corn and refined to ethanol that can be blended with gasoline. The USA is now exporting bio-ethanol to several countries in the world. Biodiesel can be made from soybean oil, vegetable oil, fish oil, and animal fats. Algal biofuels are also being considered in the energy basket; however, it is in laboratory/pilot-scale research levels. There are a number of federal policies and regulatory regimes aimed to increase the share of biomass in the renewables sector ("America's energy future: Technology and transformation," 2010; Food and Agriculture Organization of the United Nations 2020). The USA also has several demo-scale and commercial-scale units deployed on field that convert different types of residual/waste biomasses into different valuable products. Even plants that aim to produce fuels from municipal solid waste are also under construction in the USA (Sallyards and Joseph 2013).

31.7.3 Canada

In 2014, Canada had about 70 biomass-fired power plants with a gross installed capacity of 2408 MW. Canada has surplus forest biomass as well as access to by-products and residues from the forest-related industry. Some of the provinces with the most biomass availability are British Columbia, Ontario, Alberta, Quebec, and New Brunswick. Landfills and waste-to-energy facilities in Canada are increasingly generating power for nearby utilities and industry, or converting landfill gas to natural gas for transport through natural gas pipelines ("CER – Canada's Adoption of Renewable Power Sources - Energy Market Analysis - Biomass," n.d.).

31.7.4 Mexico

In Mexico, biomass energy usage and development have been taken into account in the most current general regulatory framework for renewable energy sources. Their target for reduction in national greenhouse gas (GHG) emissions is from 261 million tonnes CO_2 equivalent in 2020 to 523 million tonnes CO_2 equivalent in 2030. It is the first country to assume GHG reduction targets at the same pace as developed countries and is different from others in the Latin American region where policy tools for climate change adaptation and low-carbon strategy implementation are structured around schemes of voluntary GHG emission reduction goals. Mexico encourages the use of 2% ethanol in fuel in the country's major cities.

Biomass energy consumption in Mexico has declined since 1965, when it accounted for 15.3% of overall primary energy supply. In the past, when the rural population was comparable to that of urban areas, forest and agricultural wastes were the most popular cooking fuels. Fuel biomass now accounts for 3.2–5.3% of overall energy consumption, including its broad range of applications. Biogas has a power installed capacity of about 40 MW, with the remainder going to sugarcane mills, with a total of 500 MW (Alemán-Nava et al. 2015).

31.7.5 Australia

Biomass sources accounted for about 15% of new green energy production as of 2010 in Australia. Biomass sources are likely to continue to contribute to Australia's electricity production, and also ethanol and biodiesel are commercially manufactured in Australia.

The forestry, sugar, and grains industries are all capable of providing cellulosic feedstock for the production of electricity and advanced generation biofuels. There are several stakeholders in the Australian Bioenergy program and to name a few are Bioenergy Australia, Biofuels Association of Australia, Clean Energy Council, etc.

The condition in Australia's biofuels industry has remained unchanged. In Queensland, an innovative biofuel plant is being designed to manufacture fuel for military, aircraft, and marine applications. There is an increased demand for green energy for stationary power and transportation fuels as Australia tries to minimize its GHG emissions, which will drive the bioenergy industry in Australia to expand significantly. The production of new and emerging feedstocks is aimed at maximizing the long-term viability of existing farmland while also providing new opportunities for marginal lands. The Australian Bioenergy Roadmap process established sufficient supplies of economically and logistically available biomass resources to sustain a goal of 11,000 GWh of annual electricity production by 2020 (roughly 4% of Australia's total electricity production). The ability to generate power and heat at reasonable rates is critical in this area, which will be assisted by sustainable feedstock supply, communications and extension efforts, policy and business growth, and technological adaptation and demonstration. Sustainable feedstock production, communications and extension activities, policy and business development, and technical adaptation and demonstration can all help in this field. There is a continued creation of globally accepted sustainability standards in the implementation of sound national certification schemes for bioenergy (particularly biofuels) and related land-use policies. Land-use management programs seek to ensure that all agricultural and forestry land is handled in a sustainable way, mitigating harmful indirect land effects—supporting a broad variety of demands in various bioenergy sectors by usage transition.

There is an increased focus on usage of locally available biomass feedstocks (technical characteristics, supply potential, costs, integration with target conversion technologies), land availability mapping, and co-production benefits (e.g., soil protection, carbon storage) in order to identify the most promising feedstock types and locations for future scale-up and integration into farming and forestry in Australia. Efforts to identify promising conversion technologies, including the introduction and adaptation of technologies introduced elsewhere to Australian requirements, are being carried out in order to accelerate commercial rollout in Australia ("BIOENERGY AUSTRALIA SUBMISSION-ACT Sustainable Energy Policy 2020-2025," 2019).

Domestic and commercial food, garden waste, sewage sludge, and agricultural waste, including piggery manure and food processing materials, are the major feedstocks (red meat processing, dairy, cheese whey, breweries, and food waste) used for biogas generation.

It is estimated that usage of up to 10% of biofuels in petrol and diesel in Australia will decrease GHG emissions by 8.9 million tonnes CO_2 equivalent each year along with health benefits guided in part by the decline in the use of carcinogenic materials such as alkanes, toluene, and benzene (Galletti et al. 2012).

31.7.6 China

Residues from agricultural and forestry sectors, animal manure from medium and large-scale livestock farms, and urban solid waste are China's main biomass options. Agricultural and forestry wastes are China's primary bioenergy resource, as their development is linked to the country's main economic activity for a large portion of the population. A limited volume of timber from energy plants is used in forestry wastes. Concentrated feeding of cattle, pigs, sheep, and poultry on large and medium-sized farms has risen significantly in recent years (Jingjing et al. 2001). Straw direct-fired power generation and waste incineration power generation are the most popular biomass power generation technologies in China. Up to 2010, China's total installed capacity of straw direct-fired power generation was 2.65 GW, accounting for 62% of all biomass power generation; the total installed capacity of waste incineration power generation was 1.25 GW, accounting for 29% of all biomass power generation; other techniques, such as gasification power generation, gas generation, and mixed fuel power generation, accounted for 29% of all biomass power generation. New facilities are being focused on 1.5 generation feedstocks for ethanol processing, such as cassava, sweet sorghum, and sweet potato. For the production of biodiesel, feedstocks such as jatropha and other oilseed-bearing trees are being considered. These crops may be grown on marginal land that includes shrub land, sparse forest land, moderate dense grassland, and sparse grassland, as well as land with weak natural conditions for crop cultivation but the ability to be cultivated for growing adaptable energy crops/trees. Growing enough 1.5 generation feedstocks in adequate quantities has proven difficult in China, and other several schemes have had disappointing performance or failed to materialize. Aside from land availability issues, there is also the issue of insufficient water resources. Official ethanol figures do not differentiate between ethanol used for gasoline, beverages, or industry (Xingang et al. 2013).

Cellulosic ethanol production in China is also being explored through different routes. The off-gases from steel plants are also being converted to ethanol through the gas fermentation route developed by Lanzatech. DuPont announced in July 2015 that it had entered into a licensing agreement with Jilin Province New Tianlong Industry Co., Ltd. (NTL) to begin the construction of China's largest cellulosic ethanol manufacturing plant in Siping City, Jilin Province, China. The M&G Group and the Chinese Guozhen group had formed a joint venture to manufacture bio-ethanol from wheat straw and corn stover according to Beta Renewables (Mcgrath and Ward 2020). Around 30% of China's biodiesel output is used for transportation in cars and trucks with the rest going to manufacturing and agriculture. Used cooking oil, also known as gutter oil, is used to make almost half of China's biodiesel. There are several issues in creating a feedstock supply chain due to its uses in unorganized sectors. The scarcity of feedstock and a lack of policy support are the two main barriers to biodiesel growth (Dyka et al. 2016).

The national crop straw and stalks supplies in China are expected to be between 800 million and 1.1 billion tons. Corn stover was projected to account for 225 million tons of China's crop residue supply in 2015. China is consistently working toward achieving its standards and deadlines for commercialization of cellulosic ethanol projects. The high level of underutilized potential of Chinese bio-economy is due to the difficulties in sourcing quality feedstock (Xingang et al. 2013; Jingjing et al. 2001). Some legislative measures have been designed and executed to promote biofuel usage in China's transport sector in order to expand the market share (Ren et al. 2014).

31.7.7 Sweden and Finland

Finland is a global leader in biomass power generation. It produced 11.3 TWh of electricity from biomass in 2015 (17% of overall generation). Finland's forests occupy roughly 60% of the region. The shortage of renewable energy sources, the cold atmosphere, and the supply of waste biomass from the country's large forestry, wood products, and paper industries are the key reasons for the use of biomass in Finland. The wood used is mostly waste from such sectors, and it is of poor quality with no alternative uses. Help policies such as research grants, tax relief, and export incentives favor Finland's biomass power industry. Most of its biomass power plants are cogeneration plants that provide both heating and electricity. Around 80 of them have a capacity of at least 20 MW (Ericsson et al. 2004). Bioenergy policy is created and applied in the form of a larger energy and environmental policy framework as well as a larger political context.

Energy policy in Finland and Sweden is largely transparent and consensus-seeking. To encourage sustainable energy generation, Sweden had implemented a quota-based structure of certificate trading while Finland focused on conventional subsidy schemes. Forest owners and the forest industry are the main players on the biofuel market because almost all biomass used in Finland and Sweden comes from woods. The forest produces a variety of wood fuels, some of which are taken from the forest for use as fuel and others of which become fuel after going through the forest industry. Sweden and Finland are also rich in timber lands, with valuable forest land accounting for 52 and 66% of total land area, respectively.

The majority of sawdust in biofuel industry in Sweden has been converted to pellets or briquettes. In recent years, a number of pellet factories have been built, especially in Sweden, where pellet production capacity is about 1,000,000 tonnes per year. Finland's annual production volume is estimated to be about 200,000 tonnes. The primary potential source of forest biomass for wood fuel production is logging residues, mostly tops and branches, as well as undergrowth trees. Continuous technological advancements and improvements in harvesting logistics have resulted in lower production costs. The majority of commercial experience in Sweden and Finland has come from roadside chipping of harvested logging residues from mature spruce stand final felling. Chemically untreated wood, such as loading pellets, and some chemically processed wood, such as demolition wood, make up used wood fractions, which are relatively new on the wood fuel market. Due to improved source isolation and restrictions on landfilling combustible waste in Sweden and many other European countries, larger quantities of used wood have been available to the fuel industry. In Sweden, imported wood fuels have also competed with natural wood fuels. Except for pellets, the average wood fuel prices charged by heating plants in Finland are usually lower. Wood chips from logging waste, industrial by-products such as wood chips, sawdust, and bark, and used wood are the costliest wood fuels.

In both Finland and Sweden, the timber industry accounts for roughly 60% of industrial energy production. Internal wood-derived by-products account for about 59% and 64% of this energy market, respectively, with electricity accounting for the remainder. As a result, the forest industry is the primary biofuel customer. Sawmills and the wood-products industry, for example, are fully self-sufficient in diesel, which is mostly made up of bark and sawdust. Their excess wood fuel is used in a variety of sectors, including pulp mills, district heating plants, and in the case of pellets, households and the service industry. The spent pulping liquor, black liquor, which is burned in the chemical recovery cycle, provides the majority of the process energy in chemical pulp mills. Other biofuels are also used, such as bark, tall grease, and recycled wood chips. In Finland, commercial combined heat and power (CHP) generation is more widely used for electricity production, which is one of the few variations between the two countries' forest industries (Flach et al 2020).

Increasing the use of bioenergy is a goal for many countries; in Finland and Sweden, the use of environmental taxes has been a crucial tool in achieving this goal, making biomass the most cost-effective fuel in many applications. This, along with investment incentives, funding for technology demonstrations, and long-term RD&D initiatives, has provided the conditions for bioenergy to become more widely used. The fact that biofuel costs have decreased over time suggests that there are learning effects at work and that the industry is functioning properly. From their experience it can be learnt that relatively strong incentives are needed to start a business. In the last 20 years, Finland and Sweden have succeeded in integrating biomass into new energy systems. Biofuels and the fair use of biomass by-products in manufacturing now have increasingly broad, practical markets. The presence of existing actors and institutions in forestry and district heating has aided the response to strong and long-standing policy commitments to biomass, especially in Sweden. Biomass energy strategies have been popular in both nations, as the use of biomass for heat generation and manufacturing has increased considerably. Learning results have been achieved in the advancement of infrastructure, organization, economies, and logistics, as shown by cost savings and pricing trends. Growth has been highest in Sweden, where high carbon taxes, along with other policy initiatives, generate a powerful price signal (Ericsson et al. 2004).

31.7.8 Japan

Japan has established a number of national biofuels policies and plans that focus on four key goals. Reduced greenhouse gas (GHG) pollution, energy conservation, rural growth, and the realization of a recycle-based society are among these goals. Based on technological advancements, biofuel production's potential contribution to rural development could become significant in the medium term. To foster biofuels, Japan lacks a single policy or collection of policies. Instead, it has many national policies and plans, such as the Biomass Nippon Strategy, to support them (Goh et al. 2020). Different ministries have created these plans, and policies, and they all have different goals. The government hopes to generate about 4% of total power generation, or 40–50 TWh, from biomass by 2030. Feed-in Tariffs (FITs) were created to promote the use of renewable energy sources like bioenergy. In only 1.5 years, biomass power generation capacity had increased from 6 to 16 GWe. This is due to a booming biomass market fueled by favorable government policies and private sector investment. Japan is on target to achieve its renewable energy targets well ahead of the 2030 deadline. Green energy will account for 22–24% of Japan's total produced electricity in 2030, with biomass accounting for 3.7% to 4.6% of it. Japan has set a target ethanol blend percentage of 3%. Many countries seldom set a limit to the amount of mixing they choose to do. Since higher blending rates could result in higher nitrogen oxide emissions and oxidation of metal vehicle parts, the limit was set at 3% by volume. Ricoh is one of the Japanese companies that has adopted the use of biomass in its activities. Woody biomass fuels the entire air conditioning and hot water facilities at its Eco Business Development Centre in Shizuoka Prefecture, eliminating annual kerosene intake. In recent years, biomass plants in Japan have tended to be built near paper mills or lumber yards, where by-products are a readily available source of fuel. The heat produced can be used in the production of paper**.** Large-scale biomass producers have benefited from the market's fast expansion. Eco Green Co, a Tokyo-based company that supplies wood chips to biomass power plants, is preparing to triple its capacity to 600,000 tonnes of wood chips per year by 2030. In order to accommodate larger plants, biomass imports into Japan have been increasingly growing. Imports of palm kernel shells and wood pellets are steadily increasing. Faced with a lack of availability, power producers have also asked the ministry of economy, trade, and industry to consider other solid biomass fuels, such as rice husks, as suitable fuel. With more 75 MW plants set to come online in the coming years, including Kanda Biomass in Tokyo in 2021, Tsuda Biomass on Shikoku Island in 2023, Omaezaki Biomass in south-central Honshu, and Ishinomaki Biomass in northern Honshu, the Japanese biomass demand shows no signs of slowing down. Japan will need to import more than nine million tonnes of wood pellets per year by 2025 to satisfy demand ("Japan becoming an international biomass energy hub - Issuu," n.d.). However, increased imports necessitate better logistics for transporting palm kernel shells and wood pellets to biomass plants. The concentration of importing ports in eastern Tohoku (north-east Honshu), Osaka, and Fukuoka necessitates the storage and transportation of wood pellets to prevent spoilage. Japan's capacity for further production of domestic biomass is strong as an island nation with a forested area double that of the world's average by percentage, but uneven land ownership is impeding growth (Matsumoto et al. 2009).

31.7.9 Brazil

Brazil's National Biofuels Policy, the RenovaBio initiative, is set to go into effect in December 2019. The certification process has been demanded by over forty biofuel plants. The new ethanol mandate, which is set at 27%, has not been changed. RenovaBio is justified in recognizing the fact that the biofuels sector offers, aside from the provision of a fuel basket, a reduction in GHG emissions that are not yet assessed due to the lack of any clear demand in the market (ethanol, biodiesel, biogas, biokerosene, etc.). RenovaBio's goal is to formalize awareness of the environmental advantages of biofuels and remuneration for the sector's role in lowering GHG emissions by providing a market for carbon decarbonization credits (CBIO). The Brazilian government is yet to issue a formal statement on the abolition of the TRQ and/or the ethanol import tariff. The GOB has developed a TRQ of 600 million liters of ethanol imports per year. Under the Mercosur deal, any amount above the quota is subject to the Common External Tariff. Brazil's "National Climate Change Plan," "2030 National Energy Plan," and "Decennial Plan" set ambitious goals for greenhouse gas emissions and the phase-out of fossil fuels by expanded renewable energy production, with a special emphasis on bioenergy and large-scale hydropower. Brazil also has main energy mandates aimed at increasing the usage of biofuels in the transportation market. Brazil has enough capacity and favorable conditions to support its ambitious goals of expanded hydropower and biofuel production (Barros 2019). Brazil is a global powerhouse when it comes to biofuel feedstock productivity, and it has a lot of room to develop even further. Brazil could also be a sleeping giant in terms of future wood-based biomass resources, especially pellet production, and has significant current and potential hydropower resources. However, despite Brazil's numerous energy policies, the majority of near-term major developments in the Brazilian energy sector are/have centered on the growth of fossil fuel sectors, especially natural gas plants (Welfle 2017).

31.7.10 India

The demand for Indian electricity is mainly fulfilled by non-renewable sources, including coal, natural gas, and oil at present. The country is now emphasizing on supplementing hydrocarbon/energy requirement through renewable energy sources. The government has made it mandatory to mix biofuels into the diesel and gasoline pool. This is supported by incentives for the optimum growth and use of indigenous biomass feedstocks/residual biomass in biofuel production to promote biofuels as an alternative energy source.

The National Biofuels Policy aims a blending target of 5% biodiesel in fossil-derived diesel sold and that for bio-ethanol is 10% blending by 2022. The original target for 20% blending of bio-ethanol was 2030 and has now been advanced to 2025 showing the ardent interest of the country to adapt renewable sources on a priority basis. ("https://pib.gov.in/PressReleasePage.aspx?PRID=1727206 - Google Search," n.d.).

The vision of the National Biofuels Program is not to risk food safety and use the domestic carbon resources derived from waste/residual streams to meet the targets.

In the first four months of the sugarcane year 2021–22, the blending of ethanol in India crossed over 7.2%—for the first time. This provides confidence that the nation would be able to achieve the 10% mix by 2022 mark. Targets have been achievable primarily since the government allowed the diversion of B-heavy molasses and sugarcane juice along with damaged grains for bio-ethanol production ("India blends record levels of ethanol in first four months of 2021 | Biofuels International Magazine," n.d.). The plans to set up 5 2G ethanol plants are also underway in the country which will utilize the crop residues such as rice straw and wheat straw for the production of 2G bio-ethanol. The Ministry of Power has provided in-principal approval to launch a national mission for the use of biomass in coal-fired thermal power plants in order to reduce their carbon footprint.

The used cooking oil (UCO) collection drive is slowly gaining momentum in the country and this is helping in achieving the targets set for biodiesel blending. In addition, several tree-borne oilseeds and non-edible oil seeds are being utilized as well for biodiesel production. Pilot-scale testing of bio-jet fuel production from non-edible oilseeds has also been completed. ("SpiceJet operates India's first bio-jet fuel flight - The Hindu," n.d.). Production of biogas from press mud, which is a by-product of 1G bio-ethanol process, is also being incentivized under the SATAT scheme. In addition, the organic fraction of municipal solid wastes is also being used for the production of compressed biogas.

The country aims to achieve its submitted intended nationally determined contribution (INDC), conditional upon financial assistance, which became India's first nationally determined contribution (NDC) after the GoI ratified the Paris Agreement in 2016. India's NDC focuses strongly on action in the energy sector and includes the following energy sector-related targets ("India 2020 Energy Policy Review, International Energy Agency] - Google Search," n.d.).

- To reduce the emissions intensity of GDP by 33–35% from 2005 levels by 2030.
- To achieve about 40% cumulative electric power installed capacity from non-fossil fuel-based energy resources by 2030, conditional on the transfer of technology and low-cost international finance including from the Green Climate Fund (GCF).
- To create an additional carbon sink of 2.5–3 billion tonnes of CO_2 equivalent through additional forest and tree cover by 2030.

- To better adapt to climate change by enhancing investment in sectors vulnerable to climate change, particularly agriculture, water resources, Himalayan region, coastal regions, health, and disaster management.

India is also committed to the production of power from biomass by cogeneration. As of June 2021, a total capacity of 10,170 MW has been installed comprising bagasse and non-bagasse cogeneration ("Current Status | Ministry of New and Renewable Energy, Government of India," n.d.).

31.8 Future Challenges and Prospective

Waste biorefinery concept is still in its infancy and has a long way to go. The idea is to use waste/residual biomass at a scale sufficient to satisfy local energy requirements in a sustainable manner. They will be able to add more value to the local economy as it will provide additional income to the crop growers and generate more local employment in different stages of biorefineries ranging from collection and processing to sales of products.

As mentioned earlier, biorefinery should be capable of producing commercially viable materials/chemicals/fuels/energy. The choice of centralized or decentralized models should be done taking into account the steady supply of raw materials, potential competitiveness from other feedstocks, and long-term product market demand.

Biomass feedstock availability is the most important factor that decides the types of operations to be employed in a biorefinery and it varies from region to region. Supportive incentive mechanisms need to be provided for biomass utilization for bioenergy purposes. In developed countries or in regions where food availability is not an issue, edible feedstocks can be utilized for bioenergy purposes. In countries where food vs. fuel issue may crop up, only residual and waste biomasses may be used for the purpose of production of electricity or renewable hydrocarbons (De Jong and Van Ommen 2014).

The awareness of the quality and quantity of biomass available at a particular location can help in strategically mapping the biomass to the suitable process to produce the targeted products. Complete life cycle analysis along with an understanding of the land-use changes and carbon and water footprint would help to check if the biorefineries are really sustainable. Some of the factors influencing the waste biorefinery are types of feedstock available, suitable scalable process technology, and market demand for generated products and by-products. The biggest challenge is to integrate various biological and thermochemical processes for the complete utilization of all components in biomass (Venkata Mohan et al. 2016).

The futuristic pathway for biomass utilization globally is well established and summarized in Figs. 31.4 and 31.5 ("What does net-zero emissions by 2050 mean for bioenergy and land use? – Analysis - IEA," n.d.) and ("IRENA (2021), World Energy Transitions Outlook: 1.5°C Pathway, International Renewable Energy

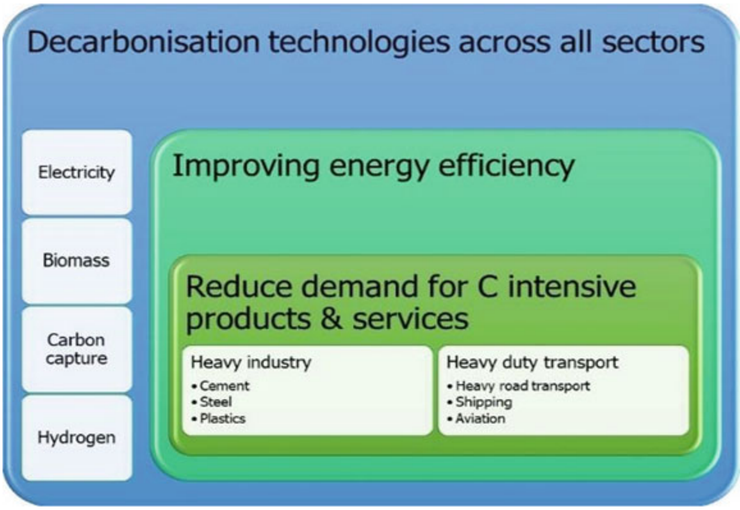
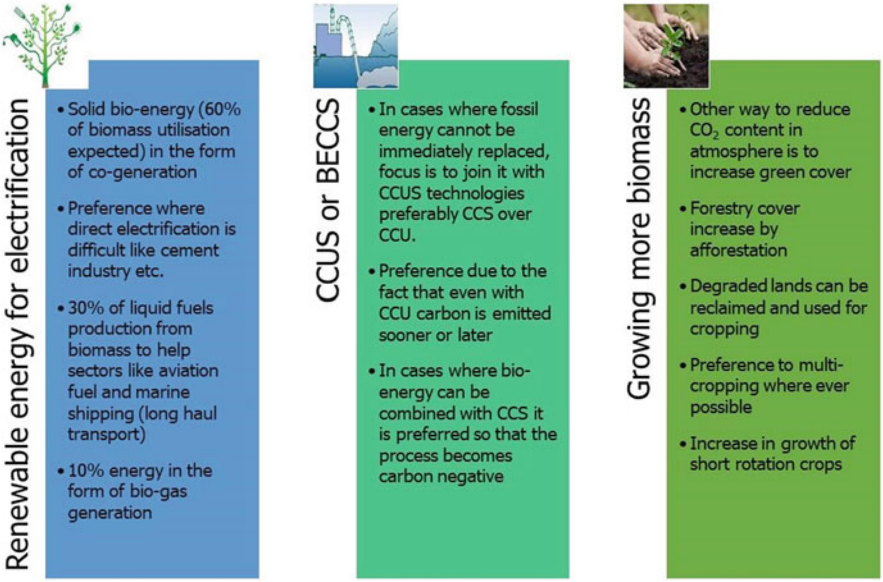


Fig. 31.4 Mission net zero by 2050


Renewable energy for electrification

- Solid bio-energy (60% of biomass utilisation expected) in the form of co-generation
- Preference where direct electrification is difficult like cement industry etc.
- 30% of liquid fuels production from biomass to help sectors like aviation fuel and marine shipping (long haul transport)
- 10% energy in the form of bio-gas generation

CCUS or BECCS

- In cases where fossil energy cannot be immediately replaced, focus is to join it with CCUS technologies preferably CCS over CCU.
- Preference due to the fact that even with CCU carbon is emitted sooner or later
- In cases where bio-energy can be combined with CCS it is preferred so that the process becomes carbon negative

Growing more biomass

- Other way to reduce CO_2 content in atmosphere is to increase green cover
- Forestry cover increase by afforestation
- Degraded lands can be reclaimed and used for cropping
- Preference to multi-cropping where ever possible
- Increase in growth of short rotation crops

Fig. 31.5 Future of biomass in the decarbonization scenario

Agency, Abu Dhabi - Google Search," n.d.). Globally decarbonization is aimed to be achieved by 2050 and it denotes the reduction of carbon dioxide emissions using low-carbon sources leading to reduced greenhouse gas emissions into the atmosphere. The global sustainable bioenergy potential in 2050 is estimated at around 100 exajoules (EJ). The paths for the same have been paved well by global experts.

The aim is to eliminate the traditional usage of biomass for cooking and heating globally. The transport industry, namely the light duty vehicles, will be run as electric vehicles (EVs) and the harder to abate sectors will use biofuels till long-range EVs or heavy duty EVs or hydrogen vehicles are well established. The heavy industries which are energy intensive will be partially supplemented with the heat from biomass in the form of pellets/briquettes. In industries like steel making where biomass can be directly used will also be encouraged. The aim is also to increase the energy efficiency of the devices used across all industries. The role of biomass in these lines is also well established and is three-pronged. The first pillar is the utilization of waste or domestic carbon resources for the production of electricity or for heating applications. Solid biofuels will constitute 60% of the biomass usage followed by 30% biofuels in the shipping and aviation industry. The mixed organic wastes available will be targeted for biogas production whose share globally by 2050 would be around 10%.

The next pillar is the combination of carbon capture and storage with bioenergy (BECCS). The use of biomass makes the process carbon neutral in nature, and when it is combined with CCS, it is very much possible to make a process carbon negative in nature.

The last pillar is to grow more biomass in cases where possible or land is available. Several countries aim to increase their forest cover. In cases where degraded lands are available, it will be restored or reclaimed. Multi-cropping or crop rotation is also being encouraged to increase the soil fertility and at the same time increase the amount of biomass produced in an area.

In a nutshell, it can be said that waste biorefineries have a lot of potential in the current generation of conscious living where fulfilling the growing requirements and taking care of the environment go hand in hand.

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Chapter 32
Sustainability Metrics on Waste Biorefineries

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Abstract Undeniably, we embark on a century in which all the functional systems that help us support this planet will prove unsustainable. Hence, developing a clearly planned approach, in which the main focus is to optimize systems already under consolidation to rearticulate and correlate environmental, social, and economic parameters, is vital. Faced with this premise, the concept of replacing fossil feedstock marked the waste biorefineries begin. This is because, in practice, fossil reserves have incorporated carbon for millions of years and therefore have met and still meet—until today—the vast majority of fast-growing energy and material demands in all social systems, resulting in the depletion of capital, as well as putting our biodiversity at risk. Besides, residue increases in the environment and the lack of efficient strategies for disposal and reuse also impelled these researches. Thus, tool applications to quantify the environmental burden is very relevant and imperative. In view of the above, this chapter addresses the value of waste-based biorefinery as a potential alternative to solve the problems of excessive waste in the various industrial sectors. In addition, the life cycle assessment and carbon footprint methodologies were presented and discussed in order to facilitate the strategy for quantifying the environmental impacts generated by these systems. Still, the last section of this chapter highlights criteria beyond sustainability, exploring the importance of the formulation of national policies in the face of the generation of a circular economy in the context of waste biorefineries, in addition to the generation of potential carbon credits. In the end, this chapter brings together future perspectives on the decision-making processes associated with the waste biorefineries.

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32.1 Introduction

Waste generations have increased substantially worldwide in the last few decades and there is no sign of it decreasing. Recently, a sense made by the World Bank announced that humanity produces approximately 2 billion tons of waste per year (World Bank 2021). Besides, the numbers for industrial waste are far less clear. However, estimates show that our global waste production is expected to up to 70% by 2050, resulting in will increase of 3.40 billion metric tons (Kaza et al. 2018). So, we will literally be living in waste if nothing is done? Probably, unless we take smart solutions, and, the time to act is now.

Currently, waste management dynamics are attributed to a mapping of unit processing operations, where critical points are identified and there is a tendency to increase the efficiency of use and reuse of raw materials so that there is less volume waste to treat and dispose of at the end (Wang and You 2021). Thus, the management hierarchy can be understood as an attempt to order different options on a preferential scale, in order to support the development of sustainable waste management strategies (Fig. 32.1). However, in practice, this approach does little to alleviate reliance on end-of-line solutions (UNEP 2011).

In view of this problem, the biorefinery concept has been sagely intertwined in the waste reuse strategy. Indeed, biorefineries are renowned for their importance in the global community. In recent years, the biorefinery idea has emerged as an alternative to face the depletion of fossil-based resources and associated environmental impacts, in addition to valuing a multitude of bio-based products (Sarkar et al. 2021). Nevertheless, when systematically designed as waste management and reuse strategy, it is capable of processing waste in a wide range of products, maximizing the value associated with raw materials, resulting in cost reduction and decreasing environmental impacts (Liu et al. 2021). But it is important to highlight that the success of waste biorefineries will be closely linked to the potential of the waste used, beyond its efficient processing. In this way, the careful sorting of the feedstock

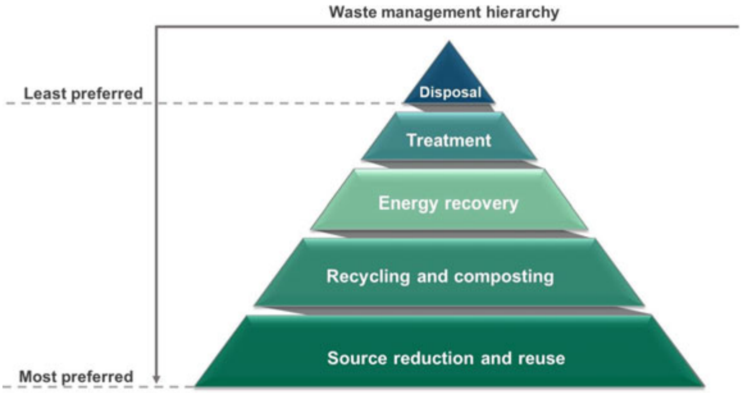

Fig. 32.1 Global perspective associated with waste management hierarchy

will be the key starting point for the environmental and economic success of these facilities.

However, although much has been discussed in the literature about the potential of waste biorefineries, in reality, these models are still far from being released. And, therefore, its commercialization seems to be further away than we think. This is because the gaps to be filled through economic and environmental indicators will be the drivers for these smart strategies to reuse waste, proven to be promising (Khudyakova and Lyaskovskaya 2021).

As a consequence, the tools of environmental and economic evaluation have been widely used as a quantification technique to assist in the decision-making of waste biorefineries. Through the life cycle assessment (LCA), it is possible to quantify the environmental burdens associated with the reuse of waste, beyond obtaining metrics and sustainability indicators that can support improvements in the processing chain. In addition, together with instruments that quantify economic benefits, using techno-economic analysis (TEA) tools, it is possible to generate estimates of financial gains in the face of this new model of waste management (Deprá et al. 2020). In addition, once the sustainable superiority of waste biorefineries has been proven, political strategies may encourage a new market model, through the context of the circular bioeconomy.

In light of what was exposed, the objective of this chapter was to promote a new aspect on ways to reduce and reuse excessive waste from the most diverse industrial sectors. Moreover, the sustainability criteria were thoroughly revised and presented in order to apply the LCA in the context of waste biorefineries. Besides, the chapter has a critical review in view of the political strategies to encourage the use of waste and economic potential associated with carbon certification and accreditation, with the aim of generating revenue in view of the environmental benefits of waste biorefineries.

32.2 Potential Feedstocks under Waste Biorefineries Context

Residual resource reuse has received considerable attention, once the products produced are renewable and exhibit characteristics of environmentally appropriate biodegradability. The waste bioprocessing in the production of value-added bioproducts and metabolites does not only address energy and environmental safety issues but also actually betters the management of waste streams (Leong et al. 2021). So, it can be recognized as an ecologically and economically viable platform, as the raw material for production is sustainable and of low cost, which in this case may be the link between environmental protection and the circular economy (Mohan et al. 2016).

Waste biorefineries classification depends mainly on the origin and nature of the feedstock (Kamm and Kamm 2007). In this way, several waste models, such as agricultural and forestry, food, municipal, and industrial waste have been efficiently reclaimed and smartly introduced in a waste biorefinery context (Leong et al. 2021). As consequence, the target market for biorefinery waste products has grown continuously despite the economic crisis of the last decade.

32.2.1 Agricultural Waste

Currently, the organic waste generation from agriculture represents a gigantic source of waste generation allocated to the environment. Among the main crops responsible for most of these residues encompassing rice, soy, wheat, cotton, and corn. However, generally, used wastes refer to any other type of lignocellulosic residue produced by the agro and food industries in their daily operations, such as leaves, roots, stems, bark, bagasse, and seeds (Nizami et al. 2017).

In parallel, animal wastes also represent another significant source of pollution in this class, particularly due to rise in contamination, as it is often dumped directly into estuaries and rivers without any pretreatment. Although these residues represent a major source of pollution (most often produced by manure, agricultural and silage residues, wood chips, oil processing, veterinary drugs, pesticides, and fertilizers), they provide a widely available, renewable, and biomass free for use in biorefineries (Sharma et al. 2019).

In view of its application potential, estimates report that today about 140 billion tons of biomass from the agricultural sector are generated each year. This volume represents a global conversion volume of approximately 50 billion tons of new raw materials that can be reused mainly as the main material for the production of various fuels and value-added products, such as bioethanol, activated carbon, biochar, organic fertilizer, natural fiber compounds, and nanocomposites (Liu et al. 2021).

32.2.2 Forest Waste

The composition of forest-based biomass consists of cellulose (40–50%), hemicellulose (25–35%), lignin (15–20%), and various extractives (2–8%) (Nizami et al. 2017), being substantially similar to agricultural wastes. As is known, the breakdown of these polymers results in sugars that can be converted into attractive chemicals. In this case, the lignocellulosic sugar conversion through biochemical fermentation or chemical conversion may result in a broad portfolio of products to be explored in the context of biorefinery, such as biofuels, organic acids, sugar alcohols, or furans (Ajao et al. 2018).

Today, the pulp and paper industry is considered a wide user and producer of energy and materials from forest-based biomass. However, this industrial sector faces an economic impasse due to new market restrictions (down selling prices, competition, and fuel expense), coupled with global attention centralized on a bio-based and circular economy. On the other hand, to the extent that some adjustments had to be made in order to circumvent the economic bottleneck while continuing to collaborate with the environment, the producing new value-added chemicals from forest-based biomass represents an unprecedented opportunity for revenue diversification (Brunnhofer et al. 2020).

32.2.3 Food Waste

The main sources of waste food come from catering, expired food, and production stages of food industries (handling, storage, processing, distribution) (Gustavsson et al. 2011). Estimates show that about 1.3 billion/ton of food and 1/3 of the total global food generation are wasted each year, costing the world economy about USD750 billion (Dahiya et al. 2018). However, the problem is not just the waste of food but the financial problems that this can generate with its treatment.

Associated with this obstacle, the negative consequences of food waste also contribute to poor waste management, and therefore, resulting in increased environmental pollution. This is because not only the emissions generated from waste degradation contribute to environmental impacts since about 90% of this waste ends up being converted into methane, carbon dioxide, and other greenhouse gases, but also the required natural resources involved in the chain of food production are important points of discussion (Tonini et al. 2018).

Nevertheless, the biorefinery point of view of residues from food residues requires a complex strategic design since the stages of collection and processing of residues require viable logistics (Kokossis and Koutinas 2012). In addition, it is necessary to identify the amount of each type of food processing and waste produced together with the quantification of the composition of the main organic fractions in each type of waste food (Rathore et al. 2016). However, the constituent profile of food raw materials represents an extremely promising character for the exploitation of this waste. This is because food residues also have high concentrations of carbohydrates, proteins, lipids, and inorganic compounds, which can be further digested into glucose, amino acids, fatty acids, etc. (Socaci et al. 2017). In this way, the exploration of these compounds as a secondary recovery alternative is in perfect harmony with the concept of sustainability, which aims to reduce the generation of substances that harm the environment while developing more ecological products or processes (Isah and Ozbay 2020). In this case, food wastes are explored as feedstock for the development of valuable chemicals and co-products.

In addition, the food waste bioconversion system consists of the utilization of routes using acidogenic and anaerobic fermentation to produce biogas, liquid biofuels, commodity chemicals, biohydrogen, and biomethane (Dahiya and Joseph 2015). Yet, some studies suggest that these residues can also act as an abundant source of electrons for electroactive bacteria capable of producing bioelectricity with simultaneous remediation of waste (ElMekawy et al. 2014). Also, various pretreatment methods (physicals, chemicals, physicochemicals, and enzymatics) have been adopted for food wastes as hydrolysis to increase biogas and biochemical production. Recently, beyond acidogenesis, other bioprocesses (such as bio-electro fermentation and solventogenesis) are gaining rapid interest. Therefore, the integration of various bioprocesses can provide a new dimension in the food waste biorefinery framework for the development of a better bioeconomy.

32.2.4 Municipal Waste

Based on the waste law, defined in mid-2012, the definition of urban waste consists of household-generated products or any resource waste produced by a community (Mesjasz-Lech 2014). Some estimates report that, in the last year, a total of 2.5 billion tons of waste was produced. Of these, only 40% were reused or recycled, while most countries send 80% of their waste to landfills.

Improper and irresponsible disposal of municipal waste deteriorates soil and water quality and can cause toxic, carcinogenic, and mutagenic effects on aquatic and terrestrial organisms, including humans. Therefore, it is mandatory to understand its toxicity, treatment methods, and implications for environmental sustainability (Ifeoluwa 2019). However, keeping in mind the number of essential nutrients opens many paths for use as an economical, abundant, and sustainable source for the generation of renewable energy, value-added products, and chemicals through the approach from a waste biorefinery (Saini et al. 2021).

Identifying the content of municipal waste is the first step in identifying possible options for optimizing waste processes. It is argued that the largest flow of urban waste comes from wastewater (household and pharmaceutical products), food waste, gardens, among others, with these wastes being its predominant profile of organic materials. For these, most technologies used are anaerobic digestion and composting (Satchatippavarn et al. 2016). However, the first technology is the most usual strategy for sludge stabilization, resulting in the biogas or to be exploited for other forms of biofuels. Sludge can also be incinerated directly to produce heat and electricity. Nutrients are recovered in solid or digested waste, which can be applied to the land as organic fertilizer or can be composted and used as a soil amendment (Sánchez et al. 2019).

Simultaneously, waste paper and plastic materials are also widely found in urban waste. Some recycling and incineration strategies are encouraged for paper waste in order to obtain a form of energy recovery. However, plastic materials can be reused as a raw material in new petrochemicals and plastics through pyrolysis and gasification processes. Furthermore, incineration may be more favorable when heating or electricity is prioritized or when there are incentives to generate energy from waste (Satchatippavarn et al. 2016). Finally, although some biogas and biomethane companies are based on sewage sludge, gas, and waste, the potential for improvement in this field is still high (GIE and EBA 2018).

At last, as there are many optimization ideas and perspectives, waste biorefineries are attracting significant interest around the world as sustainable waste management solutions, particularly in facilities for fuels, energy, heat, and value-added products (Rehan et al. 2019). Segments are already involved in extensive environmental audits and are evaluating their own waste management activities for use in biorefinery approaches. Several methods have been suggested to design waste minimization programs, such as the integration of raw materials, energy, and the quantification of natural resources, such as the establishment of water balances, all based on life cycle assessment methodology. However, although technical-scientific advances have received considerable progress, it is still necessary for most industries to carry out a detailed analysis of their waste management system at all stages of production, in order to consolidate the ownership of the biorefinery context applied to wastes. Therefore, identifying opportunities for recovery and saving of resources is often the fundamental basis for obtaining great economic and environmental benefits.

32.3 Life Cycle Assessment Standard on Waste Biorefineries

The waste biorefineries models are constantly evolving, becoming tireless in the search for ecologically sustainable processes. However, the environmental burden quantification and the functional unit definition common to all the scenarios evaluated are still bottlenecks encountered by these systems.

Currently, the LCA is by far the best instrument for quantifying the environmental burden associated with products and processes. Originated in the mid-1940s by the International Organization for Standardization (ISO), this environmental tool provides a structure that meets a growing demand for practical technological solutions found in industrial facilities. In addition, its standard methodology allows the identification of critical processing points, through a deep systemic detail. Through the four verification steps, the analysis criteria become increasingly consistent to obtain the results of LCA regardless of individual interests (Shaked et al. 2015).

In short, the LCA methodology is composed of the steps of (1) determination of the objective and scope of the study, where the limits of the system, functional units, and objections to be evaluated will be outlined and defined; (2) inventory analysis is characterized by data collection, through quantifications of the inputs and outputs of the systems under evaluation. It is important to note that in this stage, the collection can be manual or use a database available on government platforms, or by regulated organizations; (3) impact assessment is a structured step to consider the correlation between environmental impacts and the people living in the local, beyond being applied at all levels of decision-making, and (4) interpretation is a last stage of the evaluation. It is at this stage that the results of the inventory and impact assessment are classified, quantified, verified, and evaluated, resulting in appropriate conclusions and recommendations (Fig. 32.2).

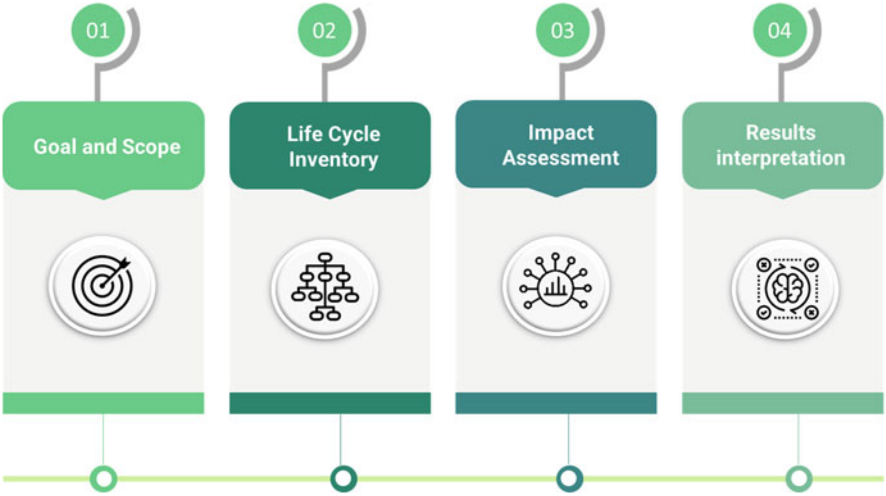

Fig. 32.2 Framework of life cycle assessment methodology principles

Basically, the general formula for quantifying the impact categories is associated with Eq. (32.1), where the sum of the process inputs is converted, through a characterization factor, into the specific impact category, and results in a score that is interpreted as the potential environmental impact of the process.

$$\mathrm{IC} = \sum \mathrm{CF} \times E_i \tag{32.1}$$

where IC is the impact category, CF is the characterization factor, and E_i is the emission inventory, expressed in mass released into the environment per functional unit.

The main midpoint impact categories are associated with global warming potential (GWP), photochemical ozone creation potential (SMOG), ozone depletion potential (ODP), acidification potential (AP), eutrophication potential (EP), ecotoxicity (ECO), energy resource (ER), land use (LU), and water footprint (WF). Whereas, the endpoint assessment can be associated with potential damage as demand for natural resources, climate change, and ecosystem quality.

However, when applying LCA in waste biorefineries systems, the complexity of evaluating the chain is high. This is because in a complete analysis, the origin of the residues, depending on the degree of depth of the evaluation, becomes unfeasible to quantify. Proof of this is attributed to the great superficiality of the data currently found in the literature. Although it is important to have an overview of the performance of these installations, the delimitation of systems is generally limited to gate-to-gate processes, and issues involving the origin of waste and final disposal of products are often omitted.

On the other hand, since most of the waste used comes from agro-industrial systems, it is necessary to assign specific quantifications for agricultural systems.

Thus, when the raw material is of agroecosystems origin, and there is the possibility of quantifying the carbon footprint, it is suggested that criteria for determining respiratory emissions of carbon dioxide (CO_2), such as CO_2 assimilated and sequestered in plants, the net production of the carbon ecosystem (NEP), are established in order to ensure greater reliability of the data generated (Yao et al. 2019).

The simplest model to quantify these variables is through NEP (Eq. 32.2), which is used to represent carbon exchange mainly in the soil, but can also be linked to the carbon released to the environment. After this quantification, the data obtained are directly computed in categories that involve land use and transformation or even associated with climate change.

$$\mathrm{NEP} = \mathrm{GPP} - R_{a+s} \tag{32.2}$$

where NEP is the difference between gross primary production and emission of soil breath and autotrophic ($\mu\mathrm{mol}\times\mathrm{m}^2 \times \mathrm{s}^1$), GPP is the gross primary production ($\mu\mathrm{mol} \times \mathrm{m}^2 \times \mathrm{s}^1$), and R_{s+a} is the respiratory emissions from soil and autotrophs ($\mu\mathrm{mol} \times \mathrm{m}^2 \times \mathrm{s}^1$).

Evidently, with regard to the choices of impact categories used in the analysis of waste biorefineries, this task is imposed by the response to which decision-makers must respond. However, driven by climate change, the high rates of greenhouse gas emissions, and the rampant consumption of fossil fuels, have resulted in greater attention to issues regarding the carbon footprint, energy demand, and global warming potential.

In view of this, the current literature presents a considerable number of researches considering the biorefinery systems of waste as an attractive solution to reuse the waste in order to generate energy. According to data obtained by Papadaskalopoulou et al. (2019), it was possible to determine that the biorefinery waste system with municipal waste—offering the service of waste management and co-generation of secondary bioproducts such as bioethanol, bioenergy (biogas and electricity), and soil conditioner—presented a performance satisfactory environmental performance. This is because the net emissions to the environment, that is, to categories of eutrophication potential of fresh water and human-carcinogenic toxicity have been drastically reduced. In addition, the total net emissions for the climate change category were estimated at -15 kg CO_2 eq per ton of biowaste.

From another perspective, research involving the environmental assessment of a waste biorefinery system using food waste, obtaining biofertilizers, biogas, and the co-generation of heat and energy, showed that in terms of the category of damage caused by climate change, it led to the economy of -73 to -173.1 kg CO_2 eq/ton of biopulp. In addition, it is estimated that about 41% of environmental impacts could be avoided using only the replacement of fossil fuels with the energy generated in the process itself (Khoshnevisan et al. 2020).

Another study regarding waste biorefinery relating to agro-industrial waste was conducted recently by Khounani and collaborators (2021). In this study, olive pomace was reused to produce biodiesel. In addition, the methanol extract from olive leaf was used as a natural antioxidant. The results show that for the category of damage to human health, climate change, and primary energy consumption, the reductions were 12.01, 11.21, and 10.62%, respectively, under the scenario of production of olive pomace oil for edible use and use of olive pomace for animal feed. The authors argue that more than 80% of environmental impacts are associated with the agricultural phase, with fertilization and soil use being the main factors of environmental pollution.

Finally, it is important to note that all human activity will have environmental impacts. However, as seen in the previous examples, waste biorefinery systems are really capable of satisfactorily reducing environmental impacts when compared to conventional systems. Thus, although they are systems whose technological immaturity still exists and are in their infancy for commercial consolidation, it is important that they be investigated and valued through public policies and tax incentives as possible ecological solutions for the new industrial perspective.

32.4 Beyond Sustainability: Circular Bioeconomy and Carbon Credits

It cannot be said that humans are not remarkable creatures. A quick look at the evidence shows that as the population has increased, the health of the environment has decreased. More precisely, in the last 50 years, we have consumed more resources than all of humanity before us. The more than 7.7 billion people, busy consuming resources, are introducing large amounts of waste into terrestrial ecosystems. The limits of global natural resources, as the world population increases, are increasingly obvious and it is no surprise that, regardless of material and technology, every product or service causes an impact on the environment. This interference, whether positive or negative, can come from the raw material, the production process, or its use and disposal (Dovers and Butler 2015).

The current economic system, denominated "take-make-use-dispose," threatens the integrity of ecosystems and the stability of economies. On the other hand, the circular bioeconomy that has the waste biorefineries as pillar aims to improve the efficiency of resource use by changing the linear model from "take-make-use-dispose" to "take, make, reuse, recycle and remanufacture." The transition to a circular bioeconomy can pave the way for the development of an emission-neutral, equitable, and resilient global economy that thrives in harmony with the environment (Ghisellini et al. 2016).

In light of this, the policymakers, mindful of the demands of combating climate change, are increasingly investing in nature as the real engine of their economies. Policies such as subsidies to support bioeconomy and circular bioeconomy companies are becoming popular with legislators and are being applied to achieve environmental goals. The European Union, China, India, Canada, Sweden, United Kingdom, Denmark, Spain, and United States are examples of countries with incentive policies. The support for unlocking the potential of the bioeconomy and

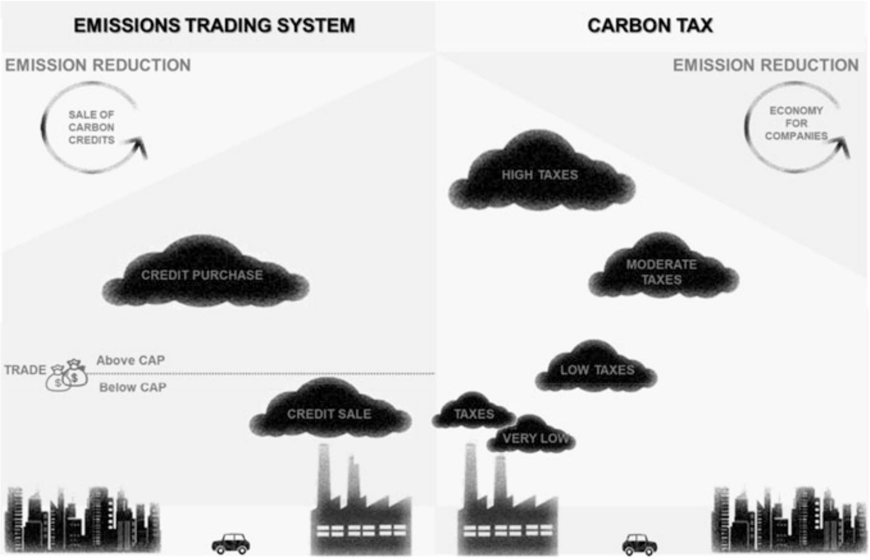

Fig. 32.3 Particularities of carbon pricing instruments

circular bioeconomy is seen by both as a holistic action plan capable of putting them on a sustainable path. Of course, that, there are still complexities that make value chains more successful on paper. However, the launch of funds from public and/or private investors brings bio-based innovations closer to consolidation in a practical sense (Mohan et al. 2019).

With regard to bioeconomy companies, a relevant economic aspect, often overlooked, is that there are activities with the potential to mitigate emissions that, if developed, can generate revenue and also lead them to reach circularity. Microalgae companies, for example, can find in the nutrient recovery from industrial wastewater and in the capture and utilization of carbon from secondary sources a way to generate credits that can be traded on the carbon market. Under a biorefinery and circularity approach there would be the use of waste as a key feedstock (Deprá et al. 2020; Nagarajan et al. 2020).

About carbon market, this is based on the emissions trading system (ETS)—also known as the cap-and-trade system, and as the carbon tax, it is one of the main carbon pricing instruments (Fig. 32.3). Carbon pricing is nothing more than a policy of climate change mitigation considered first-rate by many economists. In the case of the carbon tax, it is worth mentioning that is established a price on carbon in order to penalize emissions, and in the cap-and-trade system, an emissions limit is established. In other words, in the cap-and-trade system, issuers with emissions above the established must deliver credits to offset them and those with emissions below the limit receive credits that can be traded (Gugler et al. 2021; World Bank 2021). In the voluntary market, which involves governments and companies with no obligation to reduce their emissions, the initiative to reduce and neutralize them generates credits that can be sold to those with mandatory reduction targets. In both the regulated and voluntary carbon markets, companies that reduce their emissions have the opportunity to generate additional revenues. In this context, bio-based companies based on the circularity competency of the biological resources can adhere to emission mitigation projects and profit from it. In addition, another to generate credit to companies, regardless of the sector, is the transition from the use of fossil energy to renewable energy for the production of products. At the company level, the revenue generated by the sale of carbon credits from emission reduction projects can ultimately be used to leverage the economy of the processes and products (Severo et al. 2020).

Finally, since all interested parties are aware of the urgency of the transition from the traditional linear economic model to the circular, and that the waste generated can be integrated into biologically-based processes, the bioeconomy can benefit from its circularity potential. Closing the loop through the bio-based economy will serve well the purpose of rebinding the economy and sustaining a healthy and safe environment.

32.5 Conclusion

Exploring the availability of waste as raw materials fully capable of serving as a technological fuel for future industrial systems is the most prudent solution to restore the environmental damage already carried out and provide a measure to curb new possible impacts. However, we know that current models of waste biorefineries still need financial incentives, and the transition from thinking to a circular economy is expected to advance further in updating and optimizing processes, providing an efficient integration of energy and materials, in addition to being able to operate on industrial scales, in order to consolidate an ideal approach in techno-economic and environmental terms. Thus, putting into practice the technical strategies obtained through hard work in research and development can fill, through a multidisciplinary approach, the main gap between the remediation of waste and the recovery of sustainable products from new models of waste biorefinery.

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Chapter 33
Exergy Analysis of Waste Biorefineries

Cynthia Ofori-Boateng

Abstract Liquid and solid wastes form over 70% of total generated wastes in most manufacturing or processing plants. These wastes together with emissions/exhausts, if not utilized for value-added bioproducts or effectively controlled, may contribute remarkably to external exergy destructions thus minimizing the overall exergy efficiency of the production unit. Besides wastes generated from processing plants, plastic, agricultural, municipal and food wastes also add to the global environmental burdens if not rigorously managed. Hence, biorefineries that exploit wastes as their main feedstock and transform them into chemicals, polymers, phytochemicals, energy, etc. carry a notable segment of the sustainable waste management ladder. Nonetheless, the major unit operations involved with waste processing in a biorefinery concept are known to significantly contribute to the biorefinery's thermodynamic inefficiencies due to entropy dissipation. This chapter assesses the exergy efficiencies of common waste biorefineries which produce food, chemicals, and energy as their main products.

33.1 Introduction

According to Kaza et al. (2018), global waste generation is estimated to reach about 3.4 billion tons by 2050 with the main cause being the rapid increase in the world's population. About 30–35% of the world's total wastes generated are not efficiently managed hence contributing to about 1.5–1.6 billion tons of carbon dioxide (CO_2) equivalent greenhouse gas (GHG) emissions (Kaza et al. 2018). The major types of wastes generated globally include but are not limited to agricultural, municipal, food, plastic, medical, construction, animal, and industrial wastes. Though most of these wastes can be considered non-toxic, they may pose an environmental burden over time when they are not meticulously managed. Wastes from industries, municipalities, manufacturing processes, institutions, commercial businesses agricultural

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activities, etc. can be recycled, reused, or transformed in biorefineries into vast varieties of bioproducts such as polymers, biofuels, food, phytochemicals, biopharmaceuticals, etc. However, due to a lack of technological inefficiencies with large-scale waste conversion into useful products, solid wastes are dumped in landfill sites while liquid and gaseous wastes are deposited into water bodies and the atmosphere respectively which create environmental and health problems.

For sustainable waste management, a biorefinery becomes an excellent products' recovery alternative when all forms of waste including solid, liquid, and gaseous wastes are efficiently transformed into high-quality useful products with minimal resource inputs. This sustainability strategy can only be achieved when energy and exergy assessment tools are employed to detect thermodynamic and technical inefficiencies of unit operations within a biorefinery concept. The utilization of wastes as main feedstocks or raw materials in biorefineries is reported to reduce the external exergy destruction which results from the release of waste streams into the environment without reuse or recycling (Lee and Ofori-Boateng 2013) hence building a circular bioeconomy.

Energy and exergy are assessment tools used to estimate thermodynamic efficiencies of unit operations in a production system. Unlike energy, exergy can detect both resource quality and quantity hence numerically estimating the amount of useful energy within a resource that is available to perform work. In reality, the energy of a resource that enters a production system is not always conserved while products are being generated but mostly destroyed due to entropy generation according to the second law of thermodynamics (Fiorini and Sciubba 2005). In quantifying exergy, higher exergy loss is estimated for processes and unit operations where exergy is mostly destroyed.

Apart from energy and exergy, many authors have used other effective methodologies like life cycle assessment (LCA), emergy, exergo-economic analysis, exergetic life cycle assessment (ExLCA), etc. to estimate the sustainability indices of industrial processes (Ofori-Boateng and Lee 2014; Odum 1996; Li et al. 2022).

This chapter aims to assess thermodynamic efficiencies of different waste biorefineries with some case studies using exergy as the main assessment tool where only major unit operations are considered.

33.1.1 Energy, Entropy, and Exergy

Energy, according to the first law of thermodynamics, is always conserved and thus can never be created nor destroyed in any production process (Sorguven and Ozilgen 2010). However, due to the dissipation of energy (referred to as entropy), irreversibilities with processes cannot be ignored in real situations. For instance, during heat exchange, the medium can attain a dead state where there would be no further heat transfer indicating a complete loss of available energy to perform work though no energy has been consumed. It is therefore comprehensive to consider that exergy is what is actually consumed in a process as energy is always conserved. Due to entropy generation, the amount of resource which enters a process is not equal to the amount that comes out since some part of the resource has been consumed.

Exergy is therefore the quantity of energy that is consumed in processes hence energy analysis solely cannot help to estimate the quality of resources consumed in a process. Because sustainability stresses resource quality, exergy becomes the best thermodynamic assessment tool for quantification of energy quality and degradation rate for production processes. Exergy considers both the first and second laws of thermodynamics to estimate the overall irreversibilities and losses in a system (Peralta et al. 2010). According to Wall (2010), exergy can be defined as the maximum theoretical useful work obtainable when a system is brought into thermodynamic equilibrium with its surrounding whereby there exist interactions between the system and the environment.

33.1.2 Exergy Calculations

Depending on the type of system, the components of exergy may include chemical exergy (i.e., Ex_{ch}), physical exergy (i.e., Ex_{ph}), kinetic exergy (i.e., $c^2/2$), potential exergy (i.e., gx), and nuclear exergy (Ex_{nu}) where c, g, and x denote the velocity relative to Earth's surface, the constant of gravitational acceleration and height respectively (Szargut 2005). In biorefinery systems, only heat, materials, and work transfers are considered, hence the kinetic, potential, and nuclear exergy components are neglected.

Physical exergy is the component of exergy that depends on the pressure and temperature of resources and systems. It is generally defined mathematically in Eq. 33.1 (Szargut et al. (1988):

$$Ex_{ph} = (H - H_0) - T_0(S - S_0) \tag{33.1}$$

where $(S - S_0)$ are the enthalpy change and entropy change of the system respectively at an environmental temperature of T_0 (298.15 K) and pressure P_0 (1 atm). Entropies and enthalpies for entry and exiting streams of a process can be estimated using process simulation or computer-aided software like ASPEN Plus, ASPEN HYSYS, etc. (Ofori-Boateng and Lee 2014; West et al. 2008).

Chemical exergy is defined as the maximum useful work attainable in a system when a pure substance (including liquid and gases) is brought into absolute thermodynamic equilibrium with its surrounding of known chemical composition (Szargut et al. 1988). Chemical exergies of energy and material components are critical in determining the total exergy of the resource because they account for the quality of energy available within a resource to perform work. The chemical exergy of a resource defined mathematically by Eq. 33.2, is expressed as a function of the standard chemical exergy of individual components of the resource and Gibb's free energy of formation of the reference reaction (Szargut et al. 1988).

$$Ex_{ch,i} = \Delta G_f^{\circ} + \sum_k N_k Ex_{ch,i}^{\circ} \tag{33.2}$$

where $Ex_{ch,\ i}$, N_k, ΔG_f^o, and $Ex_{ch,k}^0$ denote chemical exergy, number of moles of the *kth* reference species, Gibb's free energy of formation of the reference reaction, and the standard chemical exergy of the *kth* reference species, respectively.

The total exergy of a process stream, resource, or system is therefore estimated using the physical and chemical exergies as defined mathematically by Eq. 33.3 (Szargut et al. 1988):

$$Ex_{system} = Ex_{ch} + Ex_{ph} + Ex_{\Delta mix} \tag{33.3}$$

where Ex_{ch} and Ex_{ph} represent chemical and physical exergies respectively. $Ex_{\Delta mix}$ is the exergy of mixing of the system which is assumed to be part of the physical exergy in this chapter.

33.1.3 Exergy Efficiency and Exergy Destruction

Exergy destruction in a system can be internal or external. When the degradation of resources is attributed to entropy generation with the dissipation of energy into the environment due to irreversibilities in a system, the exergy destroyed is termed internal. Although internal exergy destruction is unavoidable, there are efficient improvement options that can be used to reduce these losses. Equipment inefficiencies have been the major cause of irreversibilities in biorefineries (Ofori-Boateng and Lee 2014).

On the other hand, external exergy destruction is the loss of exergy due to the energy value or quality (mostly obtained via chemical exergy analysis) of resources entering a system. For instance, the use of organic solvent in a manufacturing process can help reduce external exergy destruction compared to inorganic solvents whose standard chemical exergies are high. The overall exergy destruction of a system can be more accurate if both the external and internal exergy destructions are considered according to the mathematical expressions shown by Eqs. 33.4 and 33.5 (Ayres and Ayres 1998). In this chapter, chemical exergy analysis is performed on major unit operations within waste refineries in order to ascertain the quality of wastes (that are not recycled or reused) and potential bioproducts that can be obtained from them.

$$\begin{aligned}\sum Ex_{heat} - \sum Ex_{work} + \sum Ex_{mass,in} - \sum Ex_{mass,\ out} &= \sum Ex_{destruction} \\ = T_0 S_{generation} = I\end{aligned} \tag{33.4}$$

$$\sum\left(1-\frac{T_0}{T}\right)-W+\left(\sum_i m_i Ex_i\right)in-\left(\sum_i m_i Ex_i\right)out=Ex_{destroyed}$$
$$=T_0 S_{generation} \tag{33.5}$$

where Ex_{heat}, Ex_{work}, $Ex_{mass,\ in}$ and $Ex_{mass,\ out}$ represent the exergy destruction due to heat, work, mass inputs and mass outputs respectively. $Ex_{destruction}$, $S_{generation}$, m_i and Ex_i represent exergy destruction, entropy generation, the mass of resource/stream, and exergy of resource/stream respectively. $W = Work$, Ex_i = exergy of ith component, m_i = mass of ith component, I = irreversibility, T and T_0 are the temperature of the stream/resource and environmental/reference temperature (298.15 K).

Exergy efficiency, which is the ability of a system to convert raw materials into valuable products, is defined mathematically by Eq. 33.6 (Rivero et al. 1999).

$$Ex_{efficiency}=\frac{Ex_{flow-out}}{Ex_{flow-in}} \tag{33.6}$$

Generally, in situations where the exergy destruction is low with wastes being utilized for value-added bioproducts, the exergy efficiency increases. This is an excellent alternative for sustainable biorefinery operations as waste streams with low exergy contents are transformed into high exergy content materials.

Figure 33.1 summarizes the main steps in carrying out exergy analysis of a biorefinery concept. For process simulation (which is neglected in this section's case studies), it becomes important to select the appropriate activity coefficient model (e.g., Non-Random Two Liquid, NRTL model) for the phase equilibria calculations. Again, the physical and chemical properties of each stream component as well as mass balance over each unit operation under consideration are critical.

33.1.4 Exergy Analysis of Waste Biorefineries: Current State

Though research results on the exergy of waste refineries are scarce in literature, the few existing data indicate prospective cases for sustainable biorefineries in the long term. For instance, Zhang et al. (2020) estimated an overall exergy efficiency of 60–68% for plastic wastes pyrolysis into biofuels where their simulation of the refinery pinpointed that heat carrier loading of 15–20% could improve the heat capabilities of the reactor.

Thermochemical conversion of rice husks at 1000 °C generated high-quality syngas with exergy content of about 7–8 MJ/kg (Zhang et al. 2015) which can be useful in many industrial applications. Oil palm fronds have the excellent potential of being used as waste feedstocks for biorefining into phytochemicals and bioethanol. For instance, Ofori-Boateng and Lee (2014) carried out exergy analysis on palm wastes biorefinery concept which revealed that the wastes with exergy

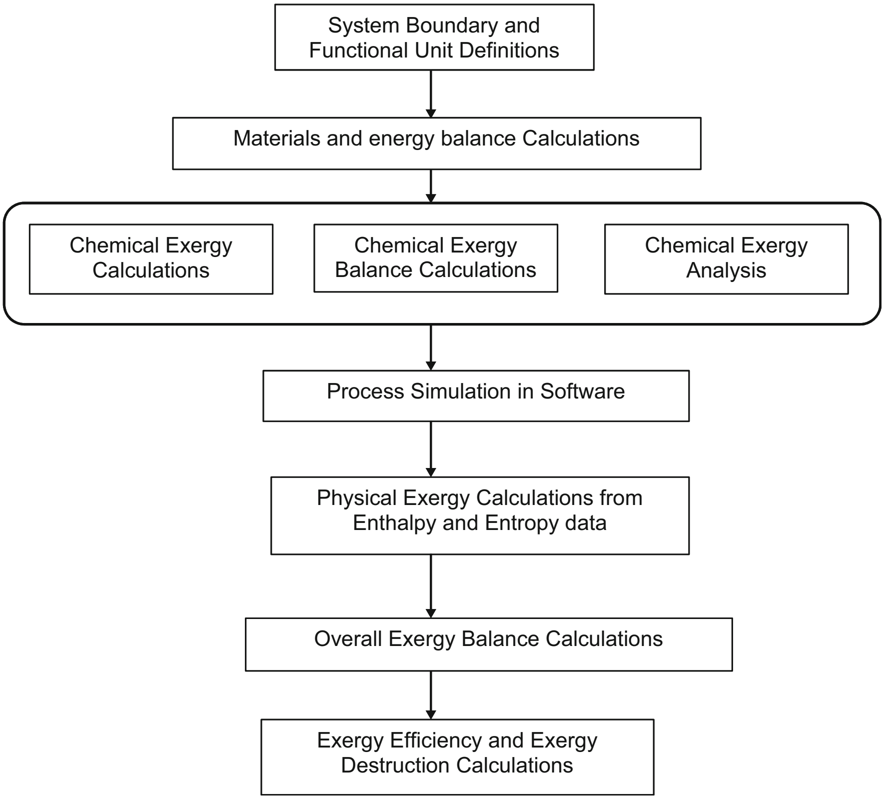

Fig. 33.1 Simplified Flow Diagram of Exergy Analysis Steps

content of ~23.3 MJ/kg were efficiently upgraded to ~25.9 MJ/kg cellulosic ethanol recording an overall biorefinery exergy destruction of about 37%. In a sugarcane biorefinery concept, the bagasse generated as wastes were utilized to produce lactic acid and electricity with an overall biorefinery exergy efficiency of about 52.71% (Aghbashlo et al. 2018). The use of fossil-based fuels as sources of energy for the sugarcane bagasse biorefinery was found to be the major contributor to exergy destruction. Hence resorting to exhausting gas recycling as well as solar energy use may improve the exergetic efficiency of the biorefinery.

In a recent finding, Vilardi and Verdone (2022) concluded that the use of municipal solid wastes as feedstock for syngas production via incineration is environmentally benign and exergetically efficient especially when gas recirculation is employed in the process. Mohtaram et al. (2021) studied the critical parameters affecting the efficiency of a waste-to-energy system using exergy as the assessment tool. They concluded that decreasing the flow's temperature to about −40 °C while increasing the inlet turbine pressure (0.6–1 M) improved the overall exergy efficiency of the system.

Food wastes are found to be very good sources of feed for an incineration system. Tang et al. (2017) carried out energy and exergy analysis on an incineration system that was fed with food wastes and concluded that about 11.6% increase in exergy of electricity generated could be realized if the food wastes are mixed with municipal solid wastes for maximal sustainability.

Oil refineries currently burn all gases emitted which is economically and environmentally unsustainable. Research and development studies have shown the possibilities of utilizing or recycling waste gases but the challenge has been the efficient or sustainable method of achieving it. In view of this, exergy analyses have become efficient tools to assess the feasibility of recycling waste gases. The exergy analysis results of Sharaf Eldean and Soliman (2017) indicated that when waste gases are used as major raw material by thermal desalination plants, overall operating cost is reduced as exergy efficiency is increased.

The transformation of waste canola oil into biodiesel via transesterification (at 55 °C and 1:8 methanol to oil ratio) resulted in total exergy destruction of 4.3 MJ/kg biodiesel and about 91.7% exergy efficiency (Khoobbakht et al. 2020). In palm biorefineries, palm oil mill effluents (POMEs) with high exergy contents are mostly discharged into the environment without effective treatment. POMEs can be converted into value-added products like methane, biodiesel, electricity, etc. Exergy destruction rate of about 167–214 MJ/s was recorded for a cogeneration plant integrated into an existing palm oil refinery for electricity generation from the liquid palm wastes (Julio et al. 2021).

33.1.5 Chemical Exergy Analysis of Wastes Refineries: System Boundary and Functional Unit

A functional unit of 1000 kg of wastes is assumed for the energy and exergy balance calculations. The production and transportation of the wastes used as feed for biorefining are assumed to be excluded from the system boundary. All unit operations considered in this chapter for exergy analysis are assumed to utilize energy (in the form of heat, steam, electricity, etc.) sourced from fossil fuels. Emissions from these unit operations are not controlled thus emissions are considered wastes in this section. For standard chemical exergies of chemicals or stream components that are not found in the list provided by Szargut et al. (1988), they are estimated using the information about their molecular structure via the group contribution method given by Shieh and Fan (1983). Ofori-Boateng and Lee (2014) have estimated most of the stream components of streams including water, steam, diesel fuel, electricity, etc.

33.1.5.1 Chemical Exergy Analysis of POMEs Anaerobic Digestion

This section assesses the chemical exergies of process streams of anaerobic digestion of POMEs integrated into an oil palm biorefinery. POME that enters the digester is assumed to be homogenized to facilitate microbial activities before feeding into the reactor. POME contains about 95% water, 4% residual oil, and 1% sediments (Lee and Ofori-Boateng 2013). Anaerobic digestate from the reactor is assumed to be a value-added product that can serve as organic fertilizer. Biogas from POME comprises about 64% methane (CH_4), 32% carbon dioxide (CO_2), 1% of hydrogen sulfide (H_2S), and 3% water vapor (Ohimain and Izah 2017; Ofori-Boateng and Lee 2014). It is estimated that about 1 kg POME is able to generate about 0.98 kg digestate and 0.023 kg biogas (Sežun et al. 2010). A closed stirred tank reactor operating at 55 °C for 40–45 days with continuous capture of biogas from the reactor is considered in this section. About 1 M of fossil-based energy (in the form of heat and electricity) is assumed to be utilized by the reactor to process about 4.35 kg of POME. Emissions in the form of exhaust gases etc. that are not captured are assumed to be about 0.5% of POME processed. The purification of the biogas is not considered in the system boundary. Table 33.1 summarizes the material and exergy values of the major streams of the system boundary considered in this section. Standard chemical exergies of stream components were obtained from Szargut et al. (1988) and Lee and Ofori-Boateng (2013). Figure 33.2 shows the chemical exergy balance of the POME anaerobic digester.

The total chemical exergy of resources (mainly POME and energy) that entered the digester was about 396 MJ per 1000 kg POME and after 40–45 days, the products generated had total exergy of about 1533 MJ. This shows that the quality of POME was improved in terms of exergy which was accompanied by the production of biogas and biofertilizer. POME, regarded as wastes, can therefore be upgraded to produce high-quality biogas and fertilizer for sustainable development. Exergy analysis reports on anaerobic digestion of waste streams from industrial

Table 33.1 Standard Chemical Exergies of Process Streams

Component	Chemical formula/ composition	Mass (kg)	Standard Chemical Exergy ($Ex_{ch,i}^0$) (MJ/kg)
Methane	CH_4	14.912	51.81
Carbon dioxide	CO_2	7.456	0.443
Hydrogen sulfide	H_2S	0.233	23.83
POME	H_2O + Oil + Sediments	1000	0.166
Water	H_2O	0.699	0.049
POME Digestate	–	976.7	0.598
Emissions	–	5.0	33.5
Utilities/ Electricity	–	229.9	1.00

Source: Szargut et al. 1988; Lee and Ofori-Boateng 2013

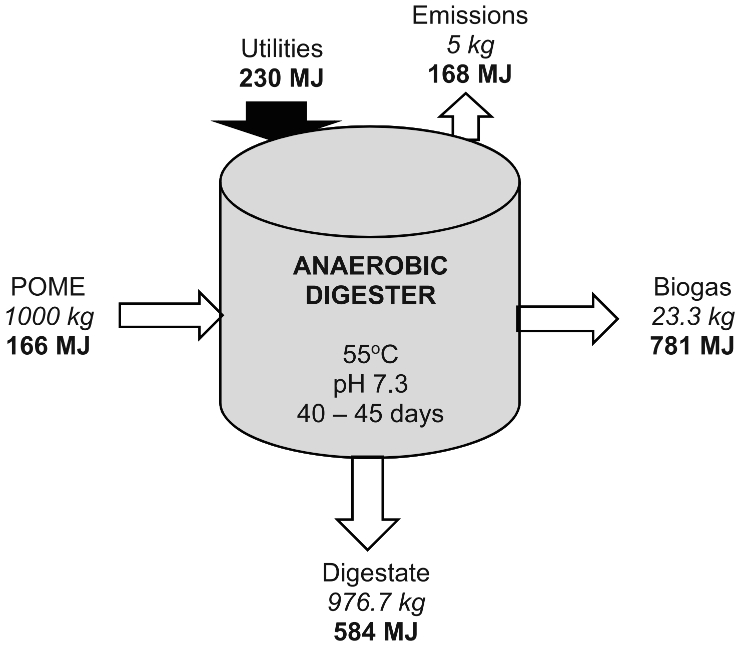

Fig. 33.2 Chemical Exergy Balance of POME Anaerobic Digester

activities show similar results where the wastes were upgraded in terms of exergy (Martin and Parsapour 2012).

33.1.5.2 Biodiesel from Waste Oil: Chemical Exergy Analysis of Transesterification Reactor

This section assesses the quality of energy content or chemical energy availability in major input and output streams of transesterification of waste cooking oil (WCO) into biodiesel. The biodiesel production process involves major steps such as transesterification, methanol recovery, washing, and purification. In this section, a one-step transesterification reactor is considered for chemical exergy analysis. WCO contains free fatty acid (FFA), triglycerides, diglycerides, and monoglycerides of about 0.169 g/g oil, 0.791 g/g oil, 0.018 g/g oil, and 0.022 g/g oil, respectively (Liu et al. 2012). Prior to transesterification, the WCO is cleaned by centrifugation and drying to remove impurities and water respectively. Alkaline-catalyzed transesterification with methanol (methanol to oil ratio of 1:8) and sodium hydroxide (NaOH) is done to convert the triglycerides in the WCO into biodiesel and glycerol at 70 °C and 1 bar. In this section, for about 1 kg WCO that enters the reactor, it is assumed that about 0.97 kg is attained as crude biodiesel (or methyl ester).

Table 33.2 Standard Chemical Exergy of Waste Cooking Oil (Talens et al. 2010)

Component	Standard chemical exergy (MJ/kg)	Mass (kg)	Standard chemical exergy (MJ)
Triglycerides	38.01	790.5	30,047
Free fatty acid	32.22	169.0	5445
Water	0.049	0.50	0.025
Others	16.65	40.0	666
Total exergy	–	1000.0	36,158

‘Others’-include diglycerides, monoglycerides and organic matter

Table 33.3 Standard Chemical Exergy Values of Major Process Streams (Szargut et al. 1988; Ofori-Boateng et al. 2012a, 2012b)

Stream	Mass (kg)	Standard Chemical Exergy ($Ex_{ch,i}^{0}$) MJ/kg
Biodiesel	970	37.55
Waste Cooking Oil (WCO)	1000	36.16
Electricity	–	1.00
Glycerol	30	22.30
Methanol	125	22.44
Sodium hydroxide (NaOH)	45	1.873

Literature data from Ofori-Boateng et al. (2012a) and Ofori-Boateng et al. (2012b) were used as basis for mass and energy balance calculations. For a functional unit of 1000 kg WCO, Tables 33.2 and 33.3 summarize the standard chemical exergies of major streams into the transesterification reactor.

Figure 33.3 shows the chemical exergy balance of biodiesel production from WCO. For about 1000 kg WCO that entered the transesterification reactor, about 970 kg came out as crude biodiesel which can be purified to upgrade its exergy content. About 30 kg glycerol was generated which has many industrial applications. WCO with a chemical exergy content of about 36,158 kg was upgraded to about 36,424 MJ (about 266 MJ increase in chemical exergy content). Though the WCO quality was upgraded via transesterification, the overall chemical exergy input (i.e., about 39,047 MJ) was degraded by about 1954 MJ indicating a chemical exergy efficiency of about 94.9%. The type of chemicals or raw materials used in the chemical reaction is very critical as inorganic inputs may increase the degradation of exergy due to dissipative effects caused by entropy generation. For instance, the catalyst NaOH which has chemical exergy of about 84 MJ was a low-quality resource compared to potassium hydroxide (KOH) with chemical exergy of about 390 MJ. KOH would have increased the input chemical exergy hence decreasing exergy efficiency (Fig. 33.3).

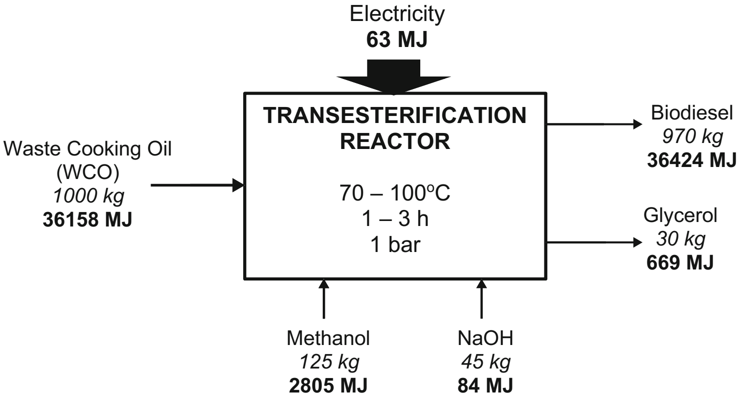

Fig. 33.3 Chemical Exergy Balance of a Transesterification Reactor

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Chapter 34
Social Circular Economy Indicators Applied to Wastage Biorefineries

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Abstract A waste biorefinery is a facility aimed to use a wide variety of biogenic waste to produce value-added products and energy. Moreover, they arise as a cornerstone in the global sphere, fostering fossil-based resources substitution. In this perspective, biorefineries have the capacity of achieving a circular economy within a sustainability context, by creating economical, environmental, and social benefits. Quantitative estimations have been assessed on the economic or environmental aspects of the circular economy (CE). However, the total assessment of sustainability in a biorefinery system involves, in addition to environmental and economic, the social impacts assessment to ascertain the potential implications derived from the process implementation to the society. In this work, we take closer regard at the pledges and expectations of the waste biorefineries within CE from the point of view of the social indicators. The social indicators are proposed to evaluate potential positive and negatives effects of the implementation and operation of waste biorefineries. The research includes an overview of Social Life Cycle Assessment (SLCA) methodology and a screening to link waste biorefinery social indicators to the Sustainable Development Goals (SDGs). As a result, we summarize key preliminary indexes to measure the waste biorefinery performance. The screening will allow decision makers to identify indicators and hotspots along the waste biorefinery and determine how these SDG hotpots can be improved.

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34.1 Introduction

In this century, petroleum derivatives are increasingly scarce and environmental damage makes their use questionable, the scientific community faces challenges and technological and economic challenges on the exploitation of renewable resources as a productive platform for countries. The industry today must comply with more and more conditions for their processes to move forwards sustainability for today and future generations. The development of agriculture, the evident growth of the population and therefore concerns about health, energy security, fuel prices from oil and the need to reduce greenhouse gases make the biorefinery a great alternative for the development of bio-based products with added value.

In the past decades, the production systems have worked under a take-make-use-dispose' model, predicated on the extraction and continuous reckless utilization of finite natural resources. With this in mind, the circular economy (CE) idea has evolved as a potential alternative for the current linear production model (Ellen Macarthur Foundation 2015). The CE centers on the efficient employment of finite resources and ensures that these resources are re-used if achievable. In this system, the use of cyclical flows of materials, renewable energy sources, and cascade-type energy flows is adopted. The purpose is to subtract only the necessary resources, which are reintegrated after their useful life, either to new production chains or to nature at the end of their maximum use. Therefore, achieving sustainable development, simultaneously, creating environmental and economic quality, prosperity, and social equity, for the benefit of current and future generations is their major target.

The biorefining model could be one of the head approaches of the CE for ending cycles of biomass materials, that is, re-utilization of forestry, agro, process, and post-consumer residues. So, biorefining can be understood as an excellent dodge for large-scale sustainable biomass utilization in the bioeconomy. It will outcome co-production of food/feed ingredients, bio-based products, and bioenergy with satisfactory socioeconomic and environmental impacts (resources use efficient, decreased GHG emissions, and others) and cost-competitiveness (Caldeira et al. 2020). However, biorefineries can also have negative effects on environmental, social, or economic sustainability. Moreover, right policies will be needed to maximize positive and minimize harmful effects of the CE strategies. So far, there has been much focus on the environmental and economic benefits of biorefineries, but significant societal concerns should still be faced (Fytili and Zabaniotou 2017).

The main challenge in addressing social dimension of CE of biorefineries is the lack of a comprehensive and robust framework of social indicators (Padilla-Rivera et al. 2020). As such, a few methods, tools, and resources have been used to assess social and sociological aspects of CE strategies, but they are not developed in connection with CE and biorefineries, thus, the tools have yet to achieve a formal consensus, and compressive indicator framework for the social dimension within CE and biorefineries has yet to be developed.

In this context, Social Life Cycle Assessment (S-LCA) is a methodology developed to assess the plus and minus social burdens of products, services, and organizations, along their life cycle embracing the feedstocks extraction and processing, manufacturing, distribution, use, re-use, maintenance, recycling, and final disposal (UNEP 2020). It could be considered as a useful tool to provide decision support in order to evaluate and monitor systems such as biorefineries to understand and improve the contribution CE strategies to the accomplishment of the sustainable development.

The present work searches to highlight the importance of SLCA and its use as a basis for CE indicators of waste biorefineries and investigate factors influencing it, in sustainability context. This work is unfolded in four parts: SLCA, social circular economy indicators and impacts and conclusions.

34.2 Social Life Cycle Assessment

The paradigm of sustainable development has created debates in all intellectual fields around the world; prompting scientists to create methods to assess environmental, social, and economic impacts. This has created great interest in the inclusion of social aspects in the life cycle evaluation of products, leading the LCA to a deeper and more comprehensive social analysis: the Social Life Cycle Assessment (SLCA).

In 2009, the UNEP published the first version of the Guidelines for the Analysis of the Social Life Cycle of Products, where the approach that should be followed to start with the SLCA studies is described; currently, there is no methodology that integrates and associates qualitative data for its quantitative management; inventories of social impacts, nor data for the preparation of SLCA, that is, the guidelines only offer an overview of the path to be followed for the development of these (UNEP/SETAC Life Cycle Initiative 2009).

SLCA's objectives are to evaluate the social and socioeconomic impacts of all stages of the product life cycle, from cradle to grave. Considering everything related to the extraction of resources, transformation, manufacturing, assembly, marketing, sale, use, recycling and disposal, among others, which can be identified during the construction of the product system.

SLCA is based on Life Cycle Thinking (LCT). This approach seeks to capture the environmental/social impacts of goods or services “from the cradle to the grave,” thus considering all the steps of their life cycle and avoiding shifting loads between geographic areas or steps in the supply chain. There are also numerous relevant gaps between the two approaches. One of them is that social concerns are diverse and subjective, depending on the context (Sala et al. 2015).

In the SLCA background, social impacts are outlined as “the effects on populations—public or private—interest that alters the style in which people experience, work, play, relate to each other, organize themselves to serve their requirements and commonly manage as members of societies”. Therefore, social impacts are the consequence of positive or negative pressures on the social areas of protection (i.e., the well-being of stakeholders). As the cause-effect chain is not well defined and a suitable impact assessment method has not yet been developed, the term “social risk” is often adopted.

Social risk concerns the opportunity that one or more stakeholders will be subjected to negative social circumstances that, in turn, damage social sustainability (Pelletier et al. 2014). “Hidden” positive social impacts in product supply chains are also taken into account in the LCA methodology, although their theoretical definition and implementation in the methodology is still under debate (Di Cesare et al. 2016).

The definition of positive impact should not be limited to the utility of a product, which, in economic terms, is “the well-being that a given good or service is capable of providing a person since it is capable of satisfying a desire or satisfying a need.” Instead, the concept of positive impact should refer to so-called “win-win” situations, in which all parties involved in the initiative benefit (or are not harmed) in terms of value created in their favor (Di Cesare et al. 2016).

Regarding this specific methodology, there are still no internationally recognized standards such as environmental LCA, but guidelines have been developed in the document “Guidelines for the evaluation of the social life cycle of products” carried out by UNEP/SETAC Life Cycle Initiative (UNEP/SETAC Life Cycle Initiative 2020). This document has been written by several experts in various fields such as sustainability, life cycle thinking and social sciences, among other disciplines, in accordance with its multidisciplinary nature. The UNEP/SETAC guidelines provide a reference set of stakeholders and impact subcategories to consider in an LCA study.

The impact categories include the social issues of greatest relevance to decision makers and also to affected parties. Among the social issues included are human rights, working conditions, cultural heritage, poverty, disease, political conflicts and indigenous rights. The social and socioeconomic subcategories of the impact have been defined based on international agreements and best practices at the international level.

Otherwise, stakeholders are defined as those potentially affected by one or more processes in the life cycle of a product, whether by resource extraction, processing, manufacturing, use, or recycling. The groups can be identified from the moment the infrastructures of these processes are built. Some of these have different geographic locations, therefore the social impacts are also related to the socioeconomic aspects of the region under study. The categories of interest groups proposed according to UNEP/SETAC (2009) are:

- Workers
- Local community
- Society (national and global)
- Consumers
- Actors in the value chain

Once the stakeholder categories and impact subcategories have been defined, the inventory indicators need to be defined. These can be of the qualitative, quantitative, or semi-quantitative types. The UNEP/SETAC methodological chips supply inventory indicators models for each subset. Therefore, given the above, the phases of the SCLA according to UNEP (UNEP Setac Life Cycle Initiative 2009) are as follows:

- Phase 1. Goal and scope definition
- Phase 2. Inventory analysis
- Phase 3. Impact assessment
- Phase 4. Interpretation of results

34.3 Social Circular Economy Indicators

Commonly, the sustainability concept has been construed dissimilarly according to the players involved, the conditions, and the indicators used to determine it. Sustainability aspects frequently show up categorized in three spheres: environmental, economic, and social. While this three-sphere rank is being discussed, no other categorization schemes have been suggested—so far—in the literature. Although the social dimension sustainability concept is broadly recognized, its deployment in the circular economy has not been very transparent determined or agreed upon. Actually, despite the variety of available social sustainability categories/aspects/indicators, Hutchins et al. (2013) observed the lack of a commonly accepted social indicator within CE.

Based on the above the methodological chips for subsets in social life cycle assessment (S-LCA) (Benoit et al. 2011) are offered as a reference for analyzing the social dimension of CE. As a result, 5 impact categories divided into 18 impact subcategories (positive and negative, qualitative, and quantitative) were selected for the four S-LCA stakeholder groups (Table 34.1).

The social subsets are reasoned on so-named type-1 indicators, which be based on semi-quantitative ordinal ranges, particularly on attribution ordinal values (e.g., 1, 2, 3, and 4) to occurred impacts during the life cycle. These ordinal-scale values generally reflect upon companies' ethical performance and legal compliance; for instance: 1 = no commitment, 2 = fulfills basic requirements and 3 = proactive behavior subsets of burdens and inventory indicators, specifying the reference framework.

The indicators set has then been applied as the collection foundation of quantifiable data, while the founding metrics were updated to the specific project features. Afterward, Performance Reference Points (PRP) were established. As quantitative data from active biorefineries could not be achieved, it was resolved to utilize companies' annual sustainability reports, which can depict the system life cycle stages. Therefore, sustainability reports gathered in the data collection phase are employed to appoint the reference spots.

It should be reinforced that, at this stage, there are no characterization models between subsets and impact categories that are usually admitted by SLCA practitioners. Thus, nowadays, the causal models in social sciences are generally not well

Table 34.1 Impact categories, subcategories, and inventory indicators proposed

Impact categories	Impact subcategories	Inventory indicators	Type of indicator
Human rights	Child labor (W)	Number of people under 15 working	Quantitative
	Equal opportunities/Discrimination (W)	Number of incidents of discrimination	Quantitative
		Percentage of working women	Semi-quantitative
	Freedom of Association and collective bargaining (W)	Percentage of workers members of a labor union	Quantitative
Health and Safety	Health and safety (W)	Number of work accidents	Quantitative
		Presence of a formal policy concerning to health and safety	
	Safe and healthy living conditions (Lc)	Number of programs to improve the health or safety of the community	Semi-quantitative
Working conditions	Fair salary (W)	Average income per capita of the household from the income of the worker	Quantitative
	Working hours (W)	Number of average hours worked/week	Quantitative
	Forced labor (W)	Number of hours of forced labor identified during the study period	Quantitative
	Social benefits/Social security (W)	Average percentage of workers who receive minimum social benefits established by law (vacation, days off, Christmas bonus, social security, flexible hours, written contract and training)	Semi-quantitative
	Job satisfaction (W)	Percentage of workers who would change job	Semi-quantitative
Governance	Community engagement (Lc)	Existence of a mechanism to receive and take into account the opinion of the community	Qualitative
	Public commitments to sustainability issues (S)	Presence of documents of agreements on sustainability issues available to the public	Semi-quantitative
	Fair competition (Vc)	Documented declaration or procedures (policies, strategies, etc.) to avoid getting involved or being accomplices in anticompetitive behavior	Qualitative
	Promoting social responsibility (Vc)	Presence of an explicit code of conduct that protects the human rights of workers among suppliers	Semi-quantitative
Socioeconomic repercussions	Access to material resources (Lc)	Number of programs aimed at creating infrastructure for mutual benefit of the organization and the community	Quantitative
	Access to immaterial resources (Lc)	Number of education programs for the community	Quantitative

(continued)

Table 34.1 (continued)

Impact categories	Impact subcategories	Inventory indicators	Type of indicator
	Local employment (Lc)	Percentage of workers belonging to local communities	Semi-quantitative
	Social acceptance (Lc)	Percentage of respondents who consider the existence of ranches to be positive for the community	Semi-quantitative

W Workers, *S* Society, *Lc* Local community, *Vc* Value chain actors

developed. Besides, the indicators might not enable a quantified rating but only qualitative or semi-quantitative, which becomes the results aggregation problematic, and, sometimes, unfeasible. Another bottleneck of SLCA is to find a good commitment between quantitative and qualitative indicators choice.

34.4 Social Impacts in Waste Biorefineries

As previously stated, social dimension is an important area in the domain of waste biorefineries. The promotion of biorefineries is an innovative way to address the growing generation of urban solid waste, which is the responsibility of local governments. Not only does it provide the opportunity to reduce negative environmental and social impacts, but it can also be beneficial for public finances. Thus, they are increasingly striving to achieve a comprehensive understanding and valid measure of social performance to influence the overall sustainability. To deal with potential social impacts in waste biorefineries, social metrics are required. In this section, a list of social aspects is presented to measure the social dimension of waste biorefineries.

After ascertaining the stakeholders list, impact categories, subcategories, and their indicators, they should be categorized accordingly to priorities and impacts in the waste biorefineries. The prioritization of impacts is aligned with the sustainable development goals based on the previous work Padilla-Rivera et al. (2020). In this context, the biorefinery concept appears as an alternative technology to follow this approach. As it was stated, the waste biorefineries were previously analyzed from an environmental a techno-economic perspective, though, the potential social impacts of this technologies type have not been evaluated. The outcome of analysis is intended to present an S-LCA of an early-stage design process and can be applied to any waste biorefinery (Table 34.2).

Table 34.2 Waste biorefinery impacts and its linkage to SDGs

Stakeholders	Positive impacts	Negative impacts	Link to SDG
Workers	Create employment opportunities	Relocation of people Increase exposure to hazardous substances	SDG8, SDG1, SDG3
Local community	Promote local development Resolve waste management issues	Increase land rights conflicts Generate environmental impacts	SDG1, SDG2
Value chain actors	Create new business opportunities Strengthen socially responsible practices	Respond to stricter environmental requirements	SDG12
Society (authorities)	Stimulate R & D innovation	Fragmented policy framework	SDG15

34.5 Conclusions

The suggested framework strived to contribute to the sustainability approach, endorsing the triple-bottom-line perspective. This proposal spotlights the social dimension of waste biorefineries, taking into account a holistic context, to supply a straightforward tool to analyze prospective social hotspots. The detailed structure is recommended as a solution option to circumvent the weakness of the current impact assessment methodology encountered when analyzing production process development. In the aftermath, methodology application could bring to the implementation strategic guideline of proper social actions at the stakeholder levels.

The research includes an overview of Social Life Cycle Assessment (SLCA) methodology and a screening to link waste biorefinery social indicators to the Sustainable Development Goals (SDGs). As a result, we summarize key preliminary indicators to assess the waste biorefinery performance. The screening will allow decision makers to identify indicators and hotspots along the waste biorefinery and determine how these SDG hotpots can be improved.

The proposed approaches can be employed in distinct sectors and countries, regardless of the processes or technologies complexity at an early development stage. The obtained outcomes give valuable information about social indicators' constraints, which can be utilized in the near future to discern processes' improvements against other processes.

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Chapter 35
How to Realize an Urban Circular Bioeconomy

Manfred Kircher and Thomas Bayer

Abstract The reduction of CO_2 emissions required in the course of climate protection is forcing the economy to switch raw materials from fossil to renewable energy and carbon sources. This also applies to the chemical industry, which can switch to biogenic carbon sources for organic chemical products. To avoid competition with the food sector, non-food biomass is also being considered. In this context, biogenic residual and waste materials, as they occur spatially concentrated especially in metropolitan regions, are of particular interest. The potential of these potential raw materials for value creation, ecological sustainability and employment is presented using the example of the Rhine-Main Metropolitan Region (Germany), where the initiative Innovation Space BioBall (Bioeconomy in a Metropolitan Region) is developing the foundations for an urban circular bioeconomy.

35.1 Introduction

The modern industrial bioeconomy has the task of integrating in particular those sectors that are dependent on carbon. These include the sectors of the chemical industry that produce organic chemistry products and those parts of the mobility sector that will be dependent on high-energy-density fuels for the foreseeable future, such as air travel. In all bioeconomy strategies, which have now been adopted by more than 60 countries (Aguilar et al. 2018), there is agreement that the integration of these industries must be done in a way in which the industrial use of biogenic raw materials does not jeopardise food supplies (Dubois and Gomez San Juan 2016) while respecting planetary boundaries (Liobikiene et al. 2019) and the limited capacity of ecosystem services (D'Amato et al. 2020). As a way out, the strategy

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of tapping agricultural and forestry by-products, so-called non-food biomass as raw material is often pursued (Khawaja and Janssen 2014). For example, the EU has set a quota for the expansion of biofuel capacity from non-food biomass (EC 2018), and the European Chemical Industry Council also favours biogenic feedstocks that do not compete with food (CEFIC 2021). Thus, there is a push to use by-products that occur at the beginning of the bioeconomical value chain, namely the production of biomass. In contrast, the potential of biogenic materials that are produced only after the use of products and during the processing of waste, i.e. at the end of the value chain, is still given little consideration today. These potential raw materials have the advantage of accumulating to a considerable extent regionally, where, depending on the regional economic structure, industrial production capacities may also be located as potential customers. In addition, cities produce primary biomass on their land in the form of green waste, whose potential as biogenic raw materials is also still largely untapped. Urban residual and waste streams can therefore close the material cycle by valorising residual and waste materials and thus contribute to urban circular bioeconomy (Kircher 2018). This chapter describes an example of the project "Bioeconomy in a metropolitan region" (BioBall), which is working on laying the scientific/technical and organisational foundations for an urban circular bioeconomy in the Rhine-Main Metropolitan Region (Germany) (Kircher et al. 2019).

35.2 Background and State of the Art

The potential and the development of an urban circular bioeconomy strongly depend on the regional conditions and the existing economic structure. Table 35.1 shows key data of the Rhine-Main Metropolitan Region on the number of inhabitants, land use, gross value added of various economic sectors and the jobs generated there. 5.8 million inhabitants live in the metropolitan region. They produce 2.86 million tons of waste, 29% of which is biowaste. 79% of the land in the metropolitan region is used for agriculture and forestry, which indicates a significant amount of agricultural and forestry biomass, including residues. At the same time, it is clear that these land-intensive sectors contribute only 0.5% to the gross value added, while the manufacturing industry produces a share of 17% on less than 2% of the area. The fact that one focus of the manufacturing industry is the chemical-pharmaceutical industry, which alone contributes 11% of the gross added value, gives an indication that, in contrast to agricultural and forestry residues, industrial residues and waste materials are produced on comparatively small areas.

Table 35.2 provides an overview of the enormously broad spectrum of biogenic residual and waste materials from agriculture and forestry, municipalities and industrial companies in the metropolitan region, the origin of these materials, the annual volume generated and the status quo of utilisation. To better classify the potential, exemplary residual and waste materials are also given that are still fossil-based today, but whose biogenic share will increase as the raw material transformation progresses (e.g. municipal waste).

Table 35.1 Indicators of the Rhine-Main Metropolitan Region (PERFORM 2021)

Inhabitants	Total	5,808,518	100%
	Thereof in core cities	1,621,592	28%
Area [ha]	Total	1,475,340	100%
	Thereof agricultural area	618,964	42.0%
	Thereof forest area	546,449	37.0%
	Thereof traffic area	105,100	7.1%
	Thereof residential area	73,926	5.0%
	Thereof industrial and commercial area	28,950	2.0%
	Thereof recreational area, sports and leisure	23.446	1.6%
	Thereof waters	22,350	1.5%
Gross value added	Total	246,088	100%
[mn EUR]	Thereof services	187,417	76.2%
	Thereof manufacturing industries (incl. Chemical-pharmaceutical industries 26,8 bn EUR (2018))	41,850	17.0%
	Thereof construction industry	11,045	4.5%
	Thereof agriculture, forestry, fishing	1295	0.5%
	Thereof other	4481	1.8%
Jobs	Total	2,435,140	100.0%
	Thereof agriculture, forestry, fishing	9708	0.4%
	Thereof manufacturing industries (incl. Chemical-pharmaceutical industries 57,000 (2018))	371,872	15.3%
	Thereof construction industry	129,844	5.3%
	Other (trade, traffic, service)	1,923,716	79.0%

As shown in Table 35.2, the metropolitan region generates an extraordinarily diverse range of residual and waste materials. The residual biomass produced in the agricultural and forestry sectors is available in large volumes in a comparatively single-variety form; examples include straw and wood. Already quasi-purified biomass fractions are the residues of industrial processing, such as lignin as a by-product of the paper industry and CO_2 captured from biogas. The situation is different for biogenic municipal waste, which consists of a complex mixture of different biomass wastes. In the metropolitan region, biogenic waste from private households is collected separately (Remondis 2021); it includes food and garden waste. In the municipal sector, green and grass cuttings from the maintenance of parks and sports facilities are worth mentioning.

The chemical composition of these materials also varies widely. Agricultural and forestry residues as well as green waste from municipalities have a high content of lignocellulose. Food residues, on the other hand, contain only little lignocellulose and more biomolecule fractions such as proteins, sugars, vegetable oils and fats. All biogenic residues and waste materials have in common that they consist of functionalised organic molecules, contain inorganic plant nutrients, and offer a partly high calorific value. Various utilisation options can be derived from this:

Table 35.2 Residuals, origin, volume and valorisation of residuals in the metropolitan region (Schebek et al. 2018; Kircher and Michels 2015; FNR 2014; Statistisches Bundesamt 2017)

Material	Origin	Volume per year	Utilisation
Rape seed residuals	Agriculture	2,500,000 t (total harvest)	Press cake: feed; other residuals not utilised
Wheat residuals		1,100,000 t (total harvest)	Straw: stable insert; other residuals not utilised
Corn residuals		420,000 t (total harvest)	Residuals not utilised
Beet sugar residuals		156,000 t (total harvest)	Leached beet pulp: feed; other residuals not utilised
Straw		70,000 t	Stable insert
Wood	Forestry (logging)	4,500,000 m^3	Material (60%) and energetic utilisation (40%)
	Forestry (deadwood stock)	22,578,000 m^3	Partly energetic utilisation
Biowaste in municipal waste	Organic waste (60%); garden and park waste (40%)	700,000 t	Composting (60%)
			Anaerobic fermentation (35%)
			Energetic utilisation (5%)
Organic share of municipal waste (bio- and fossil-based)	Organic fraction of municipal solid waste (45%)	1,400,000 t	Energetic utilisation
Sewage sludge (dw)	Municipal waste management	146,000 t	Energetic utilisation (65%)
			Fertiliser (28%)
			Landscaping (7%)
Biogenic industrial residuals	Chemical/pharmaceutical industry	no data	Disposal
	Paper industry	> 90,000 t lignin	Energetic utilisation
	Food industry	200,000 t	Anaerobic fermentation, compost, biodiesel
CO_2 (biogenic)	Biogas plant	50,000 t	Food additive (only little)
CO_2 (total)	Buildings (38%)	44,000,000 t	No utilisation
	Mobility (32%)		
	Industry (30%)		

Residual and waste materials can serve as a source of organic fractions, as fertiliser, and as a source of energy. The current status quo of waste utilisation is discussed in the next section.

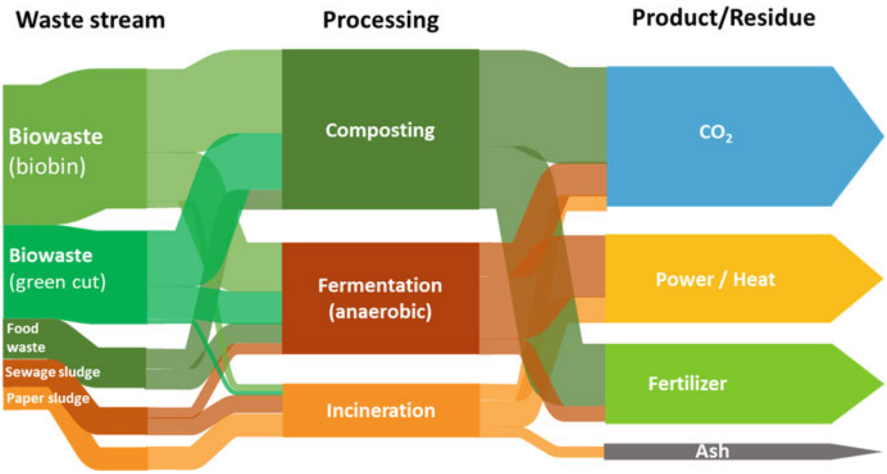

Fig. 35.1 Status quo of biogenic waste recycling in the Rhine-Main Metropolitan Region (Source: Provadis Hochschule)

Table 35.3 Contribution of biogenic residuals to primary energy in Hesse (Hessisches Ministerium für Wirtschaft, Energie, Verkehr und Wohnen 2020)

Material	Origin	Utilisation	Calorific value [kJ/kg]	Share of primary energy consumption
Wood	Forestry (deadwood stock)	Combined heat and power plants; residential heating	17,000	8.36%
Biowaste in municipal waste	Organic waste (60%); garden and park waste (40%)	35%: biogas, power generation	12,000	0.95%
		5%: incineration		
Organic share of municipal waste (bio- and fossil-based)	Organic fraction of municipal solid waste (45%)	Incineration	9000 (wet)	1.43%
Sewage sludge (dry weight)	Municipal waste management	Incineration	11,000 (digested)	0.18%

An overview of the status quo of waste recycling in the metropolitan region is given in Fig. 35.1.

Some of the biogenic waste materials are used as fertiliser according to the state of the art, i.e. composted or applied directly to agricultural land in the form of sewage sludge. In this way, the material cycle is closed for the inorganic plant nutrients contained. This also applies to the proportion of organic biomass that is ultimately degraded to CO_2 by the soil flora and released into the atmosphere as agricultural emissions.

Another part is used for energy (Table 35.3; data for Hesse, the federal state in which the Rhine-Main Metropolitan Region is mainly located). Except for wood, which contributes 8% to the energy supply, however, the share of energy generated from waste is only marginal.

Biodegradable waste from industry is incinerated, usually. For example, sewage sludge and biogenic wastes in the Industrial Park Höchst, the largest chemical and pharmaceutical site in Hesse, is incinerated, and steam for the production is produced (for more details see Sect. 35.4.3).

However, the potential that could lie in biomass for material use is not being exploited. In summary, therefore, it must be stated that waste utilisation in the metropolitan region is limited to low value-added products such as compost, biogas and energies, with significant volumes of biogenic CO_2 being emitted.

35.3 Disruptive Technological Approaches

The previous section has already indicated where the potential for future utilisation of biogenic residual and waste materials could lie in the metropolitan region. After all, these materials contain valuable inorganic and organic components that may be worth extracting or transforming into higher-value products. Figure 35.2 schematically depicts how the recycling processes of the status quo could be complemented by those that enable the waste to be valorised in a more value-adding way. Such processing of waste would recapture the carbon it contains in products, thus closing the carbon cycle in a technical way. Examples of corresponding research projects in the region are presented below and explained further in Sect. 35.4.

One of the extractable inorganic substances is the plant nutrient phosphate. Because its low-cost deposits will be depleted in the foreseeable future (Cooper

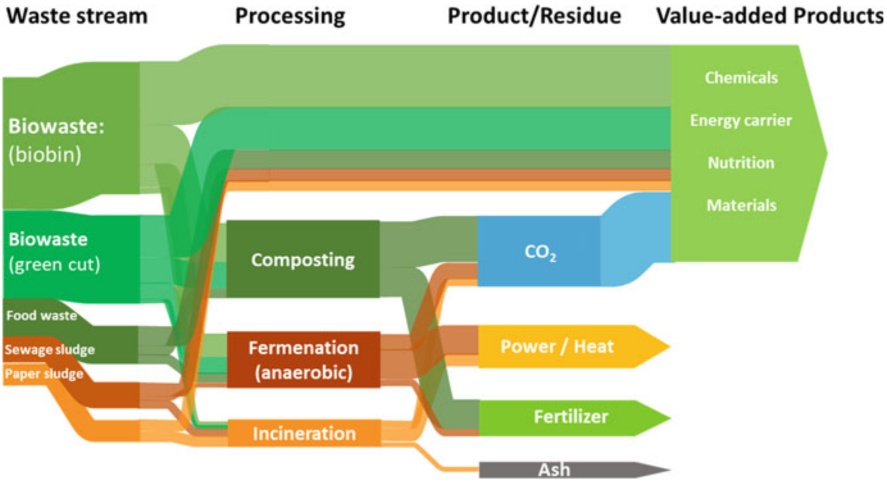

Fig. 35.2 Vision of the future utilisation of biogenic waste in the Rhine-Main Metropolitan Region (Source: Provadis Hochschule)

et al. 2011), and because the natural phosphate balance is already considered to be endangered within planetary boundaries (Sverdrup and Ragnarsdottir 2011), wastewater treatment plants of a certain size in Germany are obligated to extract phosphate from off-spec sewage sludge, which is not allowed to be spread on agricultural land because of contamination (UBA 2018), before it is incinerated. The development of a corresponding process into a phosphate fertiliser from sewage sludge is presented in Example 4.1.

The anaerobic fermentation of biogenic waste to biogas and its energetic utilisation is a standard process. However, the bio-methane contained in biogas could serve also as a feedstock for the production of basic chemicals. In this case, biogas fermentation would be a process for standardising complex wastes into methane, a product that can be further processed in many ways as a carbon source. One option is methanol, an important base chemical for the chemical industry. Interest in bio-based methanol is currently increasing as climate change mitigation calls for a raw material shift from fossil to renewable feedstocks. Example 4.2 presents the development of such a process.

Another potential carbon source generated in the course of biogas fermentation is CO_2, which is after all included in biogas with an average share of 40%. Currently, processes are being established in the metropolitan region for waxes and jet fuel that start from CO_2 (Example 4.3).

Certain plant wastes from food processing contain functionalised classes of substances that can be extracted and represent valuable starting materials for biopolymers, for example. Example 4.4. describes such a research project that recycles, among other things, cocoa nut shells.

Municipal green waste consists to a large extent of tree and shrub cuttings, i.e. lignocellulosic materials, which can also serve as a carbon source. Example 4.5 presents a project in which green waste is carbonised to produce carbon electrodes.

Considerable amounts of food waste are generated by the food industry and by end consumers, especially in metropolitan areas. It can be fed to insects. Their larvae are a high-quality source of protein that can be used, for example, as feed in aquaculture (Example 4.6). In addition, many insects contain antibiotical active peptides, in which the pharmaceutical industry is interested.

This presentation of examples of waste utilisation shows that a wide range of product and market options are possible beyond the state of the art. Phosphate addresses the fertiliser industry, methanol and jet fuel the basic chemistry and fuel sector, electrodes and polymers the apparatus engineering and chemical industry, and the transformation of waste into insect biomass opens up the feed, food and pharmaceuticals sectors. Not only the spectrum of possible applications is impressive, but also the value-added potential, because, for example, a higher added value can be expected for polymers than for compost and biogas. Because higher-value products are usually based on a longer multi-step value and process chain, the employment potential is also higher. Figure 35.3 illustrates these relationships for the examples given. Waste recycling with a higher added value therefore not only has an economic and ecological potential, but also a social one.

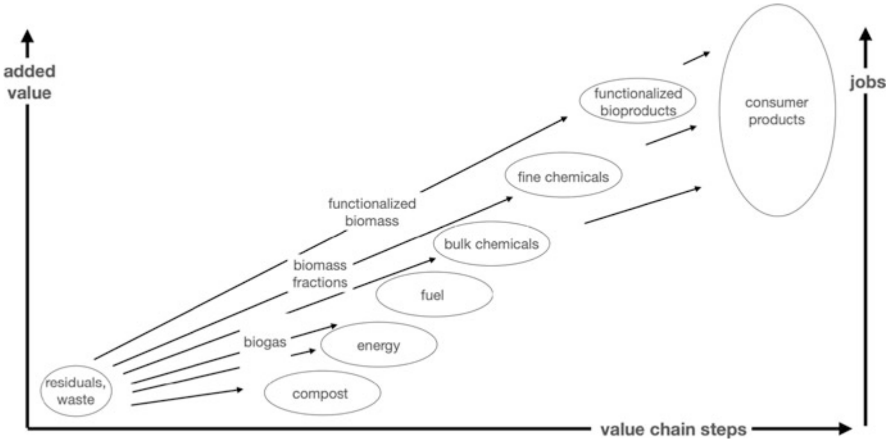

Fig. 35.3 Value and processing chain, added value, and jobs for products based on residuals and waste materials. (Source: KADIB)

35.4 Examples

35.4.1 Phosphate Recycling from Sewage Sludge

Thomas Bayer and Björn Krix

Phosphorus is an essential nutrient and building block for all humans, animals, and plants. It is used to produce fertilisers and is irreplaceable for agriculture and consequently for the supply of basic foodstuffs to the population.

Phosphorus is one of the critical raw materials and, moreover, cannot be substituted. Although sewage sludge contains an abundance of phosphorus, it often cannot be used without prior treatment due to high levels of heavy metal contamination.

Therefore, also against the background of adapted legal regulations in Germany (Sewage Sludge Ordinance), increasing efforts are being made to develop effective and sustainable implementation strategies for the recovery of the phosphorus contained in sewage sludge ash.

In the German State of Hesse, the possibility of producing a fertiliser from sewage sludge ash by adding other substances is being examined in projects funded by the European Union, the German government, and the state of Hesse.

Within the scope of the joint project RePhoRM (RePhoR 2021), a technological and organisational joint solution for phosphorus recycling in the Rhine-Main region is being developed and implemented. Based on the mono sewage sludge incineration capacity and its potential expansion in the Frankfurt-Rhine/Main metropolitan region, a cooperative phosphorus recovery from municipal and industrial sewage sludge ash is to be implemented. In accordance with the Hessian resource protection strategy, a fertiliser granulate will be produced as phosphorus recyclate, which can be used directly to close the regional nutrient cycle in agriculture. In the implementation of phosphorus recycling, it is necessary to consider the particular interests of the partners in the network with regard to the technology for phosphorus recovery and the formation of a phosphorus recycling network.

From a technological point of view, the aim is to remove heavy metals from the sewage sludge ash before the actual phosphorus recovery. The project will therefore further develop the PHOS4green technology for producing granulated fertiliser by removing heavy metals from (input) sewage sludge ash and implement the process on an industrial scale at Industrial Park Höchst. In addition to an economic and ecological analysis of phosphorus recycling, the integrated solution will be evaluated from a legal and organisational perspective.

For this purpose, laboratory tests on agronomic quality as well as planting trials on fields in Hesse are being carried out.

35.4.2 Producing Methanol from Bio-methane and Hydrogen

Thomas Bayer

Since the beginning of the last century, methanol has been produced on a large scale and used in various areas. The global demand for methanol is around 91 million tons. Approximately 99% of the methanol traded comes from fossil sources (coal and natural gas) (Methanol Institute 2019). Methanol is used primarily as a base chemical, with around 20% of the methanol traded worldwide being used for fuels and 7% to produce fuel substitutes or methanol-based blending agents such as DME (dimethyl ether) or biodiesel (Methanol Market Service Asia 2019).

The production of methanol by coal gasification and natural gas reforming has a very high degree of maturity and is suitable for the large-scale supply of methanol but produces high amounts of carbon dioxide. Production is based on synthesis gas, a mixture of carbon monoxide and hydrogen. The use of regenerative resources (e.g. solar or wind energy for electrolysis and biogenic residues to produce biogenic CO/CO_2 and sustainable hydrogen) offers a potential for sustainably produced methanol. The required carbon can be obtained from the pyrolysis of biogenic materials as carbon monoxide or via fermentation as biogas, a mixture of methane and carbon dioxide. The material use of biogas lends itself to urban centres such as the Rhine-Main region, where fermentation plants for biogenic residues already exist. The biogas obtained there can then be used materially to produce methanol. The required hydrogen can be provided by electrolysis of water with RE electricity, or as in the power-and-biogas-to-liquid (PBtL) process (Caphenia 2021), the biogas can also be used in its entirety. In this process, the methane is split into C and H_2 in a plasma (generated with RE electricity) at about 2000 °C and carbon monoxide is generated from C and CO_2 via the Boudouard reaction at about 1000 °C. The synthesis gas formed in this way can then be used to produce methanol.

35.4.3 Producing Chemicals from Bio-methane and CO_2

Thomas Bayer

Infraserv Höchst as operator of the Industrial Park Höchst, one of Europe's largest chemical and pharmaceutical sites in Frankfurt/Main, Germany had already started up its biogas plant in 2007. This plant is an optimal addition to the industrial wastewater treatment plant. A wide range of pumpable liquid and hydraulic waste can be recycled safely and efficiently. Dropping off waste at the biogas plant helps combat climate change, too: The biogas is incinerated to produce renewable electricity and steam and converted to bio-methane, as part of a waste-to-energy strategy.

This plant is one of the largest of its kind in Europe with a capacity of approx. 215,000 tonnes per annum co-substrates and a sanitisation capacity of 50,000 tonnes per annum; so, waste can be sanitised if needed. In two 30 m high digesters, each has a volume of 10,800 m^3, about 80,000 m^3 of biogas can be produced every day. The sewage sludge generated at the site is converted into biogas together with organic wastes, so-called co-substrates, from inside and outside the industrial park.

More than 100 waste codes, as defined in the German Waste List Regulation, can be processed. They include homogenised food waste from food production and pharmaceutical industry waste, food production refuse and chemical industry waste, digestible waste from biochemical processes, mother liquors or solvent mixtures, municipal and industrial sewage sludge and oil and grease trap waste and individual substances such as alcohols, glycerine and fatty acids. In contrast to many other biogas plants, no agricultural food is used. The fermentation residue of the biogas plant is dewatered and then incinerated for energy recovery in the sewage sludge incineration plant to generate steam for the companies on site.

Part of the biogas produced is used in three downstream combined heat and power plants to generate electricity and steam for the manufacturing companies in the industrial park. Since 2011 biogas is fed to a biogas upgrading plant producing up to 80 million kilowatt hours bio-methane which is fed into the public gas network. The amount is enough to supply around 4000 households with climate-friendly bio natural gas and thus reducing carbon dioxide emissions by around 16,000 tonnes per annum by substituting the consumption of fossil natural gas. A contribution to a sustainable energy supply.

As next steps into a circular economy Infraserv Höchst seek for using carbon dioxide as a raw material to produce hydrocarbons. A pilot plant producing white oils and waxes from CO_2, separated during biogas upgrading, was operated during the EU-funded project ICO2CHEM (ICO2Chem 2019) in 2021. Following this R & D project, the start-up company Ineratec (Ineratec 2017) plans to build an industrial pioneer plant for the production of up to 4.6 million litres sustainable synthetic fuels from 2022 in the Höchst industrial park, using up to 10,000 t of biogenic CO_2.

35.4.4 Novel Routes to Polymer Production Based on Glycans

Stefan Hanstein and Marcus Rose

GlyChem represents a German consortium of four research and development organisations and a global pectin producer developing a value chain for fibrous extraction residues. Partnership with a large sugar producer and a chocolate producer broadens the range of lignocellulosic feedstock comprising apple pomace, sugar beet slices and cocoa shells. The worldwide production of starch, cellulose and their derivatives as functional and structural polymers is on the same level as the bio-based rubber production, i.e. in the range of 14 Mt. (Nova Institute 2021). For both polysaccharides, market prices have dropped to 1 € per kg, demonstrating that highly efficient isolation and modification processes have been achieved. In GlyChem processes for the purification and functionalisation of industrial polysaccharides are being adapted to the production of saccharides (glycans) with a molecular weight between 1.000 and 20.000. One important target is to establish a low-cost process that provides a glycan product with a purity of 90% from a fibrous feedstock with concentrations of alkali-soluble structural sugars (hemicelluloses) below 15%. The concept for improving purity and yield is to use selective solubilisation of glycans by hot pressurised water keeping protein contamination low and to release glycans from the cellulose fraction as well (Wolf et al. 2022). For removal of smaller molecules from the extract and inherently large volumes of water, ultrafiltration is performed with state-of-the-art ceramic hollow-fibre membranes (Ebrahimi et al. 2016).

The yields of the glycan fraction from lignocellulosic feedstock can be enhanced by a partial depolymerisation based on selective catalytic hydrolysis. In conventional thermocatalytic hydrolysis using various acids in aqueous solution the major product is the respective monosaccharide, i.e. glucose in case of the historic wood saccharification process. In contrast, it has been shown that a partial decomposition towards oligomeric glycan fractions is enabled by combining the catalytic hydrolysis with significantly reduced amounts of acid and a mechanocatalytic reaction step that induced the partial hydrolysis (Jérôme et al. 2016). GlyChem optimises this process to increase the yield of the value-added glycans from various lignocellulosic feedstock.

Three glycan conversion routes covering a range of TRLs between 2 and 4 aim at bio-based coupling agents for fibre-reinforced biocomposites. Conversions will improve the solubility and dispersibility of the glycans in coating solutions and increase the reactivity in resin compositions. The solid residues of glycan extraction are used to produce C3 and C4 carboxylic acids based on extractive fermentation. The phenolic extractables from cocoa bean shells will be investigated as a source of antimicrobials for biomaterials. The elaboration of a sustainable economic concept and the evaluation of the commercial potential of the value chain for glycans and its by-products constitute an important part of the project agenda.

35.4.5 The Green Waste Biorefinery

Alexander Langsdorf, Marianne Volkmar, Roland Ulber, and Dirk Holtmann

Green waste is one of the major waste streams in urban areas, which are not recycled sustainably. In Berlin alone, about 120,000 tons of green waste are generated annually (Medick et al. 2017). The majority of green waste is currently recycled by composting and subsequent use as fertiliser or as raw material for energy production (e.g. biogas plant). The implementation of alternative recycling methods is difficult due to the strong heterogeneity of green waste. In particular, little research has been done on the material utilisation of green waste. Carbohydrates in the form of lignocellulose account for up to 60% of the biomass (Álvarez et al. 2016), making it an attractive carbon source for fermentation. For optimal utilisation of the carbohydrates, the biomass undergoes pretreatment, which serves to delignify and structurally convert cellulose and hemicellulose into monomeric sugars. In this process, the biomass is crushed, subjected to several pretreatment processes such as liquid hot water, followed by removal of toxic by-products such as furans and phenolics, and enzymatic hydrolysis to release monosaccharides for microbial fermentation. Succinic acid (Dąbkowska et al. 2019), xylitol (West 2009), or polyhydroxyalkanoates (Davis et al. 2013) have already been produced by fermentation from herbaceous biomass. Concerning the fermentative use of green waste, the combination of enzymatic hydrolysis and fermentation in a consolidated bioprocess is promising (Bokinsky et al. 2011). Through chemical conversion, levulinic acid (Girisuta et al. 2008) or furfural and HMF (Rivas et al. 2019) can be obtained. As direct extraction products, proteins, flavourings, or lignin as a by-product of pretreatment might be promising candidates. In addition, the press juice of green waste could be used as a supplement for fermentations (Boakye-Boaten et al. 2016). Another potential utilisation method is the carbonisation of green waste and its subsequent application as electrodes. Carbon electrodes can provide a low-cost alternative to conventional metal electrodes. The application of green waste electrodes in novel bioelectrochemical processes such as microbial fuel cells (MFC) or microbial electrosynthesis (MES) can contribute to a "green" economy. Yang and Chen have recently described the application of electrodes made from different biomass for use in MFCs (Yang and Chen 2020). All of the above methods for material utilisation of green waste are described in detail by Langsdorf et al. (Langsdorf et al. 2021). In summary, it is very likely that only an all-encompassing, cascade use of green waste will lead to a profitable, sustainable alternative. A potential green waste biorefinery (Fig. 35.4) could be designed as follows: First, the locally collected green waste is pressed, and valuable compounds are extracted. Afterwards, the press juice is used as feedstock for fermentation, while the solid residue is carbonised and used as electrodes in bioelectrochemical applications. After use, the "green" electrodes can be composted and used as fertiliser to close the loop.

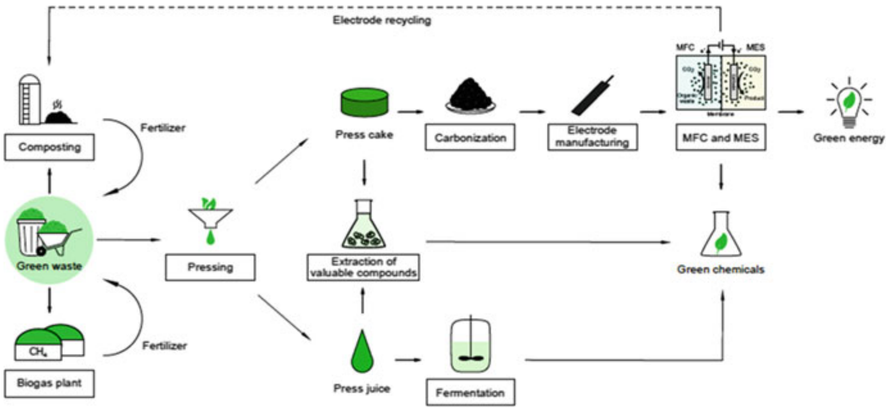

Fig. 35.4 Potential green waste biorefinery (Source: Alexander Langsdorf, Technische Hochschule Mittelhessen)

35.4.6 The Bioeconomy of Waste Biorefineries: Insects

Martin Rühl and Andreas Vilcinskas

In the European Union, seven insect species and their protein extracts are approved for industrial feeding of fish (EU Regulation 2017/893 (EC 2017)). In addition, larvae of the yellow mealworm *Tenebrio molitor* have been approved recently as novel food within the European Union. This underpins the growing demand and economic value of insects as food and feed. However, commercial rearing of insects is similar to other livestock and competitive in terms of the used feed as insects compete with conventional livestock for their food sources. In the European Union, it is not allowed to feed animal and municipal wastes to insects, even though they would grow on it. Given this background, feeding insects that have been raised on conventional feed to fish or other farm animals appear to be unsustainable and questionable. Alternative feed based on agricultural side-streams to replace the use of grain-based feed is highly needed and desired. Especially when taking into account that insect larvae can be imported from non-EU countries, whose rearing conditions are less strict. So far, most work on alternative feed has been done for the black soldier fly *Hermetia illucens* due to the fact that larvae of this species are polyphagous and can feed on diverse substrates such as manure, organic waste and side-streams from millings, breweries and agricultural industries. Industrial side-streams approved under EU regulations are generally sub-optimal for an efficient rearing when fed as sole nutrient source as shown for a lignocellulose-based side-stream (Fig. 35.5). A knowledge-based combination of different side-streams together with an improved feeding strategy can increase yields. Amongst the different nutrient parameters that have to be considered in insect rearing, the amino acid composition plays a major role when improving side-streams for insect feeding as a

Fig. 35.5 Black soldier fly larvae reared on chicken feed (top), lignocellulose-based substrate (middle) and a combination of lignocellulose-based substrates (bottom), note as the size decreases. Copyright: Fabiola Neitzel; Justus-Liebig Universität Gießen)

lack of essential amino acids results in a reduced biomass and increased rearing time. Furthermore, the feed composition has a direct influence on the larval composition, e.g. lower carbohydrate content of the feed can lead to a reduced fat content. Overall, the availability and consistency of side-streams are important for a commercial breading of insect larvae for both applications: food and feed. In this regard, local side-streams from the food industry, amongst others vegetable pomace, spent mushroom substrate, grain hulls from the milling industry or residues from the vegetable oil processing, that are available in sufficient amounts are in the spotlight of current research for the development of alternative and sustainable insect feed.

35.5 Discussion

All of the examples mentioned are projects that are currently being carried out by companies located in the metropolitan region with the participation of research institutions. Although the projects receive public funding, the companies nevertheless invest considerable resources of their own. This raises the question of the economical drivers of these developments. With the exception of phosphate extraction from sewage sludge, which is required by law, all other products are also accessible under the current framework and market conditions from conventional biogenic raw materials traded on the market in large volumes, such as sugar instead of green waste. It can also be plausibly assumed that a specified industrial raw material based on residual and waste materials, which is costly to prepare, comes with a cost handicap compared to conventional carbon sources, such as sugar from sugar cane or sugar beets. Nevertheless, companies are investing in the expansion of their raw material portfolios because they are preparing for future conditions that will be fundamentally shaped by the Paris Climate Agreement. This agreement calls for rapid reductions of fossil greenhouse emissions by 2050, to achieve a balance between anthropogenic emissions by sources and removals by sinks of greenhouse gases in the second half of this century, (UN Framework Convention on Climate Change 2015). The agreement thus forces all sectors, especially the emissions-intensive industries, to move away from fossil energy and carbon sources sooner or later. The chemical industry in the metropolitan region is also adapting to the coming raw material shift from fossil to renewable carbon sources. In principle, agriculturally produced carbon sources are suitable for industrial purposes, but even so, the industry is looking for alternatives to minimise potential land competition with food production. In addition, there is a risk that planetary boundaries, some of which are already damaged, and ecosystem services, which are already constrained, will stand in the way of increasing agricultural capacity for industrial uses (Heck et al. 2018). Given the decline in global forest cover (FAO 2020), the same is fundamentally true for wood as a raw material. In this situation, industry is increasingly turning its attention to renewable carbon sources that are available locally, that is, in the metropolitan region, and these are previously neglected residual and waste materials. The higher value-added potential is also attractive to the waste industry, to the extent that it can realise it itself. This sector is also preparing for a future change in the framework conditions such that greenhouse gas emissions from the processing of waste may be priced. In this case, processes will become attractive that do not emit the carbon contained in the waste as CO2, but instead bind it in organic chemistry products and other materials, thus closing the material cycle (Kircher 2021). This is an economically and ecologically promising option for the Rhine-Main Metropolitan Region in particular, because residual and waste materials in the densely populated region occur on comparatively limited areas in cities and at industrial sites and can be processed within a short spatial distance due to the high industrial density.

These are risks and options that a highly industrialised metropolitan region must prepare for at an early stage, because they affect the future of the business location, employment and prosperity, and not least environmental and especially climate protection. In the Rhine-Main Metropolitan Region, stakeholders from business, research and public administration have therefore organised themselves into an association called BioBall (Bioeconomy in a Metropolitan Region) in order to sensitise all stakeholders to the issue of recycling biogenic residual and waste materials, to initiate Research & Development & Innovation projects and to form consortia for their implementation. The waste management industry, municipalities and public administration have a special role to play here, because the waste management industry collects these materials and owns them, and municipalities have a stake in many of these operations and can thus exert direct influence. Another key actor is the public administration, which is responsible for the necessary adaptation of the infrastructure. For example, in the case of large-scale utilisation of CO_2, which is very energy-intensive, the supply of emission-free energy must be ensured. There are also challenges for the logistical infrastructure, because the possible raw material green waste, to give one example, has a much lower density than conventional fossil raw materials and therefore requires greater storage and transport capacities.

Circular economy is in principle not new for the chemical industry. Usage of residues from coal gas production in the early nineteenth century was the basis for a rapidly growing chemical and later pharmaceutical industry. Large sites were established using by-products from one plant in the next one as raw material, the “Verbundproduktion”. In the late twentieth century, the set out of large trusts into smaller specialised companies originated chemical and pharmaceutical parks. Their operators offer a wide range of services, in particular energy supply and waste disposal. Therefore, they are predestined to accelerate the way to a circular and sustainable economy.

35.6 Conclusion

Metropolitan regions are characterised by a high turnover of raw materials, products and waste on a comparatively limited area due to their settlement and industrial density. Manufacturing industry in industrial parks, often integrated into large cities or in close proximity to them, leads to an even more regionally concentrated turnover of industry and settlement materials. This includes raw materials for production as well as residual and waste materials from the use and disposal of products. These material turnovers are organised as multi-stage process and value chains. Today, bio-based value chains in the Rhine-Main Metropolitan Region are largely linear in design and end with waste recycling into fertiliser, heat and electricity. However, this metropolitan region with its very strong chemical industry offers the option of using the carbon of biogenic waste as a raw material for organic chemical products, for example, thus closing the carbon cycle and at the same time achieving higher added value and creating employment. This shows that industrialised metropolitan regions in particular have a special potential for closing material cycles in general and, in the case of biogenic material cycles, for realising an urban circular bioeconomy. In order to leverage this potential, it is crucial to network the actors in the targeted circular value chains and to encourage them to use their respective material flows in a value-adding manner. In this regard, the integration of waste management plays a key role.

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Chapter 36
Innovation Management on Waste Biorefineries

José Moleiro Martins, Syed Arslan Haider, João Manuel Pereira, Mário Nuno Mata, and António Abreu

Abstract Innovation management identifies the best way to create and apply new knowledge to support innovative processes. Knowledge plays an essential role in the innovation management process. Its main added value within an organizational context occurs when applied to support new processes, products, and services to satisfy market needs. Innovation under a certain complexity, uncertainty, and dynamism can only be successful if organizations pursue collaborative and innovative practices that integrate internal and external knowledge. Organizations need to determine the knowledge that will allow them to adapt to an increasingly complex, uncertain, and highly dynamic environment. The characteristics of the context to which organizations need to adapt tend to foster the replacement of known alternatives, ways of doing, and problem-solving by new and unknown ones with the potential to leverage new business opportunities and organizational performance. Based on a systemic approach, supported by secondary research, the underlying work in this chapter aims to identify the drivers of value creation within the context of waste biorefineries while bringing into perspective the determinant role of

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innovation management in the process. Additionally, the research herein, an overview of the empirical literature on creating, deploying, and disseminating biorefinery technologies is also presented.

36.1 The Current Environmental Context and Key Determinant Factors of Biorefineries

The economic development model that has marked the evolution of world economies in recent decades is now depleted, showing the inability to ensure future access and sustainable management for a set of resources that have fueled the linear economy model in which we live in. This form of economic organization representing the linear economy has become unviable for three fundamental reasons. The first is that most resources' scarcity has made their continued extraction unviable, particularly the natural resources used in the production of certain products. Most of these products end up being discarded as waste without any other utility or economic value after having fulfilled their life cycle. The impossibility of replenishing these resources highlights their scarcity as a matter of concern that requires further reflection on viable alternative solutions. The second reason is the growing increase in energy needs and the excessive dependence on fossil fuels. Besides being scarce, these resources also tend to seriously compromise climatic conditions globally, making impossible the environmental and ecological balance that is essential to the preservation of species and our ecosystem. Due to the nefarious nature of the continuous and growing increase in energy needs for this type of fuel, it is essential to consider other alternative sources of non-conventional energy, such as renewable ones. Without an alternative that promotes a better balance between the growing energy demand resulting from population growth and the new habits and needs associated with this increase, it will be difficult for societies to achieve sustainable development.

There is currently an increasing gap between environmental sustainability and economic growth (Nizami et al. 2017). This gap leads us to think that we are facing a paradox. As our economy develops through the linear model, the greater the imbalance between this current mode of development and the economic sustainability and life itself. Finally, the third and last reason is the rise of the fourth industrial revolution (industry 4.0), a term coined by Schwab (2016), and its underlying technologies. The integration of these new technologies in industrial production, namely digital, has caused significant disruptive changes in processes and the value chain. Industry 4.0 reveals a vision contrary to the one that prevails in a linear economy. At the root of this revolution is digital technology, one of the most radical changes since the first industrial revolution, highly influenced by the latest trends such as Big Data, the Internet of Things (IoT), and artificial intelligence (Niewöhner et al. 2020). This revolution currently underway is considered by several authors as one of the main drivers and catalysts of innovation, a key factor to solve some of the main issues raised by the linear economic model in place and of fundamental importance to a new era of full sustainable development. One of the merits and main contributions of Industry 4.0 and the underlying technology is improving production processes, innovation, and a greater balance between demand and supply. Companies now have more and improved knowledge of market needs and can adjust supply to demand based on that knowledge and new and innovative technologies. Therefore, it will be possible to reduce waste and the excessive use of resources through three mechanisms:

(i) A greater balance between supply and demand, with the possibility of producing in the correct measure of needs due to a greater knowledge of demand driven by the ability to collect, process, and analyze information.
(ii) Through the possibility of bringing demand, production, and delivery of products closer together in the same timeframe due to these innovative technologies and their impact on process efficiency and supply chain management.
(iii) Through the development and production of materials and products with increased and reusable life cycles, resulting from better knowledge and innovation management introduced by the underlying technologies of industry 4.0.

The devastation of our planet, by depleting our natural capital and endangering our biodiversity, through the contamination of the atmosphere and oceans to the point of eliminating their ability to absorb CO_2 (Heinberg 2018; Venkata Mohan et al. 2019) is a clear sign of our unsustainable growth. Against this backdrop of constant devastation, we must seek new models and options for societies' economic and social growth. One of the main focuses is sustainable development, which conceptually translates the idea of continuity and management of accessible resources with a search for substitutes, especially for rapidly depleting fossil-based energy reserves (Kamm and Kamm 2004).

36.1.1 The Paradigm Shift from Linear Toward a Sustainable Circular and Bioeconomy

Finding an optimal solution to our current non-renewable source of energy is another example of a window of opportunity toward the transition to a sustainable economy. The idea of a circular economy (Philp and Winickoff 2018) is considered one of its principles, and decoupling is a route forward to this economy that means that the economy can grow without simultaneous energy and resource use increase (Venkata Mohan et al. 2019). The circular economy has been subject to great attention given its aim toward a sustained growth of resource consumption and as a concept pertaining to the limitation and possible solution to environmental concerns brought forward by the opposing linear economic model currently in place. According to the Ellen Mac Arthur Foundation (2013), a circular economy is an industrial system that is invigorating or regenerative by intention and design. Unlike the linear economy, the purpose of CE is to remodel the lifecycle of a product with minimum environmental impacts at an organizational level while minimizing resource consumption and waste generation. In other words, CE is seen as an economic system that is based on the re-use and recycling of raw materials and retains natural resource resilience (Philp and Winickoff 2018).

Within the realm of a circular economy strategic objective, another form of ensuring a more sustainable economic growth is replacing fossil-based materials with biotic resources. Improving the economic condition while ensuring sustainable economic development by involving a multitude of biomass resources is the main goal of a circular Bioeconomy (D'Amato et al. 2017). According to Fernando et al. (2006), biomass is among the preferred resources to meet the challenges of sustainability while addressing environmental issues. There is no consensus in the literature regarding the definition of "bioeconomy," and as a result, various theoretical approaches and definitions are found in the literature. For some, it is defined "as set of activities in which biotechnology contributes centrally to primary production and industry" (OECD 2018, p. 14), representing a significant share of economic output.

In contrast, for others, it is perceived "as the production of renewable biological resources and the conversion of these resources and waste streams into value-added products, such as food, feed, bio-based products and bioenergy" (European Commission 2012). In essence, Bioeconomy is "the knowledge-based production and utilization of biological resources, innovative biological processes, and principles to sustainably provide goods and services across all economic sectors" (German Bioeconomy Council 2018, p. 9). The goal of the Bioeconomy is to address the issues and demands for food and energy by collaborating with researchers, stakeholders, and policymakers to apply breakthrough biological technologies. Although sustainability is assumed to be an inherent key element of a Bioeconomy, nevertheless, for some, this model is not per se necessarily sustainable. Supposedly what matters are not the crude materials incorporated alone, but also the combination of three prerequisites (Gawel et al. 2019): (a) sustainability of the resource base; (b) sustainability of both production and consumption processes and products; (c) circular processes of material fluxes. According to the literature, although the bioeconomy is mainstreamed as a circular economy, both seem to present differences in assumptions, strategies (D'Amato et al. 2017). Neither of these concepts is an integral part of each other in spite of sharing similar objectives. Bioeconomy is about the "bipolarization" of industrial value creation (Carus 2017). The approach to minimizing the carbon footprint is different in both cases. While in the circular economy the approach is to reduce the consumption of extra fossil fuels by focusing on the eco-efficiency of processes and the use of recycled carbon, in the case of the Bioeconomy the approach is to replace fossil fuels with other bio-based carbon energy, using as source economic and human activities such as agriculture, forestry, and aquatic ecosystems. It seems that while in a circular economy the main concern is to extend product lifecycle as a means of avoiding new products and, consequently, minimizing waste in return, in the case of Bioeconomy it presents an additional renewable recycling route that extends the circular economy.

36.1.2 Biorefining as a Technological Advancement and Key Driver of a Circular Bioeconomy

As mentioned previously, the transition toward a sustainable economy is mandatory, and in the process, one of the viable technological solutions is biorefining. This process involves the use of conversion platforms, also known as biorefineries (Kumar et al. 2020; Ubando et al. 2021), to convert biomass and its residues in other bioproducts, amongst others bioenergy. A fundamental aspect of biorefinery as a driver of economic growth and a net contributor to a more sustainable environment is its opportunity to reutilize by-products and transform them through various conversion technologies (Sy et al. 2018) into new value-added and environmentally sustainable bioproducts. Therefore, biorefinery is perceived as an integrative and multifunctional process in an optimized sequence to utilize every constituent of waste, to maximize the productivity for the generation of the products mentioned above (Mohan 2016) while serving as a net contributor to a more viable economy and sustainable environment.

36.2 Waste Biorefineries

Biorefineries are technological infrastructure facilities established to produce efficiently sustainable bio-based product streams (i.e., biofuels, bioenergy, biochemicals) by integrating various conversion platform technologies such as thermochemical, biochemical, combustion, and microorganism growth platforms (King and Hagan 2010; Ferreira 2017). The concept of biorefinery embraces a wide range of technologies able to separate various biomass resources into their building blocks and convert them into value-added products (Cherubini 2010). Biorefineries vary in type and complexity. In the case of waste biorefineries, the primary focus of this chapter, their difference lies in the variation and complexity of the waste/wastewater.

Social and economic growth has been achieved on account of excessive use of limited resources. In the process, a large amount of waste has been generated to the extent of jeopardizing our societies and the environment's future sustainability. A viable alternative solution to depleting these resources and the increasing degradation of our environment is to view waste as an important renewable source of energy and related by-products. According to this viewpoint, biorefinery using wastes (non-edible feedstocks and biogenic) has emerged as a viable option for the manufacture of bio-based products (Venkata Mohan 2014), such as biofuels, biogas, bioethanol, platform chemicals, biofertilizers, soil conditioners, and bioplastics (De Jong et al. 2012; Venkata Mohan et al. 2016). Therefore, waste biorefineries can create value from waste (Venkata Mohan et al. 2019), a practice usually referred to as waste valorization that involves the sustainable utilization of biowaste as inputs (Ubando et al. 2021) employed by these refineries in the production of the above-mentioned products. The technologies employed in waste biorefineries are constructed mainly on three conduits: thermochemical, physicochemical, and biochemical processes (Nizami et al. 2017). Most of these pathways and conversion technologies are mature and readily available (Ubando et al. 2020).

The literature identifies different types of waste refineries based on feedstock's origin and nature, namely agricultural, forestry, municipal or industrial waste, and aquaculture biorefinery that utilizes algae and seaweed biomass.

36.2.1 *Environmental Analysis of Waste Biorefineries*

Biorefineries will expand in developing countries to facilitate the transition from linear to circular economies, benefiting the environment and public health. Advanced and more efficient biorefinery technology will help accomplish this by shifting from fossil fuels to clean and green energy. In 2015, estimates of global emissions of human activities amounted, as carbon dioxide equivalents, to almost 47 billion metric tons of greenhouse gases (IPCC 2014). As shown in Fig. 36.1, this is a 43% rise from 1990. These are net emissions, including the impact of land use and forestry. Carbon dioxide net emissions rose by 51%, which is significant because carbon dioxide accounts for about three-quarters of overall global emissions—methane emissions raised by a minimum of 17%, with nitrous oxide emissions increasing by 24%. Fluorinated gas emissions are more than triple (WRI 2021).

Larsen et al. (2021) report that global emissions in 2019, including all six Kyoto gases, land-use and forests, and foreign bunkers, totaled 52 gigatons of CO_2 equivalent, a rise of 11.4 percent over the previous decade. China alone accounted for over 27% of total global emissions, far exceeding the second-largest emitter, the United

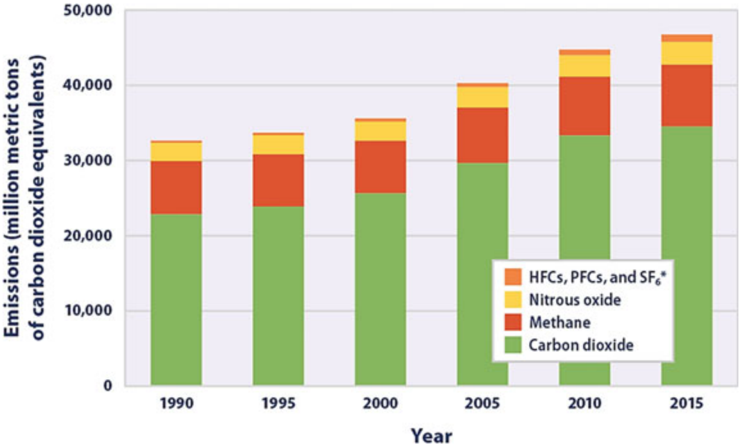

Fig. 36.1 Worldwide emissions of carbon dioxide, methane, nitrous oxide, and several fluorinated gases from 1990 to 2015

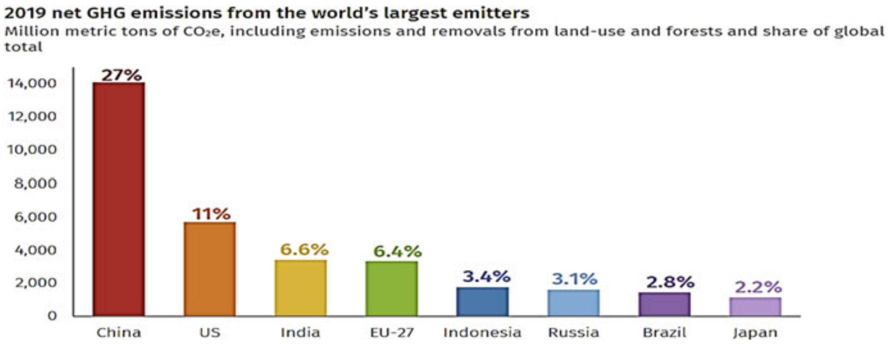

Fig. 36.2 Greenhouse gas emissions indicator based on major emitter countries for 2019—Source Rhodium Group

States (US), which contributed 11% of the worldwide total as presented in Fig. 36.2. For the first time, India edged out of the European Union (EU-27) for third place, coming in at 6.6% of global emissions.

The most important and significant environmental benefits will be reducing greenhouse gas (GHG) emissions and their adverse ecological consequences (Mohan 2016)—a GHG is a gas that absorbs and emits radiant energy in the thermal infrared spectrum, resulting in the greenhouse effect. Water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) are the main greenhouse gases in the Earth's atmosphere.

Additionally, ecological advantages include reduced waste disposal and mitigate harmful impacts on the atmosphere and public health and advanced agriculture, a range of green products, and the production of renewable energies. Waste biorefineries will save money by reducing raw materials, storage, and processing. In addition, the creation of new models and opportunities for agricultural, food, chemical, health, pharmaceutical, and logistical sectors will result in waste biorefineries in developed countries (Amulya et al. 2016).

Overall, the biorefinery produces admirably priced products and generates a gross income of €260 million. Due to intense petrochemical operations, this region has faced environmental challenges in the last few decades. The use of abundant renewable resources to produce clean energy and goods would reduce environmental pollution through biorefineries. It will also help to merge supply chains for industry and agriculture and create green jobs.

The results of the financial study are shown in Fig. 36.3 as a shared overall annual cost. The variable costs (the supply of raw material, auxiliary and operational equipment, charges in terms of disposal, and water supply) are more than fixed (write-offs, imputed interest, preservation, and insurance). This consequence is due to the enormous raw material supply required for the procedure. The cost structure of supply chains for feedstock that significantly varies between geographical locations following the cost of the supply of raw materials is a major impact on the technological performance of a lignocellulose biorefinery.

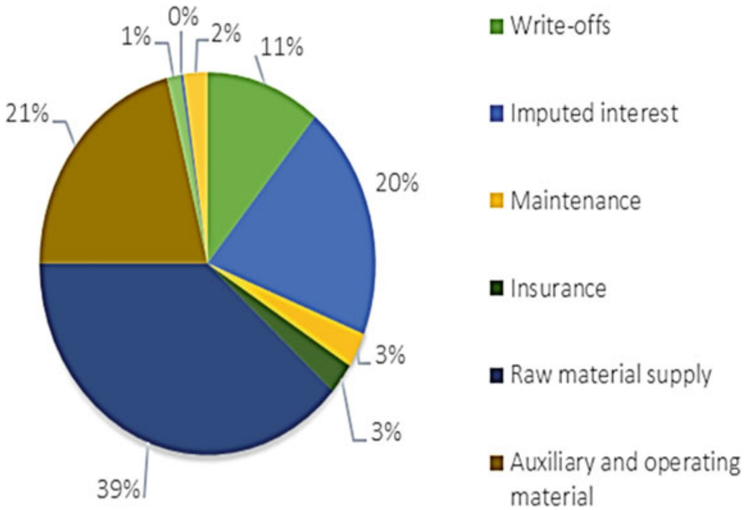

Fig. 36.3 Worldwide economic analysis

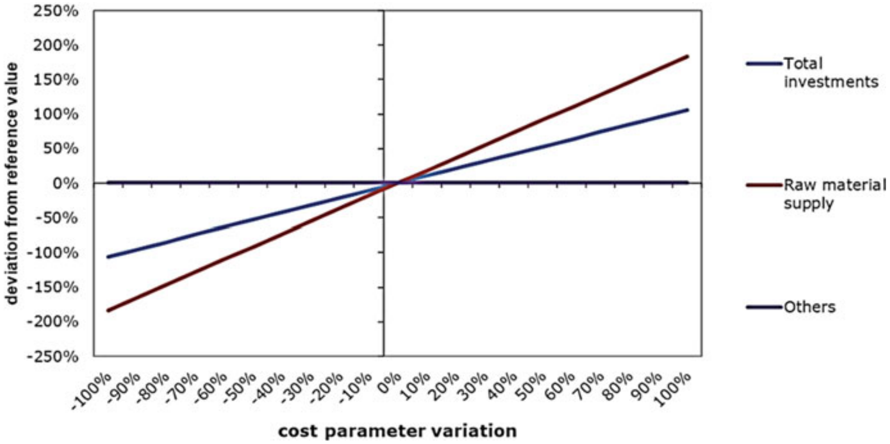

Fig. 36.4 Overall cost structure in the biorefinery

The sensitivity analysis undertaken and presented in Fig. 36.4 confirms this interpretation with variations in the cost of up to 200% depending on the input cost variation of raw material and the overall investment cost, up to 100%. Please notice that energy expenses, other costs, and operations are 0 percent decline. The self-sustaining energy supply provided by by-products inside the biorefinery has environmental and economic benefits as shown in Fig. 36.4. Due to its self-sustaining energy supply, the energy costs have no effect on the sensitivity of the global cost structure of the biorefinery.

36.2.2 Biorefinery Waste Technological and Economic Analysis

Similar techno-economic research is planned for petrol-dependent chemical refineries in residues biorefineries. In comparison to oil refining in the United States, Lynd et al. (2005) concluded that both drives have developed in small, diverse commodity producers and capital-intensive refineries that have to be managed in greater efficiency by using multiple feedstocks. However, it will take time to develop business models for biorefineries, particularly for biorefineries with lignocellulosic properties. Feedstocks, energy, capital and maintenance expenses, product usage, and consumer availability in petroleum and biomass-based refurbishments, such as pulp and paper wastes, are major techno-economic factors.

In addition to being capital-intense, many biorefinery technologies are also energy-intensive. Heat and electricity are required in large quantities in the pretreatment and purification processes and achieve the best process conditions. Many biorefinery systems, for example, are only designed for energy co-production, which means that a portion of the substrate is converted to steam and electricity to satisfy the operation's parasitic energy demands. Important additional investment in energy systems and a reduction in product yield are necessary (Hytönen and Stuart 2009; Nizami et al. 2016).

The relatively high capital investment cost of biorefinery technology is often criticized. Biochemical technologies, for instance, include long-term, low-coherence, and multifaceted biological techniques like hydrolysis and fermentation. If more lignocellulosic recalcitrant substrate, such as wood, is used instead of sugar-based raw materials, these long-term and complex problems will become much worse. As a result of these factors, the size of the machinery grows, as do the capital costs required. Furthermore, since biochemical processing processes require low, consistent requirements, separation and purification techniques add additional charges (Hytönen and Stuart 2009).

There are also major infrastructural hurdles in addition to the technological difficulties of the commercialization of advanced biorefineries. For example, these barriers are linked to the creation of innovative agricultural infrastructure for biomass assortment and storage and Waste/residue. To provide the feedstock sustainably at reasonable costs, an integrated feedstock supply system is prerequisite.

In the field, Geels (2014) describes "regime stability" as the result of active resistance by incumbent actors. Our contribution argues that this relative stability of the regime is also because the opinions of some stakeholders control certain dimensions of sustainability and exclude them. It is not so much a matter of resistance as of just partial adjustment to low-carbon societal values. Without radical changes in other elements, the main players are trying to formulate environmental tracking for biomass conversion and do not, therefore, create a deep transformation. According to Wittmayer and Schäpke (2014), profound shifts in actors' positions and their relationships with one another are essential parts of the transformation. The disconnect between technological change management, as shown by the evolution of biorefineries, and the lack of concertation processes with local stakeholders also raise concerns (Hendriks 2009). From this viewpoint, adaptation is more about influential stakeholders gradually adapting to new environmental constraints than creativity and multi-actor coevolutionary processes.

36.2.3 The Role of Technology and Innovation Management in Waste Biorefineries

In a Bioeconomy, the road to success is, to some extent, determined by the role of biorefining and, in particular, those involving the conversion of waste. However, for waste biorefineries to be effective and efficient in their role, it is mandatory to define the raw materials and altered management policies and rules vital for these conversion platforms and understand how technology and innovation can play a determinant role too. Knowledge, technology, and innovation need to be fully integrated to produce a synergetic effect in the development and exploitation of the full potential of waste biorefineries. Therefore, an interdisciplinary and cross-disciplinary approach is required to channel researchers, industry, and other relevant stakeholders toward bio-based innovations. This approach implies that researchers and industry need to be more interactive and better aligned in creating and exchanging knowledge, combined with the need for well-orchestrated research and development (R & D) focused on advanced technology development and innovation management. The term innovation management is not well defined in literature and various tasks are allocated, depending on the point of view, to innovation management (Niewöhner et al. 2020). According to Birkinshaw et al. (2008), management innovation pertains to the adoption of new management practices, processes, structures, and techniques that is new to the state of the art and is intended to further organizational goals, and that is also known to contribute the most to an organizations' competitive advantage.

Innovation as a systematic activity involving various stakeholders (Blackwell et al. 2008), also needs to be considered in the field of waste biorefineries. The focus should be particularly on the appropriate technologies and management processes for these conversion platforms to become more effective and efficient in contributing to a more sustainable economy and environment. The main drivers of innovation should be viewed from both a technology-push and market pull perspective, implying that both scientific advances and the market need to be viewed as drivers of innovation.

Waste biorefineries as drivers of a sustainable environment should be viewed as green innovations both from a technological and operations viewpoint. According to Chen et al. (2006), green innovations are hardware or software inventions relevant to green products or processes, such as energy conservation, pollution prevention, trash recycling, green product designs, or corporate environmental management. These authors divide green innovation into green product innovation and green process innovation and associate the latter with corporate competitive advantage. In a bioeconomy-related industry, green innovation management is vital to waste biorefining's determinant role, in which the key focus should be to pursue innovations with the lowest environmental impact and higher economic efficiency.

Concomitantly, it is also important to capitalize on Industry 4.0, namely the technology that has given birth to the industrial revolution on which this industry is based. These technologies include Cyber-Physical Systems that enable communication and control systems for industrial control (Zanero 2017), the Internet of Things (IoT), Big Data Analytics, and cloud computing. When integrated with IoT and machine learning, BDA can help establish smart biorefineries by generating valuable insights that can help accelerate product innovation pathways by converting intensive and costly in vivo/in vitro lab experiments to silicon simulation (Dragone et al. 2020).

36.2.4 Environmental Benefits of Other Biorefinery Products

Advances in technology show that the variety of biomass products is almost unlimited. In addition to food, feedstocks, conventional fiber products, the nutrients and biofuels, cosmetics, bulk, and sub-continuous substances, biomass feedstocks are used as a source to produce the following: foods, feeds, traditional fiber products, bio-energies and biofuels, nutrients, cosmetics, bulks, fine chemicals, and advanced materials. They are also used to manufacture the following substances. Any of the above bioproducts, such as tapestries, composites, insulation, cleaning equipment, antibody materials, industrial lubricants, and other personal care products, are already on the market. In several manufacturing stages, materials may process to produce the final products marketed.

In addition, the use and disposal of material products are generally more prolonged and more complicated, unlike the almost immediate use and disposal of biofuels. Materials may be re-used, recycled, or recycled anywhere from hours to decades until discarded (i.e., returned to the environment). Their life cycles can also be long and difficult to understand.

36.3 Biodiversity and Land Use Change

The economic and social consequences of increasing production of organic fuels (food insecurity, volatile commodity prices, poor working conditions, infringement of land rights, and an adverse Net Life Cycle of greenhouse gas emissions) and the responses they receive (Ribeiro 2013). Social learning has provided gasoline for industrial reform due to the debate (Rip 1986). The need to provide more green goods and services provided a smooth environment for creating biorefinery systems through scientific and technological development. A bio-based economy has the pledge to reduce emissions of CO_2, maintain and create new jobs, and fuel innovation through cleaner and better efficient technologies.

The production of biorefineries must be able to produce potential goods. Sustainable architecture, therefore, needs to be designed and evaluated carefully. Good assessments of the required products under various technological scenarios are necessary to this end over the next decades. There are major infrastructural obstacles to commercializing advanced biorefineries, in addition to the technological challenges. These roadblocks include, for example, the construction of new agricultural infrastructure for the production and storage of biomass and residues/waste. To provide feedstock sustainably and cost-effectively, an integrated feedstock supply system is required.

36.4 Impacts of COVID-19 Outbreak

Strong leadership, inspiration, and ambition will be needed to overcome the pandemic's challenges, not austerity. Although the COVID-19 vaccination has started, several countries have been affected by the second pandemic wave. The risk of repetitive infections and lock-up waves cannot be excluded, as the pandemic could remain until the end of 2021, creating more uncertainty for the food industry (Rowan and Laffey 2020). The specific effects of the global recession on the economy, given its particular opportunities and needs faced by emerging food-sector technologies, are unclear with any degree of confidence today. As a result, there is a greater emphasis on emerging technology to make the food sector more competitive to take advantage of the COVID-19 pandemic's opportunities (Munekata et al. 2020). The recent viewpoint on the study examines essential developments within the context of the COVID-19 pandemic and the post-lockdown period. The first developing issue is protecting the food supply chain, and cautionary measures will have to be increased while traveling from farm to gable (Rizou et al. 2020). Sustained food production COVID-19 offered challenges, for example, the clustering of food processing instances, slaughterhouses, and food production cases (Eurosurveillance 2020).

36.4.1 New Age Innovations and Disruptions

The pandemic COVID-19 has been accelerating innovation worldwide. The pattern is also reasoned as businesses that invested in the economic downturn of 2020 expanded quickly during the recession instead of only cutting costs (Weaven et al. 2021). On the other hand, it is more difficult, in hindsight downstream, to determine and predict what constitutes a disruptive technology. The foreseen food advances would be introduced during the COVID-19 pandemic period and during and after the COVID-19 century, as shown in Fig. 36.5. The chords begin during lockdowns from possible inventions and end in the post-COVID-19 periods. The more dense the

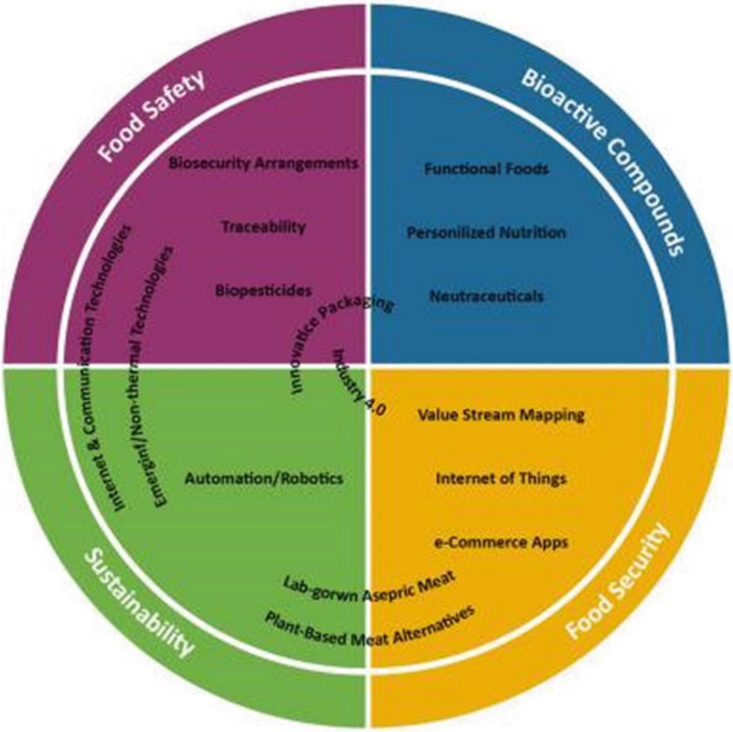

Fig. 36.5 Chord Diagrams

chords are the better the chances for advances in the modern age. In addition, the adjacent industry and digital services, which use climate modeling-related weather data, will improve these advances. Overall, the overall effects and timetables of the COVID-19 pandemic and the innovations and developments that will affect the food sector are difficult to foresee.

At present various biorefinery concepts are being developed, which display multiple phases of growth (technology maturity). Therefore, the definition itself is constantly dynamic, which is modified and leads to problems in regulating and evaluating the different purposes. Table 36.1 summarizes various biologic refinery principles, feedstocks, and the allocated TRLs (De Jong and Jungmeier 2015).

Each biorefinery concept should reliably process a number of feedstocks, produce products that are environmentally superior to their conventional components, and provide supply chains that are economically viable. In addition, government patronage from initiatives to attract the market is an essential element in deciding the form and pace of biorefinery deployment (De Jong and Jungmeier 2015).

Every biorefinery system is divided into four main types: platforms, products, feedstock, and processes (listed in order of importance). As illustrated in Table 36.2, every character has many potential subgroups.

Table 36.1 A summary of various biorefinery concepts and feedstocks

Concept	Feedstock	TRL*
Conventional biorefineries	Starch (corn, wheat, cassava), and sugar crops (sugarcane, sugar beet), wood	9
Whole crop biorefineries	Whole crop (including straw) cereals such as rye, wheat, and maize	7–8
Oleochemical biorefineries	Oil crops	7–9
Lignocellulosic feedstock biorefineries	Lignocellulosic rich biomass: e.g., straw, chaff, reed, miscanthus, wood	6–8
Green biorefineries	Wet biomass: green crops and leaves, such as grass, Lucerne and clover, sugar beet leaf	5–7
Marine biorefineries	Aquatic biomass: microalgae and macroalgae	5–6

aFederal Government of Germany (2012)

Table 36.2 Classification system features and subgroups (Cherubini et al. 2009)

Platform		C5 sugars; C6 sugars;oils; syngas; biogas; hydrgen; organic juice; lignin;
Products	Energy products	Biodiesel, bioethanol, biomethane; synthetic biofuels; electricity and heat
	Material products	Food; animal feed; fertilizer; glycerine; biomaterials; chemicals and building blocks; polymers
Feedstocks	Dedicated crops	Oil crops, marine biomass;
	Residues	Lignocellulosic residues; organics residues;
Processes	Thermochemical	Combustion; hydrothermal; pyrolysis
	Biochemical	Fermentation; anaerobic digestion;
	Chemical processes	Esterification; catalytic processes;
	Mechanical/ physical	Extraction; fiver separation; pretreatment; separation

The biorefinery classification scheme and its related elements are depicted schematically in Fig. 36.6. Task 2 established a classification and characterization system for biorefineries (Cherubini et al. 2009). The structural elements of this categorization are raw material, platform, product, and operation. It provides a standardized framework for the cataloging of biorefineries in scientific, environmental, economic, social aspects and systematic classification system. The classification system is open to extension, and procedures connect platforms to the raw materials with goods and another forum. It is probable to incorporate new product lines as well as whole platforms, for instance, if a product is to be used as the starting material for more biorefinery syntheses.

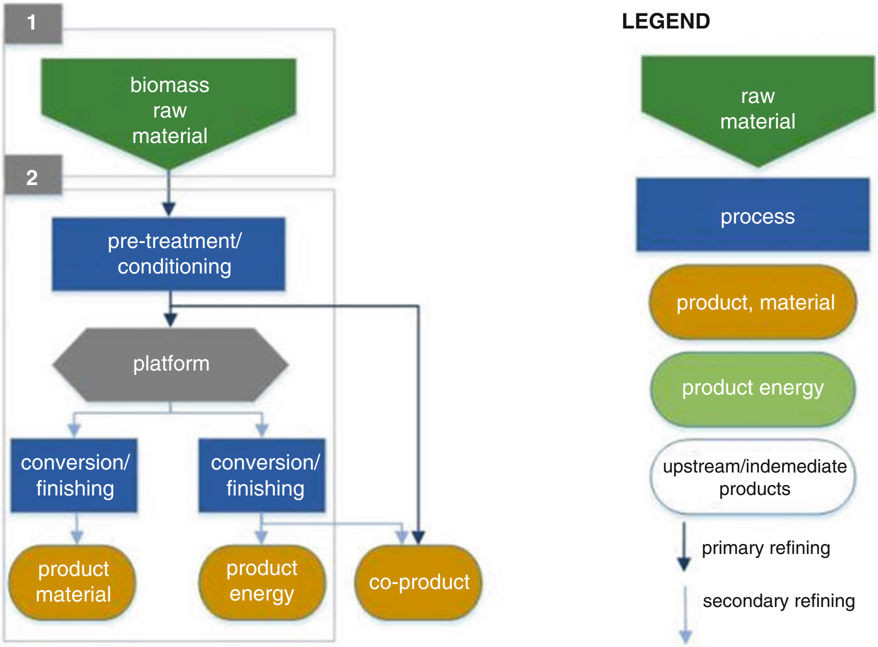

Fig. 36.6 Scheme of the classification system for biorefinery and related element

36.5 Conclusion

This literature review aims to synthesize existing knowledge on the creation, deployment, and dissemination of biorefinery technologies and at identifying actors and institutions involved in these processes. While our first main finding is based partly on the conceptual (innovation) approach, according to the studied literature, it is nevertheless crucial to note that research and experience are required to further biorefining. Due to the current emphasis on climate change mitigation, the visions for biorefinery innovations and goods have concentrated on biofuels and the bioenergy sector, which can, of course, be seen. Likewise, legislation and regulation have been essential for the development of a market for these products. Further research on how diverse welfares and actors shape the biorefinery innovation processes' material results, and how these visions and dissertations are negotiated, will be useful to provide insights into the different possible forms of biorefinery.

Waste biorefineries in developing countries are a step forward not only in terms of waste management sustainability but also in terms of generating significant economic and environmental benefits. Energy and value-added product recovery, land conservation, new markets, and market growth, and landfill cost reductions are just a few of the economic benefits. Environmental benefits include decreased GHG emissions from current disposal practices and savings in natural resources such as land, soil, groundwater, and electricity. The structural elements of this categorization are raw material, platform, product, and operation. It is based on a systematic categorization system and formal terminology and provides a coherent framework for classifying biorefineries in scientific, environmental, economic, and social aspects.

Biorefinery principles are a critical component of creating a thriving economy. Since biorefinery principles discuss some of the essential aspects of the bioeconomy plan, this is good. In closed-loop process designs, the biorefinery routes explore the critical notion of cascade-use of biomass to generate bio-based materials and energy. The paths have been investigated through a technological, economic, and environmental evaluation (TEE) method, as detailed in this work. For example, thermochemical biorefineries, digestion-based anaerobic biorefineries, and advanced (biochemically) biorefineries based on biofuels are reviewed and analyzed. Adequate biorefinery paths are selected for further TEE evaluation. Preliminary biorefinery data collected on various biorefinery set-ups was discussed and assessed through discussions with specialists. It will allow academic and industrial specialists and stakeholders to identify and select biorefineries for in-depth analysis and the subsequent creation of complete information sheets.

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Chapter 37
Incentivising Circular and Sustainable Innovations Through Patent Law

Rosa Maria Ballardini and Taina Pihlajarinne

Abstract The role of private property and ownership as well as exclusive rights, such as intellectual property rights (IPR), is often discussed in the context of incentivising developments of viable 'sustainable' innovations and practices to transit towards a more circular and sustainable future. On the one hand, IPR are important to provide the necessary incentives to innovators and businesses to move away from the traditional linear economy to a more circular one. On the other hand, IP entitlements and their interpretations, as they currently stand, do not suffice to provide the proper incentives needed to trigger the transition. This chapter addresses these shortcomings between IPR legislation and sustainability goals, via focusing in particular on one area of IPR, namely patent law. The chapter sheds light on areas where the current patent system could be further developed in order for it to better incentivise circular and more sustainable innovations and practices and pulls out several suggestions for how to trigger this change. Focus is posed on the European IP system, and concrete examples are used in particular from the biorefinery field.

37.1 Introduction

Production has until not long ago been largely based on using fossil raw materials, following a 'throwing-away' and 'always-buying-new' culture, with little emphasis on, e.g. recycling and upcycling practices. Amongst other things, this has caused serious environmental challenges. According to the EU Commission, shifting to bio-based products and processes in a sustainable way and promoting more sustainable production and consumption practices is essential to reduce the dependency of the EU on fossil raw materials like oil, coal and gas, and meet the EU ambitious

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environmental, societal, industrial and climate policy targets for 2050 (new EU Circular Economy Action Plan 2020; EU Green Deal 2019). Indeed, the development of technologies that are able to use for instance renewable raw materials or to 'transform' waste into functional products, where it is technically possible and economically feasible, is one of the key drivers for mitigating climate change and reducing depletion of natural resources.

Biorefineries implement a wide range of such types of technological innovations, holding great potential for affecting the transition towards more sustainable production and consumption practices. In this context, law and policies play a key role to provide the needed incentives for making the transition happening. Intellectual property (IP) law, a field of law that aims at fostering technological progress and creativity while also balancing societal interests, represents a very prominent tool in this respect. For example intellectual property rights (IPR), such as patents, provide legal incentives for organisations to invest R&D into technological developments, by affording inventors of such innovations with a temporary, limited monopoly right to exploit the inventions at stake. This—is believed—fosters progress in many areas of innovation, like those related to green technologies, as in the field of biorefineries. Moreover, as the patent system directs investment to certain kinds of technical inventions, it is relevant in terms of which technologies are developed and used in the market. The role of IPR becomes particularly apparent in certain areas of biorefineries that are currently facing challenges in achieving sufficient levels of commercial production with proper amounts of return on investment ratios, like biofuels. Here IPR might be essential to promote developments and secure investments in biorefineries-related technologies.

This chapter takes a broad view on the role of IPR—with focus on patent law—in relation to sustainable technologies and innovations in the field of biorefineries. In particular, the chapter focuses on key aspects of patent law under which sustainability matters arise. Emphasis is posed on issues related to the conditions of patentability. The perspective stems from the European framework, even though similar analysis and conclusions could be largely applicable also to most other (Western) patent law systems.

37.2 Intellectual Property Law and Sustainability: An Overview

Intellectual property rights are exclusive rights, giving their right owner a possibility to prohibit others from utilising the protected subject matter in certain ways. The most important forms of IP protection are patent, copyright, trademarks and industrial designs (see e.g. WTO-TRIPS Agreement for all IPR; EU Digital Single Market Directive and EU InfoSoc Directive for copyright; EU Trademark Directive and EU Design Directive for trademarks and designs; European Patent Convention for patents). However, when it comes to issues regulating technologies and technical innovations, patent law is a particularly prominent tool. Specifically, patents provide the patent owners with exclusive rights to prohibit others from utilising their invention commercially. Commercial utilisation means for example manufacturing, selling, using, or importing the invention. Patents last for 20 years after the filing date (EPC, Art. 63).

On the one hand, it could be said that promoting sustainability and sustainable development is one of the key pillars of the EU legal framework (i.e. for all fields of EU legislations). For instance, Article 11 of the Treaty on the Functioning of the European Union (TFEU) states that 'Environmental protection requirements must be integrated into the definition and implementation of the Union's policies and activities, in particular with a view to promoting sustainable development'. Indeed, this environmental integration obligation must be balanced with protection of intellectual property protection referred in Article 118 TFEU. At the same time, however, the inter-relation between patents—and IP law in general—and sustainability is not so apparent at first sight when looking at patent law legislation, as well as its current interpretations (Pihlajarinne and Ballardini 2020).

The concept of 'sustainable development' originates from the 1987 Report by the World Commission on Environment and Development (WCED), which defined it as 'development that meets the needs of the present without compromising the ability of future generations to meet their own needs'. Sustainability is a wide concept that is defined through interconnected pillars that include a wide variety of environmental, economic and social issues. For instance, the environmental pillar refers to the protection of environmental resources for present and future generations (Rodrigues 2012). Sustainability is also defined as the social foundation for humanity within 'planetary boundaries' (Rockström 2009), including core issues such as climate change and biodiversity. Moreover, concepts of 'weak' and 'strong' sustainability have been constructed: weak sustainability brings environmental concerns into existing structures and systems of business, while strong sustainability aims at integrating business into environmental systems by challenging existing structures so that industrial activities would actually fit within the capacity of the Planet (Roome 2012).

The main justifications of the current intellectual property rights system strongly rely on utilitarianism and, to some extent, also on so-called natural rights theories (Fisher 2001). Utilitarian arguments conclude that exclusive rights are necessary to create economic incentives for creativity and innovations in society, by emphasising the overall benefits derived from the intellectual property rights to the society. Exclusive rights are needed since otherwise the results of creative or innovative activities could be freely copied and utilised; such a free riding would reduce incentives for innovating. Natural rights theories, on the other hand, are based on John Locke's idea of property rights as rewards for human work, indicating that the results of a creative work or an innovative invention belong 'naturally' to the one that has made it (see e.g. Rognstad 2018; Sgaga 2018).

These theories hardly include anything that would directly address issues relating to the interface between sustainability and private rights, such as IPR. However, it is also clear that they do not preclude the possibility of taking vital societal interests such as those at the core of environmental, cultural and social sustainability into account either. On the contrary: the overall benefit for the society emphasised by utilitarianism supports the argument that sustainable welfare is a natural element of the argumentation. At the same time, however, the problem is that the concepts and doctrines of the current private law, including IPR regulation, reflect mainly the economic models (Ballardini et al. 2021), based on the developments of the first and second industrial revolutions. Production and consumption of relatively cheap mass products in Western countries, the major role of linear production and consumption models combined with unconcerns about the high demand of virgin materials, as well as overproduction and creation of waste and emissions have been the ‘business as usual’, silently assumed and supported by the current private law legislation—including the IPR system. It is clear, however, that a transition where sustainable innovations are promoted and a circular economy vision prioritised over linear models of production and consumption is needed (see e.g. IPCC Report 2021). Thus, to ensure that IPR regulation accelerates these goals instead of inhibiting them, the basic elements of IPR structures and interpretations should be re-evaluated and adapted to be in line with the principles of new types of more sustainable economic systems.

37.2.1 Patents and Biorefineries-Related Innovations: Conditions for Patentability as an Incentive for Sustainable Innovations

37.2.1.1 The European Patent Framework: Some Starting Points

Before going into issues related to patentability, it is worth spending a few words to sum up some of the key characteristics of the European patent framework.

The European patent system is a complex multilevel framework grounded on major international harmonisation processes (e.g. the WTO-TRIPS Agreement) and consisting of national patents and two centralised European nodes: the European Union (EU) node, and the one based on the European Patent Convention (EPC) (Van Zimmeren 2015). In other words, although each Member State of the European Union has their own patent offices governed by national patent laws (see for e.g. The Finnish Patent and Registration Office: https://www.prh.fi/en/index.html and the Finnish Patents Act 1967), such laws are almost entirely harmonised based on the EPC agreement and system.

The EPC entered into force on 7 October 1977. All EU members (along with some other non-EU countries) are part of the EPC, but it is to note that the EPC is an international agreement, thus not EU law. The EPC provided a solid framework for harmonising patent laws in Europe and also established the European Patent Office (EPO), which is an intergovernmental organisation (i.e. outside the institutional framework of the EU). The EPO is the primary executive actor in the EPC system, issuing and refusing EPC patents. The EPC system, however, is only a system for granting patents, as the EPO has not been equipped with a patent litigation mechanism, nor is it part of the EU judicial system. This means that once the EPO grants a patent, this is turned into a so-called bundle of rights, where patent owners will need to validate the patent in each national patent office where s/he is seeking protection. Validation is an administrative procedure that involves additional costs, such as administrative, translation and renewal feeds. Moreover, enforcement and litigation must also be done via the national route (i.e. through national courts) as at the moment, there is no centralised system for judicial review. All this adds costs and inefficiency. To solve these shortcomings, Europe has been struggling for several decades already to put forward a system that would enable also centralised validation and/or enforcement. Of the many aborted attempts, the most current proposal on the table is the so-called Unitary patent system, which aims at creating a new unitary patent, which would be valid in the participating member states of the European Union, as well as a centralised enforcement and litigation framework via a new Unified patent court (Unitary Patent agreement; see also Callens and Granata 2017; Ballardini et al. 2015). At the time of writing, however, this process is still a work in progress and it is difficult to predict when and if it will ever effectively enter into force.

Finally, it is worth mentioning that at the EU level, there is no general Directive or Regulation on patent law, but only some pieces of EU law harmonising some specific issues that had been considered by the Union as particularly important, for e.g. in the context of biotechnologies and IPR enforcement (e.g. Biotech Directive 1998; Enforcement Directive 2004).

37.2.1.2 Patentability Requirements: Perspectives from the European Framework

Generally speaking, the conditions of patentability in most patent laws are quite broad. In principle, according to Art. 52 (1) EPC any inventions in any field of technology can be patented provided they are new, inventive and industrially applicable. Moreover, the invention must be properly disclosed. In other words, issues related to sustainability play little direct role in determining whether an invention can be patented or not.

The first requirement for protection is the requirement of ‘invention’. The EPC does not provide with any positive definition of ‘invention’; however, it reveals what cannot be considered as an ‘invention’ from the perspective of European patent law. In this regard, the EPC provides both ‘exclusions’ and ‘exceptions’ to patentability. Exclusions are listed in Art. 52 (2)(3) EPC, according to which: ‘discoveries, scientific theories and mathematical methods, aesthetic creations, schemes, rules and methods for performing mental acts, playing games or doing business, and programs for computers, presentations of information as such’ are to be excluded from patentability, i.e. they are not inventions. Here the rationale is linked to policy concerns that the things listed in this provision are abstract ideas and/or fundamental concepts that should be available to all men and not restricted exclusively to none

(WIPO, SCP/15/3, Annex I). Ultimately, it is believed that providing a patent monopoly right on such fundamental ideas would stifle rather than foster technological progress (Ballardini 2012). Here it might be difficult to find any link to sustainability, especially if we look at the issue from the perspective of environmental sustainability.

More interesting, instead, are the so-called exclusions to patentability, sealed in Art 53 EPC, according to which 'European patents shall not be granted in respect of (a) inventions the commercial exploitation of which would be contrary to 'ordre public' or morality; [. . .] (b) plant or animal varieties or essentially biological processes for the production of plants or animals; [. . .] (c) methods for treatment of the human or animal body by surgery or therapy and diagnostic methods practiced on the human or animal body; [. . .]'. Here, the rationale is based on socio-economic considerations, such as the fact that allowing patenting of these types of inventions would be considered against widely accepted (European) moral values (WIPO, SCP/15/3, Annex I). So far, this provision has mostly been used in the field of biotech and gene technologies (e.g. T 1374/04 Stem cells/WARF). However, as we elaborate in Sect. 37.3 below, one can ask: is there room to expand the application and/or interpretation of this provision to also cover possible issues related to sustainable innovations?

To be patentable, an invention must also be new. According to Art. 54 of the EPC 'An invention shall be considered to be new if it does not form part of the state of the art. The state of the art shall be held to comprise everything made available to the public by means of a written or oral description, by use, or in any other way, before the date of filing of the European patent application [. . .]'. In this regard, 'state of the art' should be understood as 'state of technology', i.e. only information relevant to a field of technology is included. Moreover, the invention must be inventive. The requirement of 'inventive step' means that '[. . .] having regard to the state of the art, it is not obvious to a person skilled in the art. [. . .]' (Art. 56 of the EPC). At the EPO, the inventiveness requirement is approached using the so-called problem-and-solution-approach, which according to the current EPC Guidelines for examination, composes of the following main steps:

1. Identifying the closest prior art (i.e. the most relevant piece of prior art) and determining the difference(s) between the invention and the closest prior art.
2. Determining the technical effect brought about by the difference(s), and that define the objective technical problem (i.e., in the view of the closest prior art, the technical problem which the claimed invention addresses and solves based on reasonable expectation of success, not hope for success).
3. Examining whether or not the claimed solution to the objective technical problem would have been obvious for the skilled person in view of the state of the art in general.

As stated in the EPC Guidelines for examination 'the point is not whether the skilled person *could* have arrived at the invention by adapting or modifying the closest prior art, but whether he *would* have done so because the prior art incited him to do so in the hope of solving the objective technical problem or in expectation of some improvement or advantage' (Could/Would approach).

In sum, both in relation to novelty and inventiveness, only technical features are considered in assessing the invention, leaving apparently no room, for e.g. sustainability arguments. At the same time, however, it is interesting to note that in the context of inventiveness, an adapted version of the problem-solution approach was developed in the COMVIK decision for those applications that included claims comprising both technical and non-technical features (T 641/00 COMVIK). This is especially relevant when discussing whether issues other than technical considerations—such as, for e.g. issues related to sustainability features that are not tight to technical features of a certain invention—could play a role in assessing inventiveness. COMVIK related to the patentability of computer programmes—a field of technology where often claims include a mix of technical and not technical features. So, the difficult question about separating between technical and non-technical considerations was addressed. The conclusion, however, was that when the patent office must deal with inventions that include both technical and non-technical elements, the first step is to separate the technical from non-technical features of the invention with respect to the closest prior art. After that, only those features that contribute to the technical character are considered for inventive step purposes. In other words, this decision confirms that for the purpose of assessing inventiveness of an invention, only technical aspects should be taken into account, also in those inventions where mixed features (i.e. technical and non-technical) are included.

The invention must also be industrially applicable, that is the invention '[. . .] can be made or used in any kind of industry, including agriculture' (Art. 57 EPC). Here there does not seem to be room for specific sustainability considerations.

Finally, the invention needs to be sufficiently disclosed for the patentee to deserve the monopoly. This is the so-called sufficiency requirement sealed in Art. 83 and 84 EPC. Also in this case, it seems difficult to see how sustainability considerations could be any relevant.

All in all, from a first look at patentability requirements in European patent law, it appears that sustainability arguments do not play any (direct) role. Similar observations could be made when scrutinising most Western patent systems. At the same time, however, there could be possibility to include sustainability arguments at least in relation to assessing the requirement of 'invention' (in respect to 'exceptions' to patentability), as well as in the context of novelty and especially inventiveness of the invention.

37.3 Incentivising 'Sustainable' Innovations via IPR: How to Strike a Balance in Patent Law?

As previously mentioned, even if sustainability does not directly appear as a key principle in the patent law in Europe, it could be argued that sustainability issues could arise in specific situations related to patentability requirements. The question is whether there is the need to develop more *ad hoc* incentives inside the application or interpretation of relevant patentability requirements to promote certain desirable 'sustainable' innovations, like those related to the circular economy, as inventions in the biorefineries field.

One possibility could for instance be to look at the requirement of patentable subject matter. Here the question is whether the patent system denies (or should do so) patentability of certain overwhelmingly unsustainable technologies on grounds of *order public* or morality clauses to patentability (Art. 53 EPC presented above in Sect. 37.2.1.2), so as not to encourage investments in such technologies. In fact, the list of items presented in Art 53 EPC is not to be taken as exhaustive, while other categories could possibly be caught by the morality and public order exception to patentability. Additionally, Article 27.2 of the WTO-TRIPS Agreement specifically mentions avoiding 'serious prejudice to the environment' as one reason for such assessment, so there could be some room for sustainability arguments in the *order public* or morality assessment. Indeed the challenge relates to how to define objective criteria for making such consideration. Moreover, the issue of knowledge comes into play: patent officers are technology experts—not necessarily sustainability specialists.

One possibility would be to follow the models used in other sectors, such as in the field of biotechnologies. Therefore, the first step would be to develop legal rules to follow in order to make such an assessment—for example further develop the list of categories in Art. 53 EPC, or further develop at least the interpretation of Art. 53 via EPO case law and in the EPO Guidelines for examination (or even through national laws). Moreover, structures like those developed in some countries to deal with morality and public order concerns of biotech inventions could be considered. For example Norway had created an Ethics Committee (see Sect. 15a, cf. Sect. 25, third paragraph, of the Norwegian Patents Act) to deal with these kinds of matters. According to the Norwegian Patent Act, the Norwegian Industrial Property Office is required to consult with such a committee in cases where the Office is uncertain whether commercial exploitation of an invention is consistent with the provision regarding public order and morality based on fundamental ethical norms of Norwegian society (Sect. 1b of the Norwegian Patents Act). The use of these types of ethical committees could perhaps be helpful also to support patent offices in assessing the sustainability or not of certain inventions (see also Research Ethics and Patents 2016). Yet, several are the open questions of this type of model, spamming from the costs related to the added administrative burdens, all the way to the crucial question of who should sit on such an ethical committee and what grounds and criteria such committee members should follow in making their assessments. Indeed, these concerns are behind the reason why such ethics committees have not been very popular around Europe—with the only state implementing it being Norway. Moreover, the task of the committee is relatively limited in the end, whereas sustainability assessment could potentially cover an even wider selection of inventions, which would potentially add complexity and challenges.

In relation to the assessment of novelty and inventiveness of improvements to sustainability of products or processes, the question whether these types of inventions are novel and inventive enough in comparison to the known technologies could arise in the green technology field such as biorefineries. For instance, new, potentially more sustainable, bio-based products, such as bio-based plastics, could face challenges in terms of meeting the sufficient level of novelty or inventiveness, as the polymers themselves are often already known or the solutions obvious. This might be a problem from the point of view of incentives for these potentially more sustainable variations. Should sustainability aspects be considered while deciding on issues related to novelty and inventiveness then? For example in relation to inventiveness, would it be possible to include sustainability-related considerations in the approach currently used to assess the inventive step of the inventions? As previously mentioned, inventiveness is assessed focusing only on technical considerations. This is a core fundamental pillar of European patent law, and it would seem unrealistic to step away from this approach. However, it could perhaps be possible to develop an approach according to which, where the technical features of the inventions are tightened to sustainability improvements (e.g. reduction of CO_2, reduced use of natural resources, etc.) the level of non-obviousness required in order for the invention to meet the inventive threshold could be leveraged, when compared to inventions where sustainability benefits are either absent or negative. Indeed, in order to avoid that this type of suggestion would lead to false claims on sustainability advantages of the inventions at stake, it is important to develop clear and objective criteria for what is—or not—‘sustainable’.

In addition to trying to embed sustainability into the patentability requirements, it could be considered whether sustainability grounds could be used as further incentives in relation to the patenting process and scope. For e.g. sustainability could be a reason to justify the speeding up of patent review of certain types of inventions—like it is already done in some countries in relation to the so-called fast track of green technologies (WIPO 2013; see also the fast track system applied in Finland: https://www.prh.fi/en/patentit/applyforanationalpatentinfinland/processingofapplicationsatprh/fast-trackprocessing.html). Moreover, also the length of protection could be a tool to be tested, for instance those inventions that would be considered more ‘sustainable’ could enjoy a longer period of protection.

Indeed, one could claim that all these types of possible ‘special’ practices could go against the so-called principle of technology neutrality (also called ‘one-size-fits-all’) in patent law. Moreover, and most importantly, these practices raise questions as to what needs to be done in order for such *ad hoc* approaches to be realistic, fair and even fruitful.

The technology neutrality principle is enshrined in Art. 27 of the WTO-TRIPS Agreement, according to which patent law should have general characteristics, rather than specific technology-tailored features. This promotes statutory longevity and equal regulation of old and new technologies alike. It is believed that this principle is one of the key factors behind the patent system's success in history (Ørstavik 2021), and therefore it should be respected. Following this principle, most countries apply a technologically neutral standard of patentability in a non-discriminatory manner, regardless of the field of technology, the identity of the inventor, the place of the invention, etc. At the same time, however, it is not a secret that subjective, i.e. not neutral, policy aspects of patent law have long been part of patent law making. Patent regulation of technologies such as computer programming technologies has put out in a quite crystalline manner the need to differentiate various technological fields so as to determine exact parameters for substantive patent examination. This has indeed questioned the extent to which international patent norms are (or even should be) considering the principle of neutrality (Lee 2016; Burk and Lemley 2002). Therefore, the claim that special patent policies for better embracing sustainability would be illegitimate does not seem to hold. This is even more true when we consider that sustainability considerations could actually apply to all technology areas.

A perhaps more general problem in developing extra incentives for instance for 'sustainable inventions' is how to define them. For example the 'sustainable invention' is a concept that is dependent on the adopted goals and the phase of sustainable transition in the society. An invention that is 'sustainable' today might be deemed unsustainable tomorrow. Drawing the line between which inventions are such that they deserve special (or worse) treatment might be difficult. In a way, these challenges are also reflected in the previously mentioned ongoing efforts aiming at creating fast tracks for green patents. At the same time, however, initiatives towards further developing some standards for what 'sustainable' inventions could entail are already undergoing. For example at the International Standardisation Organisation (ISO) level a 'circularity standard' (ISO/WD 59020) is currently being developed. Once in place, these types of standards could provide solid objective criteria that could be used in the context of 'sustainable' inventions in patent law as well. Moreover, interesting perspectives on how sustainability consideration could be fed into patent law assessment, could be found by including into patenting decision-making a life-cycle assessment (LCA), or other methods of environmental assessments such Production and Process Methods (PPMs) approach. This could again be a way to provide science-based objective criteria for being able to judge on the sustainability of certain technological inventions so that such considerations could become an integer element of patent law making. Indeed, the point would not be to develop any strict definition of what is or not (a) 'sustainable' (invention) but rather to depict broad criteria and standards for inventors and (b) patent officers, but also more generally for policy makers operating in the field of IPR, as for what to take into account when asking the question what is to be considered (un)sustainable invention.

37.4 Conclusion

We are on the verge of an environmental crisis. Ecological degradation, ranging from loss of species to climate change, is rapidly spreading globally at a systemic level. Scenarios like those depicted by the so-called Anthropocene—a new epoch marred by disruptive human action on nature and its processes—convincingly point to the need for change. To reverse this trend, we need prompt action at multiple levels of society. Critically, tackling the environmental crisis calls for a radical change towards a system that prioritises ecological values and sustainability. In this transition, the legal framework could create pathways for ethically sound, yet effective, techno-socio-economic development.

Technological development and innovation impact on societies' ability to respond to the environmental crisis, both in terms of mitigation and adaptation. It is no coincidence that the Green Deal announced by the European Commission to transform the EU economy and society to a more environmentally sustainable model places deployment and development of 'sustainable' technologies in a central role. In this discourse, the role of private law regimes, such as intellectual property rights, is crucial because these legal fields regulate innovations and businesses. Thus, we need to ensure that law and policy aim at fostering rather than hindering innovations. And this requires constant scrutiny of the ethical aspects as they relate to sustainability as well.

This chapter contributed to this discussion by shedding light over the need, yet challenging task, to embed (strong) sustainability into the European IPR legislation—with emphasis on patent law. We have presented how, on the one hand, the theoretical justifications in use in the field of IP law do not preclude—albeit do not emphasise either—sustainability and private exclusive rights to come together under the same umbrella. With this in mind, the paper has contributed to the state of the art, especially by identifying new areas related to the application and interpretation of the patentability requirements where sustainability arguments could very well play a stronger role. In addition, the paper has depicted and elaborated on various possible ways for making this happening.

We acknowledge that within the current international patent system, it is probably not possible to change one single doctrine or measure in such a radical way that would make a remarkable contribution in the area of patentability and sustainability. However, adoption of several tools that could each represent a small extra incentive for 'sustainable' inventions, for instance, a combination of rejecting overwhelmingly unsustainable inventions, the consideration of sustainability for inventiveness purposes, a wider utilisation of fast track for green technologies, and an extension of protection for some very desirable sustainable inventions, as discussed in this chapter, could take patent law a step forward in the effort of considering, respecting and embedding 'strong' sustainability, this way making a key contribution in tackling unsustainable linear practices.

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Chapter 38
Industrial Economy and Technological Management in the Context of Waste Biorefineries

Ozgu Turgut

Abstract The composition of waste is very sensitive to the location or source. In general, the type of waste that can be used by biorefineries are classified into four main categories, namely food and agricultural (biomass) waste, municipal solid waste, and industrial waste. However, the optimal design and comprehensive techno-economic analysis are required for the scale-up of collecting, sorting, transportin,g and valorization processes while constructing a biorefinery system based on waste. In addition to production technologies of valorization, the surge of digital technologies will affect the way refineries are integrated into industry, and that will eventually shape total cost. The uptake of digitalization has increased the importance of operations research (OR) (ex: mathematical modelling, simulation) methodologies and all sorts of machine learning (ML) techniques through the usage of data-based decision support tools. This chapter discusses the salient economical and managerial aspects that technology management has been used in literature. From methodology point of view, the scope is bounded by OR and/or ML which comes into play for industrialisation of different types of conversions from waste to primary and secondary products. Relevant literature review is followed by a sample case study for planning transportation of feedstock, in particular food waste, for a possible refinery. The case shows how clustering and vehicle routing optimisation are used as part of a techno-economical analysis process. It concludes with the suggestions on open issues related to current constraints of practice.

38.1 Introduction

The bioeconomy concept can be understood as an economy in which "the basic building blocks for materials, chemicals and energy are derived from renewable biological resources" (McCormick and Kautto 2013). The International Energy Agency (IEA) defines: "Bio-refining is the sustainable processing of biomass into

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a spectrum of marketable bio based products (food and feed ingredients, chemicals, materials) and bioenergy (fuels, power, heat)" (Junginger et al. 2019). Increasing population and urbanisation contributes to sustainability concerns from many aspects. Biorefineries are called "vehicles of sustainable innovation" by Wellisch et al. (2010) since they have the potential to pave the way for bioeconomy. Worldwide, it is expected that more than 90% of petroleum products could be produced from renewable raw materials, and one-third of the chemicals, numerous materials, and half of the pharmaceutical market could be bio based by the year 2030 (Bünger 2010). However, only a small part of the economic activities in the European Union (11%) and the USA (5%) are based on the bioeconomy (Kuosmanen et al. 2020; National Academies of Sciences, Medicine 2020). That is, there is significant room for technical and financial improvement for the intended transition. It is possible to talk about various types of biorefineries: Organic waste feedstocks mainly consist of agricultural and forestry waste, food processing waste and effluents, sludges, yard and organic household waste. There can be proteins, sugars, lipids, fibres, vitamins and bioactive agents (antioxidants and antimicrobial agents, enzymes) among these feedstocks which are worth recovering. Also, pigments, pharmaceuticals, flavours, organic acids, biopolymers, biofuels and soil improvers can be extracted or produced through specific combinations of treatments followed by proper separation and purification procedures (Gavrilescu et al. 2015). Food waste is significant among these feedstock types and can be grouped as avoidable and unavoidable. Unavoidable waste from food manufacturing and processing systems is of interest to be used for biorefineries. This type of feedstock can be valorised into high-value functional products, through integrated and optimised systems. Biorefineries are considered as the substitute for petroleum-based systems. It should be noted that these new systems can be more efficient, flexible, and adaptable than petroleum/petrochemical systems (Sadhukhan et al. 2020). In addition, a shared infrastructure of waste/byproduct/low-value stream for industrial, municipal (household, office, and commercial settings), and public sector organisations improve environmental performance. For this reason, engineering design optimisation proficiency is a requirement for sustainable development of biorefinery systems in order to integrate with circular economy (Maranesi and De Giovanni 2020). Valorization of sustainable biomass, i.e. agricultural and forestry waste is another feedstock type for biorefineries. This conversion process has side benefits such as solving the residue disposal in addition to the other common benefits of generating renewable biofuels, creating more manufacturing jobs as well as reducing net greenhouse gas emissions. Standard biorefinery idea can be extended to an organic waste biorefinery with deeper managerial and engineered supply chain (Caldeira et al. 2020). Because waste biorefineries are likely to be more complex systems due to the variability, heterogeneity and low purity of waste materials (Alibardi et al. 2020).

The latest data published by Eurostat (2020) indicate an actual total (municipal + industrial) production potential of about 230 million tonnes/year of organic waste for EU28 in 2016, composed of ca. 42% of animal and vegetable waste, 26% of the organic fraction of municipal solid waste, 20% of wood waste and 9% of non-hazardous sludge from sewage treatment plants or food processing plants. Besides, the market targeted by waste biorefinery products has grown steadily. The global production of organic chemicals accounts for a major share of the overall chemical industry and is estimated to reach more than 300 Mtons/year, excluding fuels. The associated market was worth over USD6 billion in 2014, growing at an average rate of 8% per year from 2009 to 2014. It is expected to reach USD16 billion by 2025, at a compound annual growth rate of about 7–8% from 2019 to 2025 (Region Global Industry Analysis 2019). While biorefineries earn revenues from the sale of products, waste biorefineries can also earn income from gate fees. In the long-term, the generation of high-value products might increase the profitability, allowing for reducing or even eliminating waste gate fees (Sadhukhan et al. 2018).

Biofuels or energy carriers, soil improvers and fertilisers are the simplest outputs of a waste biorefinery which can be grouped as low-added-value products. Fractionation and separations are common phases of preprocessing at biorefineries. Parallel processing lines with a reliable supply and predictable composition become possible through waste fractionation by main chemical components. Fractionation can contain the use of enzymes and solid–liquid or membrane separation, washing and extraction, and requirements heavily dependent on the content of the waste.

The main products of the biofuels industry are fatty acid methyl esters (FAME) from wheat, barley, and sugarbeet. The chemical industry produces organic acids, amino acids, lipids, and vitamins (mainly from sugars, starch, and vegetable oils) for applications in several industries (food, feed, detergent, and cosmetics). Biorefineries started to become promising for bioplastics industry as well due to potential of producing 1,3 propanediol and succinic acid. A broader product portfolio that can be produced from tomato, potato, grape, olive and apple is supplied below as part of the case study. Caldeira et al. (2020) depicts one of the broadest valorisation pathways between food waste and industry as a chord chart.

Since the second world war, OR has spread into business, government, public services, education, defence and beyond, improving performance and helping people make evidence-based decisions.[1] Headline cover various unique approaches from mathematical modelling to simulation. With the improvements in machine learning algorithms, it is almost impossible to encounter a decision support expert who does not resort to a technique from either one of the two fields to build a state-of-art decision support tool or generate an analysis report. Accordingly, it is natural to expect that the two fields are going to increase their significance during managing and establishing the complex biorefineries systems and technologies.

In this section, we begin with a literature review on how major OR and ML techniques are used in industrial integration of biorefineries. Then we present a case focusing a region on Northwest side of Turkey for transportation planning of possible biorefineries. The section concludes with open questions and improvements points in terms of how industrial engineering tools can further contribute to waste biorefinery development.

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[1] https://www.theorsociety.com/about-or/history-of-or/

38.2 Where and How OR and AI Can Come into Play

The biorefinery feasibility is related to techno-economic parameters and their potential impact on the regional and local socioeconomic levels. According to Alibardi et al. (2020), the environmental sustainability of a waste biorefinery can be assessed by evaluating five dimensions: (1) Feedstock availability and variability since it may lead to higher proportions of rejected feedstocks that require additional disposal costs. Furthermore, feedstock composition can also be included in the dimension that will affect storage requirements. (2) Logistic issues might become crucial such as transport distance, since it can create additional need for storage capacity and various logistics costs. (3) Due to the need for complex pre-treatments, process configurations are more complex and need to be planned rigorously. (4) 'Surrounding' industrial conditions which integrates the biorefinery into waste management sectors is vital affecting many costs and profit. (5) Management of outputs such as co-products and side streams from the refinery chain are other crucial components of the value chain. In the same vein, Clauser et al. (2021) put the important aspects forward as follows: the process design, the mass, and energy integration, economic assessment, and risk and sensibility analysis. Obtaining efficient and profitable processes is closely connected to establishing and enhancing the most significant variables and parameters (Hytönen and Stuart 2011; Shahzad et al. 2017; Cristóbal et al. 2018; Bastidas-Oyanedel and Schmidt 2018; Thomassen et al. 2019; Khounani et al. 2019; Wang et al. 2020a; Padi and Chimphango 2020; D'Angelo et al. 2018; Carmona-Cabello et al. 2018; Barampouti et al. 2019; Fonseca et al. 2020). Recently, Lodato et al. (2020) developed an LCA approach specifically targeted towards integrated technologies such as (waste) biorefineries. With this study, it has been demonstrated that process efficiencies and mass, energy and substance flow within a biorefinery have subtle importance for the overall environmental performance. Producing various products and by-products to improve production costs and increase competitiveness compared to the petrochemical processes is vital to improve profitability (Zhang 2008). Similarly, in order to make the selling price of biofuels competitive with that of fossil fuels, it is also required to combine biofuel production with bioproducts that have high value and a sufficiently large market. Hence, integration of a range of different treatment processes is arising as a requirement, details of which will be shaped by the characteristics of both the waste feedstock to be exploited and the final products (Clauser et al. 2021).

In order to design the treatment train with the potential to match and buffer variations in feedstock, mixed supplies rather than a single source can be used. Seasonal flow can also be buffered using air-tight storage and preservation techniques such as ensiling or bio-drying. Combinatorial problem-solving approach will be necessary to accomplish this synthesis of these various approaches (Pyrgakis and Kokossis 2019).

Techno-economical analysis at the establishment stage can be planned to incorporate mathematical modelling while (1) organising an integrated set of suitable waste materials (i.e. feedstock) in a way to maximise the final product yield and quality (Roni et al. 2019); (2) determining the optimal capacities for the whole system. Type of the system mentioned in this context can be high-performance, multi-feedstock installations to decentralised, more specialised systems with a reduced number of platforms (Roni et al. 2019; Galanopoulos et al. 2020); (3) integrating the biorefinery with other surrounding industries to create opportunities for improved circulation of materials and energy (Caldeira et al. 2020); (4) volatility on the market side such as demands and price of products (Duan et al. 2020); (5) mitigating the impacts that the fluctuations in waste composition and characteristics can have on the array of processes adopted in a biorefinery (Matharu et al. 2016). Of the published reports in the past 2 years, 10% focused on the economics of food waste valorization (Engelberth 2020).

As mentioned before, when a waste biorefinery is compared to a conventional biorefinery an additional layer of complexity will be encountered due to the low purity of waste materials as well as variability, heterogeneity, as opposed to dedicated biomasses (Duan et al. 2020; Ubando et al. 2020; Sadhukhan and Martinez-Hernandez 2017). Low purity refers to the impurities or other undesired fractions (e.g. small plastics) that are not easily removable from the waste. In this respect one can translate sustainability assessment of a waste biorefinery to evaluating whether the use of organic waste as a starting material is less resource-demanding than the manufacturing of the same products from virgin materials (Cristóbal et al. 2018). In addition, the characteristics of final residues from complex biorefinery schemes will be different from those of traditional bioprocesses such as composting and anaerobic digestion. Hence from the environmental point of view, it should be clearly proven that simpler alternatives such as composting or anaerobic digestion have equal or less environmental benefit compared to a biorefinery (ex: Gilardino et al. 2017; Cattle et al. 2020; Sharma et al. 2019; Alvarenga et al. 2015). To this regard, ecotoxicological parameters can be used to determine more realistically the risk posed to ecosystems by complex and highly variable matrices. For these bioproducts, the approach proposed by Hennebert (2018), who suggested an array of ecotoxicological tests with aquatic and soil organisms, provides a good starting point (Hennebert 2018). In this vein, social acceptance is an important subject that should also be taken into consideration (Kokkinos et al. 2018). This should be handled both from assessing the social acceptance level as well as spending efforts in order to obtain environmentally friendly and economically feasible commercial scale biorefineries. Success of biorefineries is largely dependent on the quality and quantity of the biomass available (Dragone et al. 2020). It is possible to study these issues from the risk assessment point of view (Bai et al. 2015; Sy et al. 2018).

Supply chain analysis in biorefinery context contains generating guidance on a broad set of topics. This ranges from selecting alternative technologies at design phase, to planning required connections both from business and spatial perspectives. The technology that is economically feasible and that can be implemented within the current markets/regulations should be ensured. In this sense, many studies under supply chain planning can also be viewed as techno-economic analysis since most of the supply chain analysis models handle the system from the cost perspective. Optimisation used in biomass supply chain management includes network design, scheduling, facility location, vehicle routing and technology selection problems (Sy et al. 2018). Among others, strategic positioning of biorefineries is vital part of supply chain management. For developing and consolidating the biorefinery schemes on an industrial scale, critical factors must be identified like raw materials of the country, human resources, correct identification of future trends, world order, and value chains in the specific sector, among others (Pant et al. 2019; Housh et al. 2015).

Logistic and transportation planning can be emphasised as a separate field rather than a subcontext under supply chain management due to its deep potential, similar to many other areas. Setting up a supply chain that ensures regular collection of feedstocks and their delivery to the biorefineries is crucial. Whilst more attention is usually given to the choice of the value recovery processes and matching source and destination type of planning, the feasibility analysis for transportation options should include also the management of the supply chain (Caldeira et al. 2020; Housh et al. 2015; Pham and El-Halwagi 2012; Bai et al. 2011, 2012; Nourbakhsh et al. 2016; Marufuzzaman and Ekşioğlu 2017; Xie and Ouyang 2013; Shu et al. 2017; Martinkus et al. 2019; Chan et al. 2021).

At operational level, which can also be named as process modelling, we encounter more machine learning-related methodologies. The agro and forest industrial waste amount used for various purposes should be monitored or estimated by the governments. In addition, identifying the best ways to move on from 'one input-one output' biomass conversion processes to multi-entry and multi-output biorefinery systems depends on thorough technological planning and guidance (Wang et al. 2020b; De Clercq et al. 2020; Rall et al. 2020; Schweidtmann et al. 2018; Awudu and Zhang 2012).

Within all these studies incorporating reliable learning curves and its impact on process, improvement is also subtle in terms of generating reliable cost estimates (Hajibabai and Ouyang 2013).

38.3 Case Study: Logistics Planning for Feedstock

Food waste is elaborated based on grouping as waste and loss: Food loss often refers to the portions of the food that are lost during production steps (harvest to production and packaging) (Xiong et al. 2019). Food waste generated from growing or processing is also named as agro-industrial wastes. On the other hand, food waste refers to the portion of the food that is not used in the final food product, usually because it is an inedible portion of the food. This portion is often generated from a household or from commercial sources restaurants, cafeterias, or institutions (HORECA waste). This endeavour may require careful sorting by either the user or municipality (Abdel-Shafy and Mansour 2018). The second, i.e. 'Waste', portion of food waste is assumed to be homogeneous, continuously produced, and generated at specific points, which turns into a geographical advantage from the logistical, i.e. collecting and transporting, point of view (RedCorn et al. 2018). However,

Table 38.1 Food loss ratio for each type of food

	Tomato	Potato	Olive	Grape	Apple
Loss ratio	0.03	0.037	0.50	0.30	0.30

agricultural residues and the portion of a crop generally left on the field and considered to be of low value or limited use (Lozano and Lozano 2018).

From the economies of scale perspective, it is not unusual to expect that a biorefinery operating on both agro-industrial and commercial/residential wastes and various types of food waste would likely provide the most profit (Engelberth 2020; Cristóbal et al. 2018).

There are large scale decision support tools indicate that strategic level tools are necessary for planning biorefineries. However, they also indicate that strategic level is not enough to change the management of food waste from a grossly suboptimal level to a system that will become significant and profitable for pre-and emerging-industrial generations in a way to include valorisations of much higher value (Sheppard et al. 2020).

In light of these, a case study is presented in this section which shows logistics planning of Northwest region of Turkey for two candidate locations of biorefinery. The region is capable of supplying feedstock from various fruit types. Hence the case is focused on daily transportation of five different food as feedstock, particularly grape, apple, tomato, potato, and olive.

38.3.1 Input and Problem Definition

Tomato can be used to produce lycopene and beta-carotene. Similarly, potato can be used to produce Neochlorogenic acid, chlorogenic acid, caffeic acid, alfa-chaconine, alfa-solanine, and solanidine. Turkey's potato (1) production, (2) consumption, (3) production losses, (4) consumption losses from consumption losses in 2030 could be 5.5, 4.7, 0.094, 0.16 Mt (Melikoglu and Turkmen 2019). In addition, olive can be used to produce TPC, FAME, Squalene. Ozturk et al. (2021) state that two types of waste are formed—olive-mill wastewater (OMW) and olive pomace during olive production. According to TUIK (2017) the average amount of olives processed has been 1,030,956 tons and a total of 1,909,800 tons of waste has been produced in 1 year, including 650,000 tons of olive pomace and 1,259,800 tons of olive-mill wastewater. In addition, apple and grape are also important products of the focused area. For valorisation pathways of grape and apple, (Sirohi et al. 2020; Qin et al. 2020) can be referred respectively. However, there are not much detailed studies about the amount of available feedstock for bio-conversion in the region. Therefore 30% presented by country's fruit waste is used (Salihoglu et al. 2018). All the ratios are presented in Table 38.1. Also minimum and maximum

Table 38.2 Maximum bounds for food waste generated

	Max waste provided in kg per day				
	Tomato	Potato	Olive	Grape	Apple
Cerkezkoy	3.93	0.00	8.74	15.73	5.24
Corlu	3.93	0.00	8.74	15.73	5.24
Gebze	3.93	0.00	4.37	2.62	5.24
Silivri	3.93	0.81	8.74	78.67	28.85
Polonezkoy	5.24	0.00	0.00	0.00	0.00
Bolu	5.24	38.81	0.00	0.00	52.45
Inegol	209.79	6.47	349.65	52.45	209.79
Bandirma	104.90	0.00	17.48	52.45	262.24
Susurluk	104.90	3.23	874.13	20.98	104.90
Bozuyuk	7.87	3.23	17.48	0.00	0.00
Nallihan	10.49	1.62	0.00	52.45	26.22
Polatli	2.62	0.00	0.00	26.22	0.00
Cubuk	5.24	0.00	0.00	52.45	0.00
Sapanca	5.24	3.23	52.45	314.69	209.79
Gemlik	26.22	0.00	34.97	10.49	10.49
Izmit	0.00	0.00	0.00	0.00	0.00
Kirikkale	0.00	0.00	0.00	0.00	0.00

waste supply calculated from city-based values of TUIK[2] are provided in Tables 38.2 and 38.3.

Fifteen waste suppliers in the region are identified to supply the waste from these five food types. Within focused area, there are two petrol refineries. These locations are chosen to be the best candidates for building new biorefineries. These two biorefineries can process feedstock coming from waste suppliers, which are assumed to be located outside city centre. In this setting, we collect food waste from tomato, potato, olive, grape and apple from suppliers and ship them to the destination. The destinations can be considered either directly as biorefineries or some type of sorting stations where different types of feedstock collected, sorted and pre-processed. It is assumed the collection process starts at 8:00 AM in the morning and has to be delivered by 3:00 PM to the destinations daily. Hence the vehicle routing and delivery have some time windows to obey. The aim of whole technical process is to come up with reliable approximations to daily delivery amount, routes for feedstock collection and overall logistic costs.

38.3.2 Vehicle Routing Process and Optimisation Model

After identifying the best set of providers for each biorefinery, we optimise in order to find the best truck routes that satisfy the delivery windows. Then we build a

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[2] https://www.tuik.gov.tr/

Table 38.3 Minimum bounds for food waste generated

	Min waste provided in kg per day				
	Tomato	Potato	Olive	Grape	Apple
Cerkezkoy	0.39	0.00	4.37	6.56	2.62
Corlu	0.39	0.00	4.37	6.56	2.62
Gebze	0.39	0.00	2.19	1.31	2.62
Silivri	0.39	0.16	4.37	52.45	14.42
Polonezkoy	0.52	0.00	0.00	0.00	0.00
Bolu	0.52	25.87	0.00	0.00	10.49
Inegol	104.90	3.23	262.24	20.98	157.34
Bandirma	52.45	0.00	8.74	20.98	209.79
Susurluk	52.45	0.65	786.71	10.49	52.45
Bozuyuk	7.87	0.65	8.74	0.00	0.00
Nallihan	5.24	0.32	0.00	26.22	5.24
Polatli	0.26	0.00	0.00	10.49	0.00
Cubuk	0.52	0.00	0.00	20.98	0.00
Sapanca	0.52	0.65	26.22	209.79	104.90
Gemlik	11.01	0.00	17.48	5.24	5.24
Izmit	0.00	0.00	0.00	0.00	0.00
Kirikkale	0.00	0.00	0.00	0.00	0.00

mathematical model that tries to minimise total truck cost, which takes the predetermined routes as input. In the first stage of this phase, two algorithms are used. The first one generates feasible routes. The second set of code is the mathematical model which optimises in order to select the best set of routes generated by the first algorithm. In the first algorithm, the feasibility rules that are used for elimination are as follows:

- Total travel time should obey time windows for delivery, i.e. total travel time at each node cannot exceed 7 h in total. Total travel time is calculated as the sum of time spent between each stop (i.e. biorefinery or waste provider) plus assumed dwell time of half an hour at each stop.
- Total weight collected from each stop should not exceed truck capacity.

This first step algorithm works using random supply amounts generated uniformly between the bounds presented in Tables 38.2 and 38.3.

Then we feed the list of routes as input to the following mathematical model.

$$\text{fixedTruckCost} \cdot \text{maxTruck} + \sum_{r \in 7\text{ER}} y_r \cdot \text{totalDistance}_r \cdot \text{unitTruckCost} \tag{38.1}$$

$$\begin{gathered} y_r \geq 1 \qquad \forall \mathrm{ws} \in \mathrm{WS} \\ r \in \mathrm{7ER}, \quad (r, \quad \mathrm{wB}) \in \mathrm{RZ\pi\pi e\,V}) \int)\pi \int \nabla \end{gathered} \tag{38.2}$$

$$\begin{gathered} y_r \leq \mathrm{maxTruck} \\ r \in \mathrm{7ER} \end{gathered} \tag{38.3}$$

where FER and WS represent two sets for feasible routes and waste providers, respectively. Main decision variable is the binary y_r defined r. It takes value one if the corresponding route is selected. In addition, there is a set of sets named $\mathrm{RouteVisits}_r$ defined for all routes, which contains the waste providers, i.e. nodes, visited by each route. maxTruck is a dummy variable to track the total number of routes selected.

In this model objective function tries to minimise the cost of transportation and has two pieces. First one accounts for the fixed portion of the cost and the second one is to include distance-based cost. Then Eq. (38.2) ensures all waste suppliers are visited and Eq. (38.3) is just to set the relation between binaries and the maxTruck variable.

38.3.3 Clustering for Dispatching

The analysis indicated that few large plants would be the most profitable scenario as this allows for concentrated production, takes advantage of economies of scale, and simplifies transport logistics (Cristóbal et al. 2018).

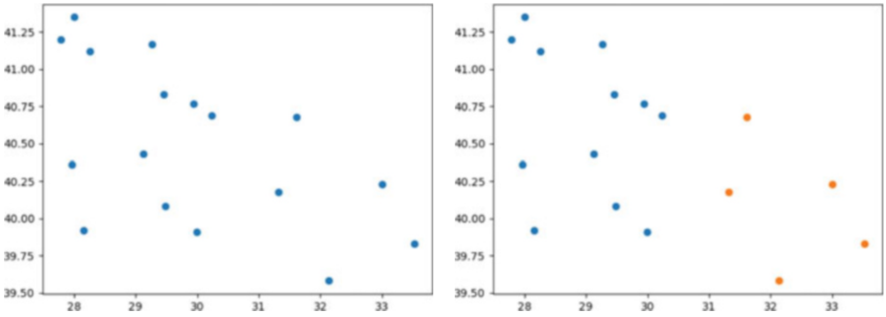
At this stage of the process, food waste providers are clustered into two in order to determine best set of providers for each candidate biorefinery site. Here *BIRCH* implementation of '*sklearn*' is used. Following figures shows the initial distribution and the resultant clusters on a *matplotlib* scatter graph (Fig. 38.1) (Pedregosa et al. 2011).

The clusters are formed according to their proximity on the coordinate axis. Number of clusters are determined based on the available candidate locations for biorefineries which is two.

38.3.4 Results and Analysis

When we run the vehicle routing optimisation process for each cluster, six routes for cluster 1 and one route for cluster 2 are generated (Fig. 38.2).

It should be noted that without clustering time spent in the first step of vehicle routing, i.e. generating feasible routes takes more than 40 h. However, after clustering the waste providers together with candidate biorefinery sites and vehicle routing



(a) Scatter for all locations (b) BIRCH clusters

Fig. 38.1 How food waste providers are scattered in terms of coordinates and how they are classified. (**a**) Scatter for all locations, (**b**) BIRCH clusters

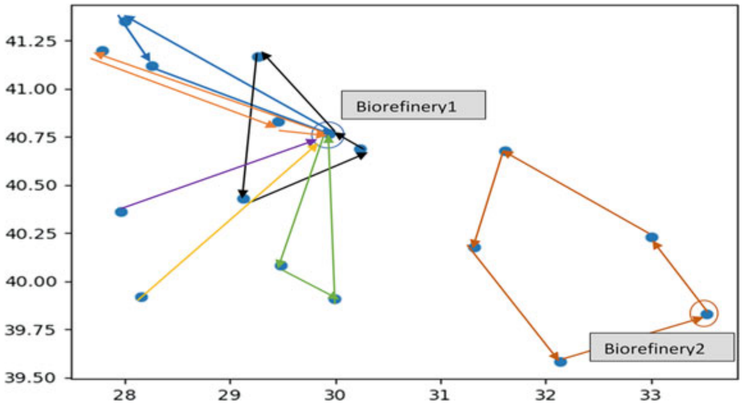


Fig. 38.2 Resultant routes for each cluster

process finishes within minutes and generates as good results for each cluster as the un-clustered version.

When we look at the carried amounts, it is possible to derive a conclusion also about the approximate capacity required for all routes. That is, none of the routes carries more than 1.7 ton daily on average. Hence any company who follows the dedicated route can offer partial load, which might lead to reduced costs; i.e. a dedicated fleet is not required.

It is possible to use this scheme for many other analysis. Here is a realistic variation on the problem setting: Consider the situation where the logistics service provider comes with a time limit. Their claim is truck drivers work for only 5 h in a day, but in two shifts. This translates into a modification requirement for the first step of vehicle routing. Specifically in the algorithm that generates feasible routes for mathematical model, the total travel time rule should be reduced to 300 from 420 min. Then resultant routes can be scheduled in different shifts based on the

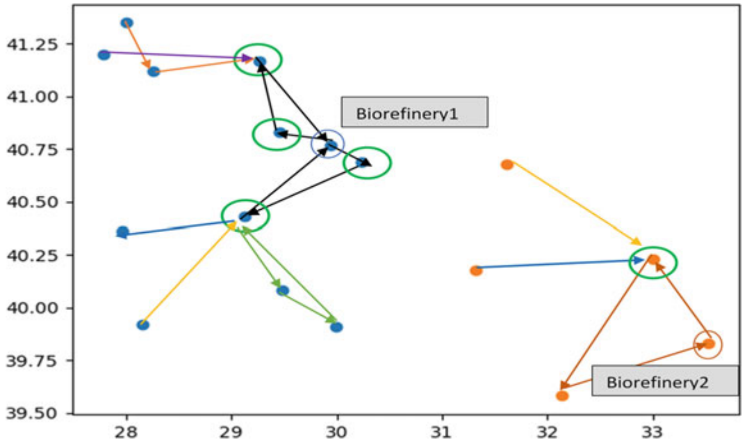


Fig. 38.3 Resultant routes for two echelon

availability. If the distances do not allow for some points to be serviced within 5 h for some nodes, then points that can be serviced in 5 h are chosen as consolidation points. Then the programme is run second time, this time to identify the best routes to connect the consolidation points to the distant nodes with another set of trucks. Figure 38.3 shows the results of this analysis for the relevant setting. In this figure, seven routes to serve Biorefinery1 and three routes to serve Biorefinery2 are needed.

It is observed that four nodes in the first cluster and two nodes in the second cluster are reachable from the biorefineries as the result of the first run within 5 h. They are marked with green circles. Then these nodes are fed to the vehicle routing algorithm as origins in the second run, and the best routes to reach the remaining ones from these nodes are generated. Hence the network is converted into a two echelon in order not to violate 5-h-service time constraint of the logistics company.

Without doubt, this solution is built on the assumption that the intermediate nodes which are reachable within 5 h are willing to act as consolidation nodes. As the result, total number of routes increased by one in the first cluster and two in the second cluster. None of them carrying more than 1.5 tons daily.

38.4 Concluding Remarks and Open Issues

The analysis of Bauer (Bauer 2018) shows that the studies in literature which lie at the intersection of technology management and waste biorefineries are serving basically in three ways: the significance of different kinds of products; the importance of generating new or applying current knowledge, the need for a comprehensive agenda of state interventions to support a transition towards a bioeconomy. They conclude that pathways to very different bioeconomies are indeed open, but policy should remain attentive to the existing conflicts and not presume consensus among actors who claim to support innovation for a bioeconomy. There are currently weaknesses in the innovation system related to fragmented and coordinated policies, especially regarding other biorefinery products than biofuels (Hellsmark et al. 2016; Hellsmark and Söderholm 2017) and that significant challenges regarding capacity building and collaboration remain to be solved (Palgan and McCormick 2016).

Holistic OR models can help to communicate the benefits, integrate complex systems and support robust decision making at any stage of this route.

The literature summary presented in this study shows clearly that OR and ML communities have great interest in the topic as well as their proven potential to improve decision support process. Afterwards a sample case study is supplied with novel data and analysis in order to prove how problems of waste biorefineries lends itself to OR and ML methodologies naturally. This case study focuses on specifically transportation side of the system using a clustering integrated vehicle routing approach.

In line with this, city logistics and challenges related to transportation and distribution in urban areas have received a huge interest lately. While extending the supply network of waste, it is an inevitable barrier to overcome where OR and ML techniques can come into play with significant contribution.

For all the major supply chain planning and analysis studies and even for techno-economic analysis, volatility at various levels of the new biorefinery systems should be taken into account. In addition to data-based tools, stochastic modelling techniques can play an important role in terms of identifying risks as well as planning in a robust manner in the future.

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Chapter 39
Techno-economic Aspects and Circular Economy of Waste Biorefineries

Raquel M. Balanay, Rowena P. Varela, Anthony B. Halog, and Rey Y. Capangpangan

Abstract Biorefineries mushroomed in the late twentieth century to generate biofuels in the pursuit of environment-friendly solutions to industrialization. Biomass from many crop species can be converted into biofuels using the advanced technologies in biorefinery. However, most species used as bioenergy sources are grown massively for food and feed. The food security goal may be compromised as a consequence of the food/feed and bioenergy competition. Technologies in utilizing wastes from processing food crops into sugar, oil, flour, and other food products into biofuel have proliferated in recent years. These technologies can provide solutions to the competing demands for food and biofuel. The integration of green chemistry into biorefineries, and the use of low environmental impact technologies by recycling food-processing wastes are keys to the efficient production of biofuels and high-value chemicals, which can encourage circular economy and sustainability. This chapter describes the technical and economic aspects of waste biorefineries, focusing on the integration of green chemistry and valorization of innovative products from the various forms of waste generated. Understanding the entire food production and waste generation chains and the technological aspects in valuing the wastes for economic goal would consequently develop a circular economy for biowaste refineries.

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39.1 Introduction

The search for sustainable approaches in generating biofuels and bio-based products (e.g., food, chemicals, feeds) has been on the rise since the turn of the century. Biorefineries mushroomed to generate biofuels and other industrial products in the pursuit of environment-friendly solutions to industrialization. The targets of biorefineries are to supply the global requirements for biofuels, provide integral components for the production of innovative materials with disruptive features, creation of enterprises, valorization of wastes, and reduce greenhouse gas (GHG) emissions. The growing importance of biorefineries has made countries around the globe to actively pursue business in biorefineries. Marketwatch (2021) released that the global biorefinery market size is projected to reach USD52,680 million by 2027, from USD45,370 million in 2020, at a CAGR of 2.2% during 2021–2027. This covers the key players in North America (United States, Canada, and Mexico), Europe (Germany, UK, France, Italy, Russia, and Turkey), Asia-Pacific (China, Japan, Korea, India, Australia, Indonesia, Thailand, Philippines, Malaysia, and Vietnam), South America (Brazil, Argentina, Columbia), and the Middle East and Africa (Saudi Arabia, UAE, Egypt, Nigeria, and South Africa).

In biorefineries, technological and economic aspects are important considerations. Nonetheless, in spite of the significance of these two key aspects, the social and environmental dimensions are also critical considerations for sustainability. The governmental and stakeholder supports for green materials and chemicals and for bioenergy are also important factors for the biorefineries development. Technologies in converting agri-food wastes into biofuel have proliferated in recent years. These technologies can provide solutions to the competing demands for food and biofuel. The integration of green chemistry into biorefineries and the use of low environmental impact technologies by recycling food-processing wastes are keys to the efficient production of biofuels and high-value chemicals, which can encourage circular economy and sustainability. Green chemistry as a technology in the biorefinery industry has been promoted across decades (Morais and Bogel-Lukasik 2013; Clark et al. 2006, 2012; Clark 2007). Although present technologies in biorefinery have resulted to economic benefits, more researches are needed to make biorefinery as an approach towards sustainability. De Albuquerque et al. (2019), for instance, concluded that the application of knowledge acquired from the cutting-edge researches is necessary to consolidate the lignin use in an integrated process in biorefinery.

Techno-economic assessment (TEA) is also indispensable in evaluating the technologies applied in biorefinery, including the economic and ecological aspects. TEA research has been developed to provide information about the performance of the biorefinery concept. In recent years, more TEAs have been conducted to evaluate the performance of biorefinery. Studies related to TEA have been done for glycerol biorefinery (D’Angelo et al. 2018); food waste biorefinery (Bastidas-Oyanedel and Schmidt 2018); mango processing waste refinery (Arora et al. 2018a, b); corn stover-ethanol biorefinery (Bbosa et al. 2018). Recently, Liu et al. (2021) reviewed the waste biorefinery development towards a circular economy. Likewise, Ubando et al. (2020) made a comprehensive review of biorefineries in circular bioeconomy. More information related to the technology and economic scenario analysis along the circular economy concepts for waste biorefinery may give new inputs for policy directions, particularly in the developing countries.

39.2 Policy and Issues Associated with Biorefinery

Biorefineries are important in the pursuit of biofuels development and bioenergy upscaling for numerous reasons. Having biorefineries for the conversion of biomass into bioenergy is a crucial decision as it indicates a determined action towards securing a future with reliable production of renewable energy consistent with the Sustainable Development Goal 7 (Affordable and Clean Energy) (Kumar and Verma 2020; Noh et al. 2016; Ubando et al. 2020). However, over the recent period, bioenergy and biofuel are at the crossroads in terms of the ways forward, because of the confusing outcomes resulting from energy choice. There are conflicting outcomes between food, feed, and bioenergy and environmental repercussions to include contamination of water sources and biodiversity problems that can eventually lead to environmental degradation (Giri et al. 2016; Ubando et al. 2020). Countries have mobilized various R & D programs to document observed phenomena for critical decision-making, making the bioenergy option a highly-political and economic matter.

Renewable bioenergy and its logistical requirements (e.g., biorefineries) induce structural changes whose repercussions to society and the environment take shape in gradual terms, thus, taking antiquated research and development findings to the fore ensures that associated uncertainties are cautiously dealt with considering the optimal balance of a nation's welfare objectives (Kurian et al. 2013; Pradhan and Mbohwa 2014; Ullah et al. 2015; Ozturk et al. 2017). The keenness of the optimal balance that developed and developing countries have mostly embarked in-depth studies to explore more viable sources and outcomes of providing support facilities and logistics (e.g., biorefineries) to induce the gradual shift to renewable energy sources (Katakojwala et al. 2019; Bhuyan et al. 2020; Ozturk et al. 2017). The works of Pattanaik et al. (2019) for India regarding the valorization of agricultural wastes for biofuel production demonstrated this, Vian et al. (2018) in exploring sugar and energy linkages for future bioenergy policy actions, and Pierossi and Bertolani (2018) in accounting the agricultural and logistics issues with biorefineries for sugarcane waste feedstock in Brazil. These bioenergy efforts are global spanning across several continents to examine the viability towards bioenergy shifts for a sustainable future (Noh et al. 2016; Giri et al. 2016; Tapia et al. 2019; Awasthi et al. 2020).

The Philippines' bioenergy initiatives are enshrined in its two landmark legislations-Republic Act (RA) 9367 (The Biofuels Act of 2006) and Republic Act (RA) 9513 (The Renewable Energy Act of 2008) (Rosellon 2017). The key features of these two laws promoting renewable energy through biofuels and other sources are showcased in the table below (Table 39.1). Upon the signing of the second law (RA 9513), the country already progressed to become the second-largest producer of geothermal energy in the world after the US and the first Southeast Asian country to have a commercial wind farm and a grid-connected solar photovoltaic power plant (Corpuz 2017). However, the progress of the country on its biofuel pursuit had plateaued, particularly in increasing the blending rate of biofuel with its current fuel products (Corpuz 2017). The main reason lies with the production capacity not capable to outpace demand in the country (Rosellon 2017; Corpuz 2017), although other issues have contributed to the deceleration of achievements towards biofuel production and consumption, particularly towards increasing the blending rate of biofuels in the country.

The economic reasons for the observed slowdown are associated with the production aspect, such as high production cost, low productivity, and lack of production capacity of the current distilleries-making importation much cheaper than in-country production for the Philippines (Rosellon 2017; Corpuz 2017). Rosellon (2017) examined the debate on renewable energy, particularly biofuels in the country, looking at the barriers causing the slowdown on the aggressiveness of the Philippines towards the national advocacy of biofuels and renewable energy. On the issue of capital intensiveness of developing biofuels and other renewable energy sources, Rosellon (2017) suggested to continue the search for innovative strategies to reduce the production cost requirements in biofuels and renewable energy production and to continue supporting the key players in tax incentives and business process facilitation. The academia continually undertakes R & D support on this in partnership with the Department of Energy and other relevant organizations. The works of Sy et al. (2018), Ubando et al. (2020), and Benjamin et al. (2020) on the biorefinery development in the Philippines, focused into the optimal design of an integrated biorefinery, explored on biorefineries in support to the development of a circular bioeconomy, and analyzed for the risk and resilience potentials of integrated biorefineries, respectively.

39.3 The Biomass Supply Chain in the Philippines

The Philippines is determined to pursue a low-carbon national economic development with its aggressive steps towards securing significant progress in the production and consumption of renewable clean energy sources, of which biomass is a critical component (DOE 2017a). The country aims to secure bioenergy from indigenous sources over the next two decades until 2040 (DOE 2017a). The latest statistics of bioenergy projects in the country shows tremendous increase in the number of projects since the country decided to go forward with bioenergy in 2008, indicating biomass projects at 67 (grid: 45; own-use: 22) with potential energy of around 326 MW as well as biofuel projects at 21 (up by 5 from 2014 to 2016; broken down into 11 for biodiesel with a total annual capacity of 584.9 million liters and

Table 39.1 The key features of the renewable energy/bioenergy laws in the Philippines (Source: Rosellon 2017)

Republic Act title	Key features
Biofuels Act of 2006 (RA 9367)	• Mandatory use of biofuels. All liquid fuels for motors and engines sold in the country shall contain locally sourced biofuels components, following the mandated proportion or blend. The initial mandated blend is a minimum of 2% by volume for biodiesel and 5% for bioethanol. • Phasing out of the use of harmful gasoline additives and/or oxygenates. • Fiscal incentives: zero specific tax on local/imported biofuels component per liter of volume; value-added tax rate (VAT) exemption for sale of raw materials used in the production of biofuel • Exemption from wastewater charges (under the Clean Water Act) for all water effluents as they are considered "reuse." • Financial assistance: Government financial institutions (GFIs) will extend financing with high priority to Filipino citizens or entities (at least 60% Filipino-owned shares) involved in biofuel activities from production to transport, including blending of biofuels with petroleum. • Creation of the National Biofuel Board (NBB) to monitor the implementation of the National Biofuels Program; provide recommendations to the DOE on matters concerning biofuels and biofuel blends. • Security of domestic sugar and feedstock supply. The Sugar Regulatory Authority (SRA) will formulate guidelines in ensuring sufficient supply of sugar to meet the domestic demand and stable price of sugar. • Security of domestic biofuels feedstock supply. The Department of Agriculture (DA) will ensure reliable supply of biofuel feedstocks. • Development of a social amelioration and welfare program for workers in the production of biofuels. • One-stop Shop is created for processing applications for feedstock production, biofuels, and biofuel blends production and distribution.
Renewable Energy Act of 2008 (RA 9513)	• Renewable Portfolio Standards (RPS), which is set by the National Renewable Energy Board (NREB). • Feed-in Tariff (FiT) System—for electricity produced from wind, solar, ocean, run-of-river hydropower and biomass. The Energy Regulatory Commission (ERC) will formulate the FiT rules and set the FiT rates • Renewable Energy Market (REM), which will be operated under the Wholesale Electricity Spot Market (WESM). A Renewable Energy Registrar will be established by the Philippine Electricity Market Corporation (PEMC) that issue, keep and verify RE certificates used for compliance with the RPS. • Green Energy Option program that provides end-users the option to choose RE resources as their source of energy. • Net Metering agreements with qualified end-users who will be installing the renewable energy system.

(continued)

Table 39.1 (continued)

Republic Act title	Key features
	• Fiscal incentives: income tax holiday; duty-free importation of renewable energy machinery, equipment and materials; special realty tax rates on equipment and machinery; net operating loss carry-over; accelerated depreciation; zero percent VAT; cash incentive of renewable energy developers for missionary electrification; tax exemption of carbon credits; tax credit on domestic capital equipment and services. • Exemption from universal charge for renewable power and electricity generated for the generator's own consumption and/or for free distribution in the off-grid areas. • Fiscal incentives for farmers engaged in plantation of biomass resources. • Fiscal incentive for end-users in renewable energy system hosts communities/LGUs whose monthly electricity consumption does not exceed 100 kWh. • Financial assistance: GFIs will provide preferential financial packages for the development, utilization, and commercialization of RE projects (with endorsement from DOE). • Creation of the Renewable Energy Management Bureau (REMB) under DOE to develop, formulate and implement policies, plans, and programs to accelerate the development, utilization, and commercialization of renewable energy resources and technologies; develop and maintain a database; conduct technical and impact studies; information, education, and communication services. • Creation of the National Renewable Energy Board (NREB), assisted by a technical secretariat from the REMB. The NREB is primarily tasked to recommend policies to DOE and monitor the implementation of the Renewable Energy Act. • Renewable Energy Trust Fund to enhance the development and greater utilization of renewable energy.

10 for bioethanol with a total annual capacity of 282.1 million liters) (DOE 2017b). The establishment of biomass plants has already covered Luzon, Visayas and Mindanao (DOE 2020).

The Philippines' Department of Energy (DOE) has also recognized the importance of progressing towards bioenergy production as advantageous to its agriculture sector, with the additional opportunities for the farmers to improve their farm incomes and for the sector to induce further rural employment (DOE 2017b). Biomass supply for the country's bioenergy plan is expected to increase at an average rate of 4.4% per annum or 13.8% of the total primary energy supply under the clean energy scenario by 2030 due to the expanded capacities of the biomass-fed power plants (DOE 2016). More biomass is needed for the targeted increases for biodiesel and bioethanol fuels, particularly with estimated 21.3% and 9.7% annual average increase of the said alternative fuel products, respectively (DOE 2016).

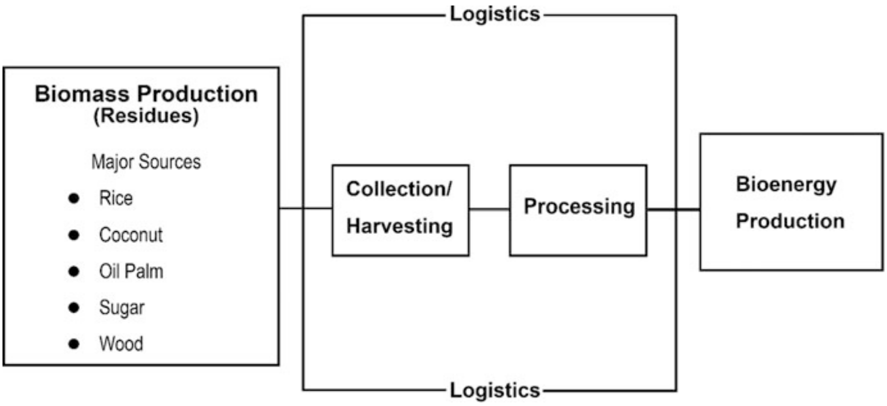

Fig. 39.1 The biomass supply chain for bioenergy production in the Philippines

The agriculture and forestry provide massive support to the bioenergy initiatives and endeavors of the country for clean energy (Shead 2017; Zafar 2020). An estimate of 16 million tons of residues from various production in the said sectors provides buoyancy to the bioenergy production in the country (Shead 2017). The supply chain through which the biomass is converted into bioenergy is shown in Fig. 39.1. Analysis on the available literature of the biomass supply chain indicates that the critical activities in bioenergy generation is the production of the biomass feedstock that should be collected and handled properly for the conversion process to produce the forms of bioenergy for distribution (Goyal 2020; Raychaudhuri and Ghosh 2016).

Along the chain, logistics is essential and critical at the same time (Goyal 2020). Transport, rural infrastructure and efficient storage systems are the crucial logistics to consider for efficient operations along the chain. Technological innovations, policy environment, and funding are likewise critical in developing the biomass supply chain for efficient bioenergy production operations, which Raychaudhuri and Ghosh (2016) suggest examination of capacity towards cost-effectiveness, policy support and strategic planning as viable measures. Conversely, Shead (2017) recommends to pay attention to “the development of agricultural residual recovery systems, the improvement of the agro-forestry systems, the introduction of the latest energy conversion technologies, and the development of biomass supply chains” as these aspects are key to further development of bioenergy production in the Philippines. Raychaudhuri and Ghosh (2016) and Ambaye et al. (2021) purport that optimum level of utilizing residues along the biomass supply chain for bioenergy fosters efficiency in energy generation.

39.4 Green Chemistry and Biowaste Valorization

To contend the worsening consequences of climate change, implementing regulations on the production and management of biowaste materials has been intensified. Sustainable development in addressing issues such as energy crisis, resource scarcity, pollution, among others, has become the foremost priority for policymakers worldwide (Ahuja and Tatsutani 2009).

Valorization of biowaste materials is a process of converting waste debris into valuable products, including chemicals, materials, and fuels (Arancon et al. 2013). Valorization approaches depend on the type of waste materials and the intended products. Agricultural waste materials are predominantly present in countries with a large agriculture-based economy. In fact, agricultural wastes ranked second-highest among wastes generated globally (3.35 kg/capita/day), next to industrial wastes (World Bank n.d.; Usmani et al. 2020). These wastes, which are largely organic, can be valorized to serve as feedstock for further agricultural activities (Usmani et al. 2020). There are several promising valorization techniques in producing valuable products. Waste valorization technologies such as biowaste-based biorefineries using agricultural or food-processing waste have gained popularity in recent years. Generally, each technology can extract the potential chemical energy of biowaste to produce electrical and thermal energy, value-added chemicals (organic acids), and energy fuels (Usmani et al. 2020; Matsakas et al. 2017).

(a) Continuous-Flow Chemical Technology

This new approach in converting biowaste materials into valuable chemicals and fuels addresses the high level of the structural and chemical complexity of biomass, deep chemical changes, and multistep processing (Serrano-Ruiz et al. 2011, 2012). Controlling the reactivity in biomass derivatives is a prerequisite to direct the conversion to the desired products. Some of the significant advantages of this process are: (1) allows better control of reaction conditions, particularly in dealing with reactive feedstocks such as those derived from biomass; (2) facilitates scaling up, which is important, especially that most biomass processes are still in the lab-scale; (3) allows intensification of the chemical processes, which significantly contributes to simplify technologies that have direct economic implications; (4) do not require catalyst separation after the reaction and regeneration, unlike with the usual batch processing technology; (5) allows continuous removal of unwanted gases (e.g., CO, CO_2, O_2) that potentially leads to increasing pressure.

(b) Microwave-Assisted Technology

Microwave heating is another green valorization technology, which is immensely useful, particularly in degrading highly stable biopolymers and recalcitrant compounds (e.g., lignin). The microwave-assisted valorization of biowastes has been successfully demonstrated in converting lignocellulosic wastes such as shells, sunflower husk, vegetable, and fruit peels, and food wastes were used to produce environmentally benign insecticides (Tukacs et al. 2017). Similarly, the microwave-assisted process was also used to produce the levulinic acid from waste biomass (Galletti et al. 2012). Likewise, it has been noted that this valorization strategy can revolutionize the industrial process since it generates products fast due to microwave heating on one continuous run (Tukacs et al. 2017; Verma et al. 2020).

(c) Pyrolysis

Though it is an old method used to produce char materials, pyrolysis is another green valorization strategy whose significance has recently been recognized in producing smaller molecules from very stable biopolymers (Zaman et al. 2017). Pyrolysis is usually used in the synthesis of fuels. The process involves heating the biomass at high temperatures in the absence of oxygen to produce decomposed products (Canabarro et al. 2013). Mohan et al. (2006) provide an excellent review of the recent development of pyrolysis utilizing biomass to produce products utilized as an energy source and a feedstock for chemical production. Fast pyrolysis from carbonaceous feedstocks gave high yields of primary, nonequilibrium liquids and gases, including valuable chemicals, chemical intermediates, petrochemicals, and fuels. It also been used in the production of advanced materials, including carbon nanotubes and graphene-like materials, which have been used in various applications. Despite its importance in biorefinery, innovations are needed, particularly in exploring and adapting innovative chemical thinking to advance this valorization technology. Catalytic process in pyrolysis reactors for producing purified petrochemicals and coming up with established quality norms and standards for pyrolysis products are just some areas that require research.

(d) Solid-State Fermentation (SSF)

Aside from its use in enzyme and antibiotic production, the solid-state fermentation (SSF) process is recognized as a green valorization process in producing value-added and industrial interest products from solid biomass, such as bioactive compounds and organic acids (butyric acid, succinic acid, itaconic acid, lactic acid, fumaric acid, malic acid), bioethanol and biodiesel products, biosurfactant molecules, among others (Lizardi-Jiménez and Hernández-Martínez 2017; Marzo et al. 2018; Cerda et al. 2019). SSF is a three-phase heterogeneous fermentation wherein microorganisms grow on the surface of a porous solid substrate with enough moisture to maintain microbial growth and metabolism (Marzo et al. 2018). Solid particles represent the main phase, and the process is carried out in the absence or near-absence of visible water between particles (Diaz et al. 2016). Industrial enzymes (pectinases, xylanases, and cellulases), which can be used for the hydrolysis of different agro-industrial residues in order to produce monomeric sugars that can be fermented to a wide range of high-added-value products, were successfully produced through SSF technology.

(e) Microbial Digestion/Degradation

Fermentation-based biowaste valorization strategies are increasingly recognized among the promising routes in waste valorization strategies. In this process, the degradation of complex wastes is facilitated with biological microorganisms

(Arancon et al. 2013). Researches in bioconversion have been intensified in past years, taking advantage of the revolutionized technology to re-engineer the metabolic pathways of microorganisms and increase the yield of the products. There have been substantial reports on the use of microorganisms for waste conversions (Wulff et al. 2006) and the use of microbiological processes for waste conversion to biofuels (Hnain et al. 2011), which demonstrate the potential of this technique as a green process in waste valorization.

39.5 Challenges in the Techno-economic Aspects of Biorefinery in the Philippines

Like other countries, bioenergy production in the Philippines is one of the potential sustainable solutions to address the demand for energy and reduce carbon emissions. In fact, a biofuel roadmap for 2017–2040 and a biomass energy roadmap for 2018–2040 illustrate the direction and the commitment of the country in attaining energy independence and implementing power market reforms as stipulated in RA 9367 (Biofuels Roadmap 2017–2040, DOE). Currently, available academic resources on biorefineries in the Philippine setting are limited. The technical difficulties in establishing biorefineries in the country may be the reason, aside from political, economic, and logistical constraints.

Technical challenges requiring discovery and application of new and efficient catalyst technologies such as fermentation processes, biomass fermentation, and hydrolysis, advanced gasification are factors that influence the performance of biorefineries. Technologies from other countries can be verified on the R & D stage. Likewise, the development of new catalysts is a painstaking task that needs to undergo rigorous research and optimizations. Thus, the development of new catalysts for existing processes with a less tractable substrate, high yielding, excellent selectivity, self-assembly of catalytic spaces under certain reaction conditions is essential for a successful establishment of biorefineries. In addition, the country still lacks the regulatory standards in standardizing the quality requirements of biorefinery products, which may limit the establishment of the biorefinery. Such standardization will help focus future research on attaining products with a specific quality.

39.6 Economic Implications of the Competing Demands for Food and Bioenergy

Trade-offs in relation to bioenergy production are a general knowledge with current pursuits in clean and renewable energy causing environmental footprints. For biofuels, these trade-offs have greatly induced the expansion of the exploration of biomass sources to non-land-based alternatives (Borines et al. 2011), creating three-generation technologies so far to secure alternative biomass sources (Ambaye et al. 2021). Land-based biomass particularly that of the first-generation technology entails issues about conflicts with food and environmental security as bioenergy efforts are intensified (Borines et al. 2011; Ambaye et al. 2021). The food-bioenergy nexus is established with the natural resource support common to these two essential goods in their production (Guo et al. 2020). Agriculture and forestry play a key role as major sources of biomass necessary for the production of bioenergy essential in the decarbonization of energy forms used in households and industries (Ambaye et al. 2021; Guo et al. 2020). Food and bioenergy security share the same resource requirements, such as water and land, which put the former at stake with biofuels advancement in view of sustainable development (Benjamin et al. 2021; Ambaye et al. 2021; Guo et al. 2020).

First-generation biofuel production has a huge impact to the food security objective, because the biomass sources are mainly edible crops such as corn, soybean, sugarcane, and rapeseed (Pattanaik et al. 2019; Arora et al. 2018a, b). Expansion in biofuel production means reduction of arable land and water for food production (Pattanaik et al. 2019; Guo et al. 2020), creating issues in the food-bioenergy nexus. Such massive volume can provide an environment-friendly alternative to biofuel production, which can save forest ecosystems from degradation (Pattanaik et al. 2019). However, by-products from lignocellulosic biomass have added values because of hemicellullose and lignin content that can be turned into xylitol, ethanol, polyhydroxybutyrate, xylose, furfural, xylose furfural, k-carrageenan/locust bean gum and polymeric blend films in commercial biofuel, biochemicals, and animal feed production (Arora et al. 2018a, b). Exploring further alternative biomass sources can find economic values in the extended uses of by-products, aside from securing food baskets and ecosystems, as demonstrated by Arora et al. (2018a, b). Dias et al. (2018) also documented the benefit of expanded energy yield from electricity and heat co-generation from the production of sugarcane's second-generation bioethanol.

Bioenergy products as yet to replace the fossil fuels used today for an eco-friendly and sustainable future are still undergoing numerous challenges typical of breakthrough products in the economy, especially concerning uncertainties with biomass supply regularity, processing plant optimal operations, process coordination, and logistic issues (Dias et al. 2018; Pulighe et al. 2019). This shows that overall cost-effectiveness of producing bioenergy is still sought and that shifting energy dependence favoring those clean energy forms is coupled with extremely high investment requirement (Xu et al. 2018; Dalena et al. 2019). Considering this, research and development efforts to expand biomass sources and yield that do not compete with food security and environmental integrity is a laudable mechanism to reckon with (Antar et al. 2021; Dalena et al. 2019). Review done by Awasthi et al. (2020) has shown the technological updates being shared regarding that aspect in scientific formats to provide the basis for the ways forward. Integrated biorefineries are noteworthy technological innovations to address the need to synergize efforts on this matter. Integrated biorefinery designs may be the remedy ensuring food security, environmental integrity, and clean energy via efficient reutilization of biomass towards a sustainable future.

39.7 Conclusion

Understanding the technical and economic aspects of waste biorefineries, particularly on the integration of green chemistry and valorization of innovative products from the various forms of wastes is crucial in preventing the competing demands for food and biofuels. The adoption of circular economy for waste biorefineries can be explored, particularly for the developing countries like the Philippines. The integration of green chemistry in the entire supply chain from the production to processing of agricultural crops can reduce the dependence of biorefineries on virgin raw materials, thereby minimizing the environmental footprints. Moreover, the use of non-food resources (fast-growing trees and grass species) can lessen the competing use of edible agricultural products for food or biofuel. Nonetheless, the concept of circular economy has not been fully explored in the developing countries. Thus, the need for more research to examine the production and waste generation chain and the technological aspects in valuing the wastes for economic goal and develop a circular economy for biowaste refineries. The information and scenarios generated from research are necessary inputs in strategic planning, particularly in developing countries. In the case of the Philippines, where national policies have been in place, the inputs derived from circular economy studies can be used in making action plans to fully implement what has been stipulated in the national development plan.

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Chapter 40
Unlocking the Global Potential of Waste Biorefining: Scaling Up or Scaling Down?

Ozgul Calicioglu

Abstract The value of organic waste and residues as a resource has been recognized since ancient civilizations; yet, modern bioprocessing technologies promise to increase this value. Besides, industrialization and urbanization levels, and population growth, impact the spatial distribution, quantity, and quality of organic waste globally and locally. In this respect, the scale and type of feasible biorefining solutions across the globe are affected by several factors, such as (1) readiness and availability of technology, (2) Comparative advantages of urban centers and associated waste streams, agri-food industries, and agroforestry activities, and (3) scale at which the supply and demand of the waste meet for efficient value chains. This chapter explores the approaches for unlocking the potential of organic waste as a feedstock for biorefining. In this regard, the chapter outlines global organic waste stocks concerning the abovementioned factors to analyze the current state of organic waste valorization approaches and exemplifies solutions for country archetypes.

40.1 Background: Waste Biorefining as a Potential Means of Circular Bioeconomy

The increase in the world population and the urbanization rates have led to a significant increase of waste generation rates. Partly, these phenomena are fueled by industrialization, which, in turn, has created a linear economy, reliant on the products of petroleum refineries. Analogous to petroleum refineries, biorefineries would receive materials of biological origin as a feedstock (Naik et al. 2010). When the feedstock is selected from an array of organic waste streams (e.g., organic fraction of municipal solid waste, agri-food industries, agroforestry activities, etc.), the produced bioenergy, biochemicals, and biomaterials would offer the potential to offset the negative value of waste. This paradigm shift, once enabled by technologies

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and policies, can unlock the potential of waste as a resource (Venkata Mohan et al. 2016).

Waste biorefineries can produce a broad range of end products and create production systems with drastically less inputs. In addition, incorporation of biorefinery principles in mainstream and traditional production pathways can reduce the amount of waste generation. This development can further support novel bio-based industries. Unlocking the global potential of waste biorefining offers multiple prospects for sustainable bioeconomy; for example, can contribute to transforming Europe's from net imports of oil to exports of technology, Know-how, and bioproducts (European Commission 2011).

Waste biorefineries offer a closed-loop alternative to linear economy. Waste biorefineries eliminate the concept of waste, through its valorization into marketable products (Venkata Mohan et al. 2016), in alignment with the concept of circular economy. The circular economy was first conceptualized by Segerson et al. (1991), but the definition from the Ellen MacArthur Foundation, "*An industrial economy that is restorative or regenerative by intention and design*," is most widely used. This approach eliminates the concept of waste, as its components return to natural or industrial cycles. The components of the economy with organic origins biodegrade, while technological or industrial origin will be energy-efficiently looped back into the economy (Potocnik 2014). The essence is one of closing the life cycle of products, i.e., moving from a linear model of the economy (produce, use, and discard) to one that is circular, as of course occurs in nature. Circular economy, by designing out waste and using (bio)renewable sources (Allesch and Brunner 2014), opens an avenue for the biorefining of waste (Zorpas et al. 2014).

With respect to the abovementioned circular economy approaches, the following sections are organized to regard waste as a resource and place the waste biorefinery to the center of the operations. First, waste streams and their potential as biorefinery feedstocks are discussed as part of the waste biorefinery upstream. Then, factors affecting the technical feasibility of waste biorefineries are discussed as the mid-stream of waste biorefineries. Finally, ways for creating markets to ensure the financial viability of biorefinery products at scale are discussed as part of the waste biorefinery downstream operations (Fig. 40.1).

40.2 Waste Biorefinery Upstream: Waste Streams and Their Potential as Biorefinery Feedstocks

A multitude of waste streams can be used as biorefinery feedstocks, provided that they are organic. These waste streams include, but are not limited to organic fraction of municipal solid waste, agri-food inductees waste, and agroforestry waste.

Global municipal solid waste generation data suggests that there is a high potential of using waste as biorefinery feedstock, as the largest waste category is food and green waste, which constitutes 44% of global waste (Kaza et al. 2018).

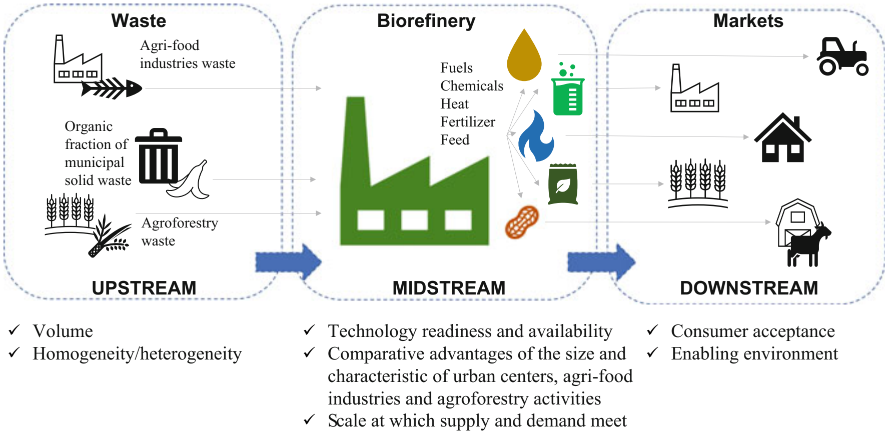

Fig. 40.1 Upstream, midstream, and downstream of waste biorefineries. Bullet points exemplify factors at each stage, affecting large-scale applicability

There is an inverse correlation between the income levels of the countries and the organic fraction of the municipal solid waste (Fig. 40.2). Paper and plastic consumption is higher in higher-income countries compared to lower-income countries. The availability and resolution of data improve by the income level of the countries, which enables creating detailed accounts for materials such as wood and rubber waste. Global food loss and waste account for a significant proportion of food and green waste.

In the food value chain, prior to retail and consumption, waste is generated during the production in agri-food industries. These industries are another major source of organic waste, with potential to be used as a waste biorefinery feedstock. Some examples of agri-food industry waste that can be valorized as a feedstock are peels, and other residues from fruit and vegetable processing (Arora et al. 2018; Awasthi et al. 2021) spent grains, and filter cakes from breweries (Outeiriño et al. 2019; Parchami et al. 2021), and bagasse and molasses from the sugar production (De Buck et al. 2020).

Agroforestry waste examples include the lignocellulosic biomass or green biomass. Lignocellulosic biomass can include agricultural residues such as corn stover (Bbosa et al. 2018) and rice husk (Offei et al. 2021). Green biomass examples include duckweed grown on wastewater (Calicioglu et al. 2019, 2021) and clovers, other grasses, and herbaceous plants (De Buck et al. 2020).

Organic fraction of the municipal solid waste tends to be more heterogeneous, versus the agri-food and agroforestry wastes can be more uniform and homogeneous. These properties provide different opportunities and flexibility in the midstream of the biorefinery processes and are further discussed in the next section.

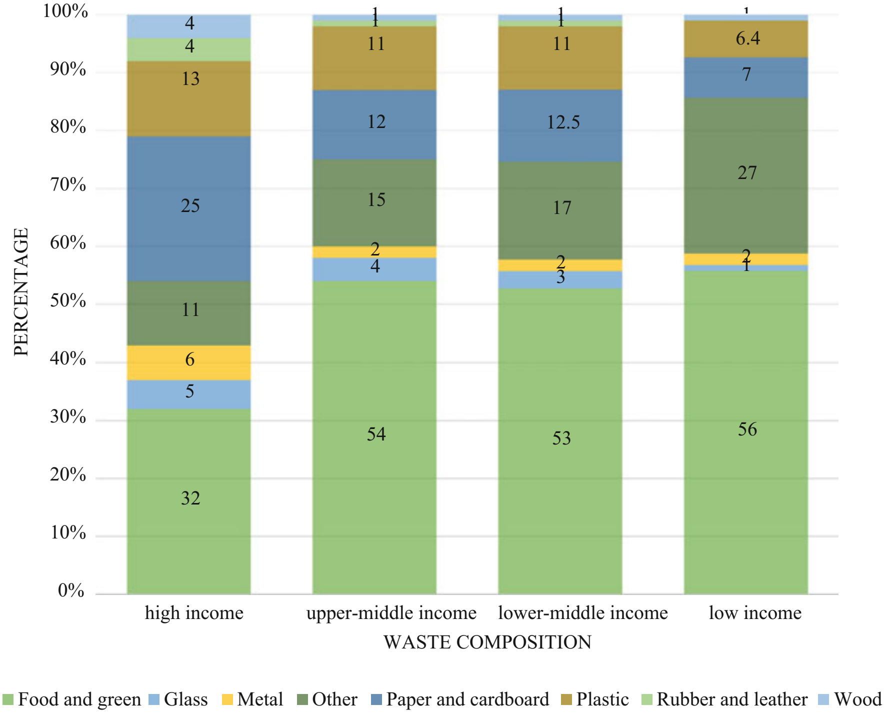

Fig. 40.2 Waste composition by country income levels. Adopted from World Bank, What a Waste 2.0 report (2018)

40.3 Waste Biorefinery Midstream: Factors Affecting the Large-Scale Technical Feasibility of Waste Biorefineries

Petroleum refineries, as their name imply, receive one category of feedstock. However, the feedstock options for the biorefineries are broad. There are a few factors in the selection of waste types, the biorefinery processes to be implemented, and the selection of the appropriate scale, processes, and final products. This section further discusses these factors.

40.3.1 Technology Readiness and Availability

Technology readiness of waste biorefineries varies for different feedstocks, processes, and end products for large-scale applications. Currently established products, processes, and applications include compost from the organic fraction of the municipal solid waste, volatile fatty acids and biogas from the organic fraction of the municipal solid waste or suitable agri-food and agroforestry wastes, feed from industrial byproducts, biodiesel from waste vegetable oil, and bioethanol from lignocellulosic waste or residues (Taherzadeh et al. 2019).

Short-term future prospects for large-scale waste biorefineries include novel processing technologies for valorizing industrial side products in the form of high-value bioproducts, such as pharmaceuticals, high-value alcohols, or bioplastics, by integrating biorefinery concepts into mainstream production. Another technology to reach scale is lignin valorization from lignocellulosic compounds, in agroforestry sector (Stafford et al. 2020).

40.3.2 Comparative Advantages of Urban Centers and Associated Waste Streams, Agri-food Industries, and Agroforestry Activities

It is very important to ensure feedstock availability, in turn, technical feasibility at scale. In this respect, comparative advantages must be realized for urban centers and associated waste streams, agri-food industries, and agroforestry activities.

Despite great potential, many European countries still struggle to manage the organic fraction of municipal solid waste at the higher levels of the waste hierarchy, and over 100 million tons of organic waste produced end up in landfills as an untapped potential and missed opportunity (European Commission 2011).

Urban centers provide a comparative advantage by concentrating waste, predominantly food waste, at large amounts. It was estimated by United Nations Environment Program that in 2019, 931 million metric tons of food waste was generated worldwide. Of this value, 61% originated from households, 26% originated from foodservice and 13% from retail. The report also estimates that the total share of produced food in the food waste mix can be up to 17%, with 11%, 5%, and 2% coming from households, foodservice, and retail, respectively. It must be noted that priority should be given to the interventions for avoiding the food waste, particularly of the edible fraction. Nevertheless, there is an adequate amount of inedible food waste, particularly in low-income countries, that can benefit from circular approaches. In contrast to the common belief that in developed countries the post-consumer food loss predominates the mix and the production and processing loss predominates the mix in developing countries, the study found that action on food waste across the whole value chain is relevant in all income groups (United Nations Environment Programme 2021).

The characteristics of the urban centers play an important role in the selection of the appropriate feedstocks to ensure overall sustainability of waste biorefinery operations. For example, in arid and semi-arid regions, conversion processes that can use seawater instead of freshwater could be prioritized (Bastidas-Oyanedel et al. 2016; DomínguezdeMaría 2013). Another alternative to fresh water in urban settings can be the municipal wastewater, as the centralized collection and drainage systems pose an advantage for the economics of scale for circular approaches. For example, nitrogen-and-phosphorus-rich domestic wastewater can be used in the production of plant biomass such as willow (Sas et al. 2021) and phytoplankton such as microalgae (Calicioglu and Demirer 2015), which can be further processed into biochemicals such as energy carriers (Bhatia et al. 2021). This integrated process also serves as a biological carbon sequestration mechanism, which results in a reduction of life cycle impacts of biomass production processes (Sharma et al. 2020).

An important comparative advantage of any waste stream is the lack of contamination, which can be relatively easily achieved in agri-food industries (Cristóbal et al. 2018). This characteristic allows for targeting higher-value products. Similarly, although more prone to contamination during the collection stage from farms, agroforestry waste can be very homogeneous, opening the avenue for the production of higher-value biomaterials. Nevertheless, non-homogeneous feedstocks can have the potential to be converted into value-added bioproducts, such as methanol (Lavoie et al. 2013).

40.3.3 Scale at Which the Supply and Demand of the Waste Meet

Waste type and amount have implications on technical feasibility of the biorefineries as they govern the scale and can be interpreted in terms of the potential for waste biorefining per country income levels, and are discussed under the next section on factors affecting the technical feasibility of waste biorefineries, scale at which the supply and demand of the waste bioproducts meet for efficient value chains.

Opportunities for scaling up Proper collection programs, where administrative capacity exists, can tap into the potential for valorization of the organic fraction of municipal solid waste. For instance, San Francisco city in the USA initiated a program for collection of residential and commercial collection of food waste. Under this program, over 1 million metric ton of food and green waste have been converted into compost for local agricultural consumption (Kaza et al. 2018).

In addition, highly industrialized countries with large urban centers bear a high potential for large-scale urban biorefineries to produce higher value bioproducts such as bioplastics and jet fuel precursors with a biorefinery value cascade approach (Calicioglu et al. 2019).

Opportunities for Scaling Down Homogeneity of the waste plays a major role, yet it is usually achieved at a smaller scale. Scattered agri-food industries may benefit from small-scale biorefining practices. These can target higher-value products such as pharmaceuticals, if the technology allows, owing to the homogeneity of the feedstock and the less susceptibility to contamination. Similarly, agroforestry residues can find uses as feedstock at smaller scales. For example, Stafford et al. (2020) revealed various pathways and assessed technology readiness levels and market feasibility for the production of a variety of products using biomass residues of the production systems, which can reach up to 50% of the raw material. Another small-scale and technologically ready alternative biorefining option with would be farm-scale biodigesters, producing biogas and soil amendment (Oleskowicz-Popiel et al. 2012).

40.4 Waste Biorefinery Downstream: Creating Markets to Ensure Financial Viability of Biorefinery Products at Scale

Market for the waste-derived bio-based products needs to be strengthened for creating a "pull mechanism" for long-term financial viability. In this regard, standards, certifications, and labeling schemes can play an important role. The information conveyed by the standards, certifications, and labels increases market access of the products and elevates brand value. In developed countries, consumers are prepared to purchase goods and services with reduced environmental footprint, even if it comes at an expense of "Green Premium" (Carus et al. 2014). Therefore, bioproduct certification schemes can facilitate market development by enhancing social acceptance (Bracco et al. 2020).

Commitment of policy makers is also important for enhancing the enable environment of large-scale waste biorefineries. For example, waste, predominantly food waste, contributes to approximately 5% of total greenhouse gas emissions globally, and simple improvements on the waste management systems can cut this value down by 25% (Kaza et al. 2018). Therefore waste can be listed as one of the primary sectors in countries' Nationally Determined Contributions for reaching climate targets (Powell et al. 2018). Such commitments can enable better waste management systems; in turn, enabling environment for large-scale waste biorefineries.

40.5 Conclusions

There are well-established technologies for waste biorefining and integration of these principles into already-existing industries. Highly industrialized countries with large urban centers bear the highest potential for large-scale urban biorefineries to produce both low and high-value bioproducts such as bioplastics and jet fuel precursors. Countries with lower income levels or scattered agri-food or forestry residues may benefit from small-scale biorefining practices such as farm-scale biodigesters. Regardless of the country archetype, analyzing the local context and surrounding the biorefining operations with enabling policy environment are key for the long-term sustainability of waste biorefining applications.

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Chapter 41

Development and Scale-Up of Waste Biorefineries Systems: Lactic Acid as a Case Study

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Abstract This chapter aims to discuss relevant topics for successful development and scale-up of industrial biotechnological process in the context of a biorefinery. Lactic acid will be explored during the text since more than 90% of the world's production occurs by bioprocesses. From this perspective, some critical aspects should be considered according to the maturity level of the technology, since scaling-up investments and time estimates are not directly proportional to what is dispended at the bench level research. Misunderstandings in the design of some development stages may represent increase in investments and spent time reducing then the chances of implementing a promising technology at the industrial reality. In the following sections, a description is provided on main aspects of an industrial biotechnology and is illustrated how an integrated approach among bioprocess development, including the construction of industrial strains, fermentation, and downstream process development, along with scaling-up features and sustainability assessment, can predict possible bottlenecks and guides the research and the development of an industrial biotechnological process.

41.1 Introduction

Biological conversion of non-food and renewable feedstocks, such as lignocellulosic biomass, oil residues, industrial and municipal wastes, into a wide range of valuable bio-based products has been considered a promising approach within a waste-based biorefinery concept to promote carbon-neutral bio-economy (Ferreira et al. 2019; Ko

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et al. 2020). Bio-products or bio-based products refer to chemicals and materials derived from waste feedstocks. Examples of bio-products include enzymes, organic acids, polymers, amino acids, alcohols, fatty acids, both with wide application in the pharmaceutical, cosmetics, food, plastics, and fuels industries.

The development of a promising new technology from lab to industrial scale is a significant challenge for biotech processes as this is a high-risk venture that requires time and investment. However, it is highly recommended to have pilot plant and demo plant stages during the process development of biotech routes to validate key important technical aspects of the new process. Furthermore, process scale-up provides information for the design of the industrial equipment and generates first samples of the product, which can be after validated for a specific application. Once planned properly, scale-up can be executed successfully. This means that the new process technology can produce the target bio-product according to a required market specification in an intermediate scale matching the initial timeline and cost estimates. In other words, the success or failure of the scale-up depends on how close rate, yield, and purity at the larger scale matches up to those results from the lab bench scale. Successful scale-up also means the issues related to transport phenomena which does not appear in the lab scale are faced and resolved in a larger scale. Sometimes, even a complete understanding of the mass and heat transport phenomena was not achieved, a background for future development has been established (Reisman 1993).

The scale-up of industrial process often takes place in two stages if there is a high degree of novelty in the process. The first stage is the pilot plant with fermenters and the required downstream equipment. Frequently, at this phase, the process is not yet fully integrated, and each unit operation is operated batch-wise. The second stage is the demonstration plant with higher fermenters and the respective downstream. At this phase, the process runs continuously and has the same equipment that will be used at the industrial plant. The unit operations run fully integrated considering all the recycling streams, and the feedstock is the same that will be used in commercial unit. Sometimes, if there is low degree of novelty, demo plant may be skipped (Crater and Lievense 2018).

The time required to complete the transition from lab bench scale to manufacturing process is typically 3–10 years, which means the biotech developments are long-time projects with high financial risk. Scaling may require from 6 months to 3 years, depending on if a facility exists or need to be constructed and on the degree of novelty introduced by the new process. Any deterioration in process performance during the scale-up will be costly and can lead to the project failure. Even a short deviation, such as 4–10% of underperformance or delays (6–12 months), can significantly reduce financial results of the endeavor (Crater and Lievense 2018). This reinforces the need to have a good approach with a good planning, and an experienced team before going to the scale-up. Some important points for a good scale-up, such as think about full-scale from the start and perform the preliminary techno-economic analysis, will be stated here. Many experts in biotech scale-up state that it is important to “begin with the end in mind,” which means the final industrial full large scale should be thought of before experimental work begins. Start from the large-scale operation and not from lab scale work (Noorman and Heijnen 2017).

A realistic view of how the process looks like at production scales provides key inputs to guide the research program. Beginning with the end in mind allows the teams to prepare a detailed conceptual design of the envisioned manufacturing process. Even working with many unknown, taking realistic premises, it is possible to build process flow diagrams, material and energy balances, unit operation designs, and techno-economic models. With this approach, some problems can be anticipated, increasing the chances for success, expenses are reduced, and scale-up can be faster (Crater and Lievense 2018).

The techno-economic analysis (TEA) at the early stage of the industrial project gives the first feeling of the economic attractiveness to develop a bio-based product. TEA is also important to understand the critical performance metrics such as fermentation titer, productivity, yield, and downstream recovery that affects the rentability of the project. Every time there is a significative new input from the research, the economic model must be updated. TEA drives the go/no-go decisions for next steps of the scale-up and prioritizes goals and efforts for the research.

Usually, the development of upstream, midstream and downstream processes is carried out in separate groups. However, these teams must interact. From the beginning of the research, it is important to develop the entire process from the raw material to the final bio-product. All processes are intricately connected to each other. For example, the microorganism selected for the bioprocess significantly impacts the conduction of the development of the fermentation process, as well the yield and titer of the bio-product that can be obtained. The culture medium used in the fermentation can affect the efficiency and cost of the downstream process. Through collaborative problem solving, whole team can find solutions to overcome the barriers during the development program.

A successful case of a biotechnological process application is the bio-based lactic acid production. Lactic acid is a molecule widely used in cosmetic, chemical, food, textile, leather, pharmaceutical, and polymer industries to produce PLA (polylactic acid), which is a biodegradable and renewable polymer. It can be obtained by two routes, chemical synthesis or fermentation. The chemical synthesis results in racemic mixture of DL-lactic acid, while the fermentation route results in an optically pure L-lactic acid. The latter is metabolized by humans and finds applications in food and pharmaceutical industries and can be used in the synthesis of the biodegradable PLA polymer (Babele and Young 2020; Komesu et al. 2017a; Oliveira et al. 2018). Considering the current production of lactic acid, over 90% of the commercial production is performed via fermentation due to several advantages over the chemical synthesis route, such as the use of low-cost and renewable feedstocks, lower energy consumption, and the likelihood of obtaining high optical purity of the acid, depending on the strains used (Djukić-Vuković et al. 2012; Singhvi et al. 2018).

The following sections in this chapter will discuss relevant aspects of the development and scaling-up industrial biotechnological process, considering four synergic steps: (1) upstream process that develops robust strains capable of producing a desired bio-products using waste as renewable resources; (2) midstream process that optimizes the bio-product synthesis through fermentations/cultivations; (3) downstream process that recovers and purifies the desired bio-product to achieve industrial level requirements; (4) sustainability assessment that guides the whole development to have a good trade-off between economic and environmental aspects. Lactic acid will be used as background to discuss these steps and highlight the importance of this integrative development.

41.2 Bioprocess Upstream—Industrial Strains Development

Microorganisms isolated from nature can produce a variety of interesting bio-products (e.g., antibiotics, enzymes, amino acids, lipids, polymers, organic acids, fuels), and for this reason, they have been employed by industry for over 100 years. However, these native strains hardly meet industrial demands because of some undesirable characteristics, including (1) unable to produce high titers and yields of the target bio-product, (2) not optimized to consume a wide variety of carbon sources, (3) low tolerance to toxic components present in bio-based feedstocks and industrially relevant stress, (4) can produce high by-products titers, which make the downstream process complicated and expensive (Yu et al. 2020; Zhang et al. 2011).

To overcome these general challenges and fully exploit the potential of microorganisms, intense efforts have been made by academia and industry to synergistically develop high-performance strains and customized bioprocesses capable of efficiently converting waste-derived carbon sources into bio-products in industrial level.

Industrial strain development requires several strategies and decision points, as discussed in excellent reviews and perspectives (Ko et al. 2020; Lee and Kim 2015). The early stage of this development includes the selection of a suitable host microorganism (also known as chassis, microbial cell factory or platform microbial). This choice is not trivial and depends on the type of product, on several physiological factors, such as capability of utilizing carbon sources, abundance of key intracellular precursors, growth in an inexpensive medium, oxygen requirement (anaerobic versus aerobic microorganisms), in addition to techno-economic, regional legal, and regulatory factors intrinsic to an industrial process (Lee and Kim 2015; Liu et al. 2020).

In recent years, the rapid progress of tools and strategies for strain optimization has opened new avenues for the development of high-performance strains, enabling the production of high “TRY” (Titer, Rate, and Yield), high level of optical purity, low nutritional supply, the use of complex agro-industrial wastes, or minimal by-products production during industrial fermentation and downstream steps. Here, we show relevant classical and advanced metabolic engineering approaches that have been evaluated to develop an increasing number of industrial strains using lactic acid production as a successful case study.

As already mentioned, the selection of a suitable host is also crucial to meet the commercial requirements of lactic acid production. Although a wide range of microorganisms can naturally produce lactic acid, the most commonly used by the industry is the homofermentative lactic acid bacteria, due to their ability to convert over 95% of sugar into optical pure lactic acid, with a maximum theoretical yield of 2 mol of acid per mol of glucose and 1.67 of acid per mol of xylose (Singhvi et al. 2018; Wang et al. 2015). Among the homofermentative bacteria, the genus *Lactobacillus* and *Bacillus* are the predominant chassis for commercial production. Some of the advantages of these strains are: (1) can naturally produce optically pure lactic acid as the primary metabolic end-product with high yield and productivity; (2) consume hexoses, disaccharides and pentoses, enabling the use of several different renewable substrates, such whey, starch, molasse; lignocellulosic materials; (3) most of them are Generally Recognized As Safe (GRAS status) (Hofvendahl and Hahn-Hägerdal 2000; Klotz et al. 2016). However, one of the major problems associated with bio-based production of lactic acid by lactic acid bacteria has been its reduced tolerance to low pH levels. To avoid the pH drop by lactic acid production and prevent growth inhibition, neutralizing agents are frequently employed to maintain a neutral pH during fermentation. However, at pH around 5–7, a substantial proportion of the product exists in lactate form (since pKa ~3.8 at 25 °C). During lactic acid purification, acidification step is required to recover the free lactic acid, increasing the cost of the process and generating a large amount of waste, such as gypsum that poses economic and environmental problems (Datta and Henry 2006; Lee and Kim 2015; Singhvi et al. 2018). In addition, lactic acid bacteria generally require complex nutrients due to their inefficiency in naturally synthesizing B vitamins and amino acids, essential components for their growth and lactic acid production (Komesu et al. 2017a; Wang et al. 2015). In general, according to Tejayadi and Cheryan (1995), the culture media, especially nitrogen supplementation, can represent about 38% of the capital costs of a bioprocess (CAPEX).

To overcome these current limitations in industrial bio-based lactic acid production and several other bio-products, traditional non-GMO (non-Genetically Modified Organism) strain modification approaches, including random mutagenesis (using physical or chemical agents), protoplast fusion, and adaptive evolution, have been widely investigated. These classical strain improvements are random processes wherein it is not possible to predict which type of mutations would arise. Random mutations are introduced into the genome of the strain of interest, followed by a screening and selecting steps in an attempt to obtain strains with desired characteristics (Saxena 2015). Joshi et al. (2010) induced mutations in *Lactobacillus lactis* using classical physical mutagenesis to improve D-lactic acid production from hydrolyzed cane and molasses sugars. Repeated UV-irradiation exposure was able to generate a mutant capable of producing 110 g/L D-lactic acid with 98% of optical purity from 150 g/L of sucrose from hydrolyzed cane sugar in shake flask culture. In another study, a low-pH tolerant mutant of *Lactobacillus delbrueckii*, previously obtained by chemical mutagenesis using nitrous acid, was subjected to genome shuffling strategy through protoplast fusion. After three rounds of genome recombination between this mutant and an amylase-producing *Bacillus amyloliquefaciens*, the resulting mutant produced 40 g/L of lactic acid from 83 g/L of liquefied cassava bagasse (starch content 50%, w/w), a non-food and low-cost feedstock, with minimal addition of nutrients (only 0.2% of yeast extract and peptone) and low concentration of neutralizing agent (2% $CaCO_3$) (John et al. 2008).

Adaptive Laboratory Evolution (ALE) has become another powerful and non-genetic engineering tool to facilitate and streamline industrial microbial development. ALE consists of adapting cells in a chosen environment with a selection pressure for a prolonged period. After hundreds or thousands of generations, it is possible to naturally obtain mutant strains with desired phenotypes, such as increased product yield/titer, growth rate or substrate utilization, and stress tolerance to pH, temperature or inhibitors (Choi et al. 2019; Cubas-Cano et al. 2019; Sandberg et al. 2019). To improve L-lactic acid production from agro-industrial wastes based on potato stillage and sugar beet molasses, Mladenović et al. (2019) performed ALE of *Lactobacillus paracasei* NRRL B-4564. The first phase of the adaptation was conducted under sequential batch cultivations for 15 days by increasing gradually the concentration of molasses in the medium from 5 to 25%. After another 15 days of adaptation under fed-batch culture, a resulting mutant was able to produce 170 g/L of lactic acid, which was 59% higher compared to parental strain.

Although powerful, classical strain improvement technologies require considerable time for downstream screening and selection, and, when applied alone, can generate an increased number of mutants, containing mostly unimproved strains (Zhang et al. 2018). In this context, recent advances in rational genetic modifications tools have significantly accelerated the development of industrially competitive microorganisms. Over the past three decades, metabolic engineering approaches are being widely used to introduce rationally directed genetic changes into various microorganisms, including those less studied ones, using recombinant DNA technology. These genetic modifications, including eliminating unwanted biochemical reactions, increasing the activity of specific genes, and/or introducing new genes to enhance or redirect metabolic flow in the desired direction, have allowed the construction of customized chassis for the bio-products and bioprocess of interest.

Several studies are evaluating suitable metabolic engineering strategies to improve lactic acid production. Lee et al. (2017) focused on enhancing L-lactate production by *Kluyveromyces marxianus*, an emerging non-conventional yeast with various phenotypes of industrial interest, such as a fast growth rate, various stress tolerance, and wide substrate use. Promising L-lactate dehydrogenases, enzyme responsible for converting pyruvate to L-lactic acid, from heterologous sources and with distinct pH optimums were identified and introduced into *K. marxianus.* A strain co-expressing two L-lactate dehydrogenases simultaneously (one enzyme with an optimum pH of 5.6 and other of 5.3) was able to produce 16.0 g/L of lactic acid with a yield of 0.32 g/g glucose without pH control, whereas the strains expressing those enzymes individually produced a maximum of 8.4 g/L of lactic acid. In another study, *Lactobacillus plantarum* was engineered to increase the optical purity of L-lactic acid during fermentations using raw corn starch (Okano et al. 2018). After deleting simultaneously, the D-lactate dehydrogenase gene and the lactate racemase operon (which catalyzes the interconversion between D-lactate and L-lactate) and introducing an α-amylase-secreting plasmid to catalyze the hydrolysis of starch, the resulting strain could produce L-lactic acid with a high titer (50.3 g/L), yield (0.91 g/g), and optical purity (98.6%) using raw corn starch as renewable feedstock.

Combined approaches of classical mutagenesis and rational metabolic engineering have also been employed successfully to create industrial strains more efficiently. For the low-pH production of L-lactic acid from both glucose and xylose, Qiu et al. (2018) reconstructed the pentose phosphate pathway for xylose assimilation by introducing four heterologous genes encoding transketolase (tkt), transaldolase (tal), xylose isomerase (xylA) and xylulokinase (xylB) into the *Pediococcus acidilactici* chromosome. Additionally, the endogenous genes phosphoketolase (pkt) and acetate kinase (AckA2) were knocked out to decrease the flux through acetic acid production. The engineered *P. acidilactici* was able to produce 9.8 g/L of L-lactic from xylose. Subsequently, ALE was also applied to accelerate the xylose assimilation rate and increase the L-lactic acid yield. After 66 days, the resulting strain showed about threefold higher L-lactic acid production from xylose.

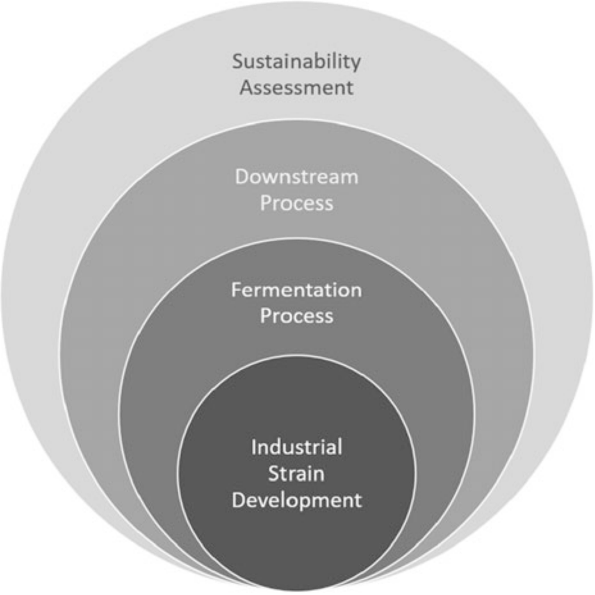
As described, there are several classical and innovative approaches to develop robust and efficient strains for the biotechnology industry. The choices and results of the upstream process significantly impact the next fermentation and purification developments and scaling. In this context, the integration of processes and teams is crucial for the successful development of industrial bioprocesses based on waste feedstocks.

41.3 Bioprocess Midstream—Fermentation

The fermentation process involves the cell growth to obtain the product of interest, which can be the cell itself or a bio-product produced by it. The bioreactor is the tool used in fermentation process that allows to create environmental conditions to maximize cell and product production. In the bioreactor, parameters such as pH, temperature, agitation, aeration, and dissolved oxygen can be monitored and controlled.

The fermentation can be performed by batch, fed-batch, or continuous mode. In batch process, after culture medium and viable cell inoculation, nothing is added or removed to the culture, except air or another gas, antifoam and acid or base to pH control. Usually, the concentration of nutrients, cells and product vary with process time. In fed-batch fermentation, besides the addition of gas, antifoam and acid or base to pH control, feed can be carried out with one or more nutrients. The feed medium can be continuous or intermittent (pulse-feeding), and the rate can be constant or vary with time. The low concentration of the nutrients supply can minimize the shift in microbial metabolism and/or the inhibition effect by-product or substrate and consequently enhance yield and productivity. In continuous fermentation, after a batch phase period, the culture medium is fed to the bioreactor.

Fig. 41.1 Interactions between the biotech process development teams



The reaction volume in the bioreactor is maintained constant by continuously removal of the fermented broth. It can be performed by the chemostat method, with a limiting substance, or by the turbidostat method, with constant cell mass. Continuous fermentation allows productivity improvement, however, keep the sterile operation is a challenge (Bailey and Ollis 2018; Shuler and Kargi 1992).

The final objective of the fermentation process is to produce an economically and sustainable industrial bioprocess. For this purpose, it must pass through the process development at bench scale, identification of the operational challenges at pilot scale and scale-up to industrial scale.

The development and scaling of the fermentation process involve a constant communication exchange with developers (Fig. 41.1) of the strain, downstream process (DSP) and sustainability assessment (technological, economic and ecosystem analysis), which must become part of routine of the process development team. The main objective is to develop and scale a process to promote metabolic and physiologic conditions to maximize cell and product production.

The strain must be stable from the cell bank, through the inoculum train, until the production scale (Thiry and Cingolani 2002). In the metabolism, the stress can induce metabolic shift, which can result in misincorporation of amino acids in both native and recombinant proteins, impacting the product quality (Fenton et al. 1997; Schmidt 2005).

Culture media are an important environmental factor for microbial metabolism and strongly impact the efficiency of a bioprocess. These cultures can be classified as defined or complex. The carbon source is an important component of the medium. Complex media, composed of nutrients such as yeast extract and tryptone, can be easily prepared and results in fast cell grow, however, it has a variable composition and variation between batches can occur. On the other hand, defined media has a chemical composition well known, which can be reproducible and facilitate DSP for secreted products (Thiry and Cingolani 2002).

Other important fermentation process parameters are agitation, aeration, pH, temperature, dissolved oxygen, and pressure. Agitation and aeration supply microorganisms with oxygen and promote mix of the broth to obtain uniform suspension and an accelerated mass transfer rate of the metabolic product. Bioreactors with mechanical agitation break the air bubbles and intensify the turbulence of the liquid. The pH and temperature are important parameters for cell growth, but also to stability of the bio-products. Oxygen supply for microbial cultures is often a limiting factor for aerobic microorganisms since oxygen has a low solubility in liquid medium. Dissolved oxygen levels can be increased by supplying pure oxygen (highly expensive and dangerous at large scale) or increasing total air pressure in the bioreactor (Aiba et al. 1973).

In the fermentative process scale-up, it is supposed to transfer the data obtained in laboratory and pilot plant to industrial scale. The scale-down can also occur for well-established process, to make improvement of the process, strain and medium.

Scaling usually follows three steps, laboratory, pilot/demo, and industrial plant. For the most part, the laboratory involves shaker flasks and bench bioreactors. More recently, laboratory high throughput for process development and optimization has been used microtiter plates, instrumented shaker flasks, and miniaturized stirred bioreactors (Marques et al. 2010). More knowledge of the interactions between fluid dynamics and cell physiology in a heterogeneous environment has to receive performed by computational fluid dynamics (CFD), metabolic flux analysis and agent-based modeling (Delvigne et al. 2017).

The pilot plant is indispensable to confirm the improvements of the strain and the medium before going to industrial scale. A instrumented pilot plant can provide valuable physical and metabolic data for a rational scale-up or scale-down.

The success of the scale-up is not result of a straight-lined transposition of experimental data, requiring improvement on each scale. The main relevant physiologically parameters are substrate concentration, biomass, cell viability, metabolites, products, pH, temperature, partial oxygen pressure (pO_2), partial carbon dioxide pressure (pCO_2), and exhaust gas composition. The physical parameters employed for scale-up are mainly those which affect mixing, heat transportation and oxygen supply, such as power input, aeration and agitation rate, heat transfer coefficients, pO_2, and oxygen mass transfer coefficient (kLa). The physical parameters can be combined one each other, or with other variables, in dimensionless numbers that are kept constant, as scaling criterion (Marques et al. 2010; Najafpour 2006; Schmidt 2005).

The dimensionless kLa is the most used physical variable for fermentation scale-up, since it includes parameters that influence oxygen supply. Volumetric power consumption, constant Reynolds, constant impeller tip speed and equal mixing and recirculation time, are also occasionally employed (Garcia-Ochoa and Gomez 2005; Najafpour 2006). Another simple and common scaling method is variation of the stirrer speed and aeration rate in function of the maintenance of the constant pO_2 (Schmidt 2005).

Lactic acid production via fermentation is the process most widely used by industry worldwide. Microbial lactic acid production has several advantages when compared to chemical route, such relatively lower temperatures, lower energy consumption, and high purity (Oliveira et al. 2018). Industrial microbial production of lactic acid is still predominantly performed with carbohydrates such as glucose, lactose, starch, and sucrose from sugar beet, molasse, and whey. However, in recent years, several laboratory-scale fermentation studies have aimed to evaluate different renewable materials, as well as to validate and improve the performance of the lactic acid-producing strains and find the optimal production conditions in order to develop more sustainable and economically viable bioprocesses for large-scale lactic acid production.

Batch mode fermentation is typically used for industrial production as it can allow higher lactic acid titers with reduced risk of contamination despite the disadvantage of generally resulting in lower productivities (Ahmad et al. 2020; Ghaffar et al. 2014; Rawoof et al. 2021). However, continuous and fed-batch modes, with initial high cell density culture or cell recycle have also been reported. Simple batch and repeated-batch processes with cell recycle were evaluated for L-lactic acid production using wild-type *Enterococcus faecalis* and hydrol (an efficient carbon source derived from glucose production), soybean curd residues (a potential nitrogen source derived from soybean products), and malt as renewable substrates (Reddy et al. 2016). Ten repeated batches with cell recycle were performed at 38 °C and pH 7.0 controlled automatically by the addition of NaOH, with a total fermentation time of 200 h. Biomass concentration increased during repeated-batch fermentations, reaching 26.3 g_{DCW}/L, removing inoculum preparation step at each fermentation. The productivity of L-lactic acid also increased significantly from 3.20 to 6.37 g/L·h, indicating that repeated-batch fermentations with cell recycle are an efficient bioprocess for industrial production of lactic acid. Carpinelli Macedo et al. (2020) evaluated the production of lactic acid by *Lactobacillus amylovorus* using hydrolyzed cassava bagasse and corn steep liquor as renewable feedstocks. Batch without pH control and fed-batch with pH controlled automatically at 6 using NaOH strategies were carried out at 37 °C. The maximum lactic acid production and productivity under batch mode were 31.6 g/L and 0.11 g/L·h, respectively. In contrast, higher titer (66.9 g/L) and volumetric productivity (0.46) were achieved when controlled fed and pH maintenance were performed.

Many bioprocess variables, as temperature, pH, neutralizing agent, aeration level, substrate concentration, inoculation size, sterilization, have been adapted and optimized for improving lactic acid production. The definition of these variables depends on the type of raw material, chassis, expected yield/titer or purity. The effects of critical parameters, such as temperature (25, 30, 35 and 40 °C), inoculum size (5, 10, 15 and 20%), and sugar concentration (8, 13, 18, and 35 g/L of reducing sugar concentration) were examined separately during batch fermentations of *Lactobacillus casei* using soybean straw hydrolysate for L-lactic acid production (Wang et al. 2014). The maximum L-lactic acid yield and productivity were obtained with the higher initial reducing sugar concentration (35 g/L) and intermediate conditions for temperature (30 °C) and inoculum size (10%). Other critical parameter in bioprocess is pH, mainly during acid organic production. pH is closely related to the enzymes involved in the metabolism process and cells nutrients transport, and changes in pH can affect microbial activity and the efficiency and final titers of the bio-product. Furthermore, as mentioned earlier, the choice of neutralizing agent for pH control is pivotal for a sustainable bioprocess. In this context, Liu et al. (2014) studied the effects of KOH, $Ca(OH)_2$ and NH_4OH as neutralizing agent for D-lactic acid production by a genetically engineered *Escherichia coli* strain. Fermentation neutralized by $Ca(OH)_2$ achieved a volumetric productivity three times higher in addition to a slightly higher yield of D-lactic acid compared to that achieved by KOH or NH_4OH. According to the authors, $Ca(OH)_2$ is the cheapest neutralization agent compared to the other two in the Chinese market, which makes it a potential base for industrial production of D-lactic acid. Nakano and co-workers compared the employment of $Ca(OH)_2$, NH_4OH, and NaOH as neutralizing agents for lactic acid fermentation and evaluated its impact on lactic acid recovery. In Simultaneous Saccharification and Fermentation (SSF) process with *Lactobacillus delbrueckii*, $Ca(OH)_2$ as neutralizing agent resulted in higher lactic acid productivities (3.59 g/L) compared with NH_4OH (1.51 g/L) and NaOH (1.4 g/L). The molarity of the lactate in the fermentation broth was reduced using calcium hydroxide, besides that, it suggests that the divalent cation (Ca^{2+}) was more effective in neutralizing cultures compared with monovalent cations (Na^+ and NH_3^+) (Nakano et al. 2012).

The choice of nitrogen source in the culture medium also plays a key role in the development of economically viable bio-based processes. Balakrishnan et al. (2020) evaluated the production of D-lactic acid by *Lactobacillus delbrueckii* using the low-cost Kodo millet bran residue, an abundant grain in India, Africa, and China, with significant amount of starch, protein, and other essential nutrients. The effects of several types of nitrogen supplements (yeast extract, beef extract, bacteriological peptone, brain heart infusion, soy peptone, whey protein hydrolysate, casein enzyme hydrolysate, urea, and sodium nitrate) and its optimized dosage on D-lactic acid production was studied. The results indicated that casein enzyme hydrolysate is the most suitable low-cost nitrogen source and that increased dosage of this nitrogen source has a positive effect on LA production. However, no significant increase in specific growth rate and D-lactic acid productivity was observed in fermentations with casein enzyme hydrolysate concentration above 5 g/L. Therefore, an optimum casein enzyme hydrolysate dosage of 5 g/L should be considered for a more economical bioprocess.

As described above, there are different approaches for fermentation development and scaling process. For each process, for each bio-product, there is a different strategy that can be elaborated. The process must be well characterized, and all variables that impact the product yield and quality must be known. In most cases, the scaling will not be a result of a conclusive and straight-lined experimental data, but rather a result of an accurate analysis of the experimenter, which depends on their experience, ability and intuition (Marques et al. 2010; Schmidt 2005). The interaction with other developers must be frequent, since the strain development, the fermentation process, downstream process, and sustainability assessment work like a chain, and are strongly linked.

41.4 Bioprocess Downstream—Separations and Purification

Downstream process (DSP) is an important pillar of the industrial bioprocess to obtain a purified bio-product. It follows a sequence of unit operation, which usually consists of initial recovery, purification, and polishing.

In the initial recovery, there are a cell separation from the broth, step performed mainly by centrifugation, filtration, or flotation. For intracellular bio-products (Fig. 41.2), the cells must be broken, and the cell debris removed. The cell lysis could be performed by operations such as high-pressure homogenizer, mill, or an enzymatic method. The clarification obtained from cell homogenate can follow steps such as concentration, purification, or formulation. Already for extracellular bio-products (Fig. 41.2), the clarified broth can be concentrated by precipitation or ultrafiltration, followed by purification and formulation (Harrison et al. 2015; Roque et al. 2004; Sutherland and Chase 2011). Therefore, DSP usually entails several unit operations to obtain the product to the required specification. However, it is not just about to achieve the required purity, the DSP must be robust, reliable, and scalable.

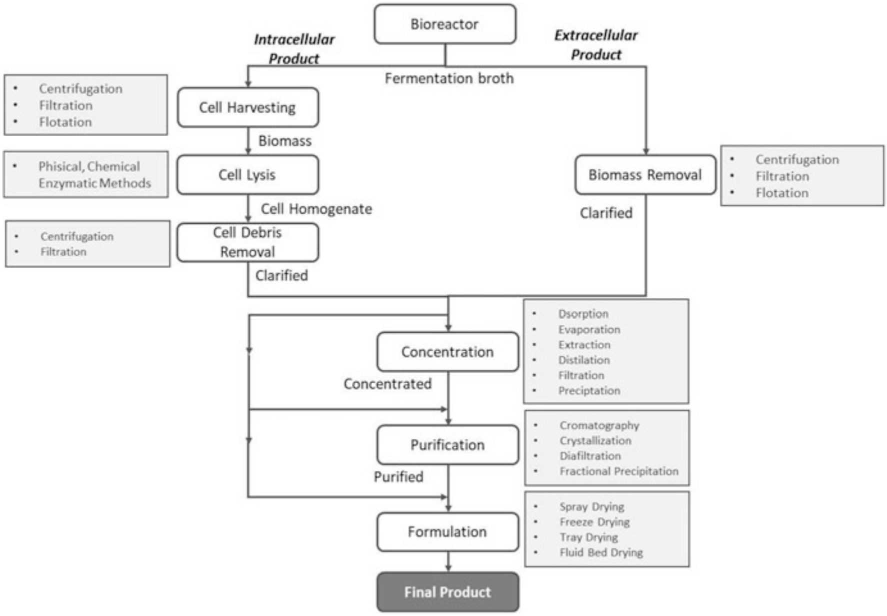


Fig. 41.2 General steps and operations involved in a bio-product purification

For that, essential parameters such as purity and recovery yield must be monitored (Rosa et al. 2010).

In this section, we will focus on lactic acid purification produced by fermentative route. Indeed, depending on the application of the lactic acid, a specific purity is required: industrial grades 88–90%; food grades 25–90%; pharmaceutical and cosmetic grades 90%, and specialty grades 80–98%. Therefore, a set of DSP steps are necessary to achieve the purity grade (Komesu et al. 2017b).

After fermentation process is generated, a whole broth composed by cells, residual of sugars, components from previous steps (pretreatment and hydrolysis of lignocellulosic materials) to obtain fermentable sugars, salts, media components, by-products, besides the lactic acid, which demand multistep for lactic acid recuperation and purification. Downstream process is a key element to obtain cost-effective production of lactic acid in high purity, since the DSP is estimated for over than 50% of the production cost (Datta and Henry 2006; Kumar et al. 2020; Pal et al. 2009).

The fermentation for acid lactic production is carried out at near-neutral pH, hence, during the neutralizing process, it produce salt instead of acid, which is a challenge for purification. A traditional process applied for lactic acid recovery is precipitation, which is detailed below.

41.4.1 Precipitation

Precipitation process is an operation downstream, which consists of an obtention of solid from a solution. This step is usually carried out in the first stages of purification. The precipitation process allows to reduce the reaction volume by precipitation of the interest product and its resuspension in a smaller volume. Also, it can be used to purify through the fractional precipitation of the interest product, leaving the contaminating in the mother solution. This technique is relatively inexpensive, can be carried out continuously, and with simple equipment (Harrison et al. 2015).

During fermentation, lactic acid is produced and accumulated in the broth, decreasing the pH, which is inhibitory to the cell. In the traditional microbial lactic acid production, calcium carbonate ($CaCO_3$) or calcium hydroxide ($Ca(OH)_2$) are usually employed to maintain the pH control around 5–7 producing calcium lactate salt. After fermentation, the broth is treated with sulfuric acid to convert the calcium lactate into lactic acid and calcium sulfate ($CaSO_4$), followed by filtration to obtain free organic acid. Then, the filtrate is evaporated to recover the lactic acid, which achieve technical grade between 22 and 44% (Fig. 41.3) (Datta and Henry 2006; Komesu et al. 2017a). For high purity (Fig. 41.3), it is required additional steps of esterification with ethanol or methanol, distillation to recover the ester, hydrolysis with water and evaporation to recycle the alcohol and obtain the pure acid lactic (Datta and Henry 2006).

Despite precipitation be a simple technique, it consumes high quantity of sulfuric acid and produces a huge quantity of calcium sulfate as a solid low-cost waste

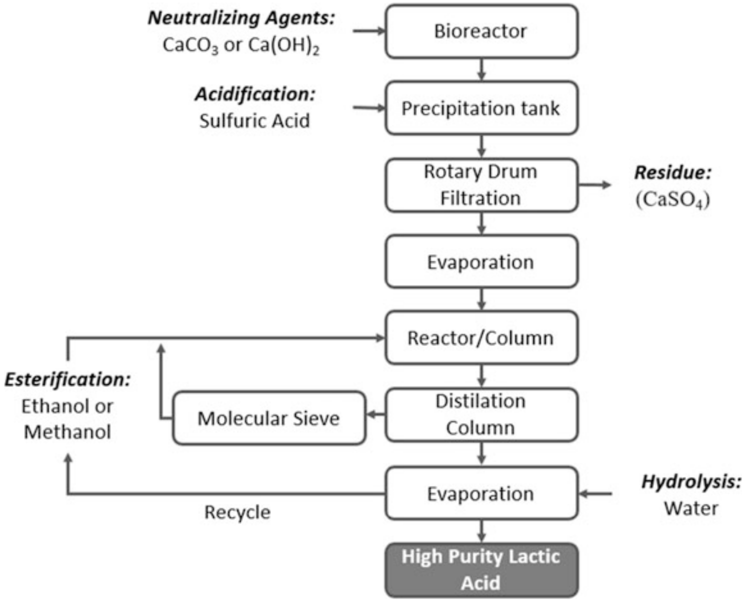


Fig. 41.3 General sequence of lactic acid recovery by precipitation

residue. Besides that, low purity of lactic acid often is achieved, demanding other steps to increase its purity (Kumar et al. 2020; Pal et al. 2009).

Approaches to improve the efficiency of lactic acid precipitation have been carried out. Kwak et al. (2012) proposed a precipitation process to recover alkyl lactate from ammonium lactate. Recovery of lactic acid from ammonium lactate solution by acidification with sulfuric acid is a difficult task, since ammonium sulfate [$(NH_4)_2SO_4$] has high solubility and lack of precipitation. The addition of methanol during the acidification of ammonium lactate decreases the solubility of the $(NH_4)_2SO_4$, which could be separated by filtration. The clarified with lactic acid was transformed into methyl lactate by an esterification reaction with methanol, which could be separated by distillation. The processes can be performed at room temperature with simple equipment, and the residual ammonium sulfate can be used to produce ammonia and sulfuric acid or be sold as low-cost fertilizer.

A patent issued to ZeaChem Inc, an alternative bioprocess using $CaCO_3$ as a neutralizing agent during fermentation and nitric acid as precipitation agent is described. This strategy allows lactic acid recuperation and concomitant production of ammonium nitrate processed as nitrogen fertilizer and $CaCO_3$ can be recycled in the process (Verser and Eggeman 2006).

41.4.2 Membrane Process Separation

An alternative lactic acid purification process is based on membrane separation, detailed below. Filtration process is an operation of downstream, which consists in a separation of a particulate from a suspension, according to their size, by flowing under a pressure differential. The filtration process can be conventional, where the fluid flows perpendicular to the filter element, or crossflow filtration, where the fluid flows parallel to the filter element to minimize buildup of solids on the filter. In bioprocess, conventional filtration is used for sterile filtration and for extracellular products, where the conventional filtration is employed to retain the cells in cake (solid phase) to obtain the product in the clarified phase (liquid). Crossflow filtration is used for separation of cells and its components, concentration and for exchange and remove of salts. A membrane process can achieve high levels of separation and purification and can be integrated into other operations such as bioreactors, eliminating the separation step in a compact design (Harrison et al. 2015; Pal et al. 2009).

In lactic acid production, the decrease of the pH is a bottleneck that can result in a reduction of the productivity. Membrane-coupled continuous fermentations (Fig. 41.4) have been carried out in order to remove the lactic acid produced (maintaining pH desired for fermentation) and ensure high cell concentration and productivity (Pal et al. 2009). Membranes of microfiltration, ultrafiltration, nanofiltration, reverse osmosis and electrodialysis can be employed to separate fermentation products from lactic acid produced. Depending on membrane porous size, different fermentation products are separated. Crossflow microfiltration retains only cells, while the permeate removes unconverted carbon sources, nutrients, proteins, salts, water, and lactic acid. Differently, crossflow ultrafiltration, retains cells and proteins, while removes unconverted carbon sources, nutrients, salts, water, and

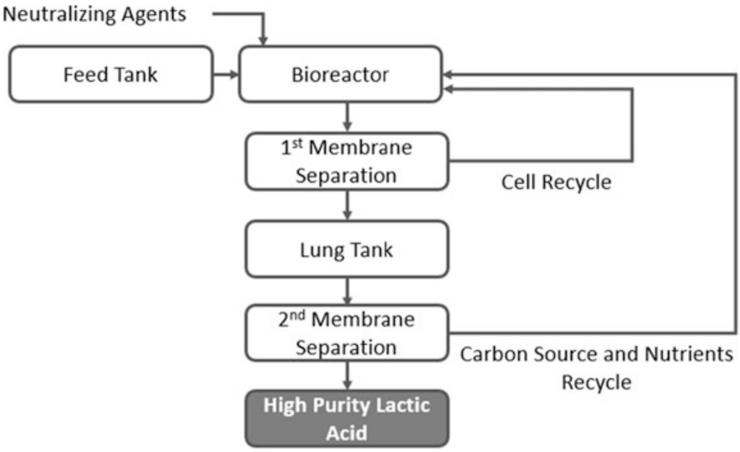


Fig. 41.4 Integrated continuous fermentation with membrane process in two stages. First stage—microfiltration or ultrafiltration membrane; second stage—nanofiltration or reverse osmosis

lactic acid. However, the permeate flux can be decreased due to membrane clogging, fouling and concentration polarization (Crespo et al. 1992; Diosady et al. 2005). The use of microfiltration is recommended before the ultrafiltration to increase the ultrafiltration efficiency, avoiding the fouling of the membrane by high molecular weight protein. Indeed, the fermentation with cell recycle by microfiltration or ultrafiltration results in a culture with high cell density and consequently in an increase of the viscosity and lowering of permeate flux, which can be overcome by cell bleeding (Crespo et al. 1992; Diosady et al. 2005).

Nanofiltration membrane can retain cells, unconverted carbon sources, nutrients, proteins, and salts, while removing water and lactic acid. The membrane process coupled in a bioreactor in two stages, first microfiltration followed by flat sheet crossflow nanofiltration as second step, can achieve monomer grade lactic acid with high productivity (Fig. 41.4) (Pal et al. 2009). US Patent employed a ceramic tubular ultrafiltration in the first stage for cell separation and a nanofiltration in the second stage, resulting in a long-term operation (Russo and Kim 1996).

In reverse osmosis, the separation is based on solution diffusion mechanism, which demands a high operating pressure. Reverse osmosis, as well as nanofiltration, retains cells, unconverted carbon sources, nutrients, proteins and salts, while removes water and lactic acid. In both strategies, unconverted carbon sources and nutrients can recycle in the bioreactor, while allow the lactic acid purification (Pal et al. 2009).

In electrodialysis (ED) the separation is based on the electromigration of ions through a stack of cation and anion exchange membranes. Applying an electric potential between the electrodes, cations migrate to cathode and anions to the anode (Pal et al. 2009). Electrodialysis is applied to remove salts from solutions or to concentrate ionic substances. It involves two stages: first, monopolar electrodialysis (MEP) separates and concentrates the lactate salt from the fermentation broth, while in the second stage, the bipolar electrodialysis (BED) converts the lactate salt into lactic acid (Hábová et al. 2004). For electrodialysis efficiency, it is necessary a cell-free broth, therefore, studies have been performed with microfiltration, ultrafiltration or nanofiltration prior to electrodialysis (Bouchoux et al. 2005).

Membrane-based technologies show high selectivity, resulting in high levels of separation and purification. The integration of the membrane with a fermentation process allows simultaneous production and purification, avoiding additional equipment and reducing equipment investment cost. However, the high cost of membranes, polarization and fouling are still a challenge for the use of these processes.

Other lactic acid separations include liquid–liquid extraction, molecular distillation, and reactive distillation (Datta and Henry 2006).

41.5 Sustainability Assessment

During the stages of development of a new process technology, it is extremely important to assess the sustainability of the process which is being scaled-up. Despite several advantages are being reported for the biochemicals production, not all biochemicals are consistently more sustainable than equivalent petrochemicals. This stresses the need for metrics to evaluate the new process's sustainability to guide the research decisions during the development.

The three key principles of sustainable development are economic, environmental, and social aspects. This section covers methodologies to assess the economic and environmental aspects during the scaling-up stage of the project. Social principal is not less important, but still a challenge in terms of methodology.

In typical industrial biotechnology, several decisions are made when designing an industrial plant, and these choices have impacts that need to be evaluated. For instance, during strain optimization, strains are mainly selected based on yield, titer, and productivity. However, the presence of some specific bio-products may lead to higher associated downstream processing costs. Likewise, for proper downstream separation of impurities, extensive use of chemicals or utilities may increase environmental impacts. Very often, the environmental and economic performance implies trade-offs that should be considered and evaluated early in the technology scale-up. An iterative approach considering techno-economic and environmental impacts can optimize the final biochemical process.

Assessing the economic viability of future technologies is part of the product development in biotechnology. This chapter focus on economic assessment during the scale-up stage of a process.

41.5.1 Assessing the Economic Sustainability (Techno-economic Analysis)

The cost estimation methodology for the scale-up stages of biochemical development is similar to the methodologies applied to estimate the cost of the industrial plant. Here it is important to stress the main goal of the process scale-up is to design a complete process, from the feedstock to the final product for a specific application and to decrease the technical and economic risks for the investment. The cost of the final industrial plant must be assessed as well as the cost of the scale-up step, which includes the cost of operation of a pilot or demo plant.

The economic feasibility of any new process depends on the overall yields and costs associated with the production process. The costs can be classified as capital and operational costs. Capital costs are related to acquisition of the required equipment, automation, infrastructure, buildings, engineering and construction and contingencies, and others, that are required to build an industrial unit. The operational costs refer to the expenses to run the process and are proportional to the plant output or operation rate. It includes raw materials, utilities, consumables (chemicals and catalysts), effluent disposal, packing, maintenance, and labor.

Specifically for the scale-up steps, it must be considered if there is an existing pilot plant facility. In this case, scale-up planning should first consider whether a retrofit would be necessary and must estimate the related costs of it. Secondly, the scale-up should establish the experimental program and schedule and estimate the operation costs related to this plan. The former mentioned costs related to the equipment are Capital costs (CAPEX), while the costs related to the operation of the facility are the operational costs (OPEX).

A pilot plant is a collection of equipment designed and constructed to demonstrate technical feasibility of a new process and its performance.

In some cases, a company may desire to invest in his own new multipurpose facility to have a research installation where the innovation project portfolio can be proven. This is not the general case once high investments are necessary to build and erect a new installation.

However, most of the time it is more advantageous to contract services of a pilot plant platform and the scale-up development team. There are some examples of facilities in the world dedicated to the development of new processes, such as BBEU (Bio Base Europe Pilot Plant), CBP Fraunhofer, BPF (Bio-based Process Pilot) and Pilot Plant at LNBR/CNPEM [Brazilian Biorenewables National Laboratory (LNBR), part of the Brazilian Center for Research in Energy and Materials (CNPEM)].

41.5.1.1 Capital Cost (CAPEX)

Cost estimation strategies for pilot or demonstration plants are similar to the costing of the industrial facility, however, the small scale of these facilities implies more error, and final estimate can have lower accuracy. The installation costs, construction, labor and overhead represent a larger percentage in pilot and demo plants.

There are three basic methods for estimating the costs of a new pilot plant: similarity, cost ratios and detailed labor and materials (Palluzi 1991)

- Similarity involves estimating the cost of design and construction of the new pilot plant based on a similar unit. It is a fast method, nevertheless, it has low accuracy with errors of ±100%. It can be used as an order of magnitude at very early stages of the research when little piece of information about pilot plant cost is available.
- Cost ratios involve estimating costs by relating the overall cost of the pilot plant or part of the pilot plant to a known factor such as the cost of main equipment, the number of control loops, the size of the equipment, or a variety of similar factors. The cost is estimated by using the ratios to develop the cost of the entire unit or of some subsystems. Although cost ratios are a widespread methodology for plant-estimating tool, the cost ratios are rarely available for pilot plant equipment. Typically, the accuracy is ±25–50%.

- Detailed labor and materials estimation involves breaking the pilot plant construction down into a detailed series of small tasks and estimating the labor and materials required for each separate task. This method has accuracies of ±10–20% but requires more effort than the previous methodologies.

A good practice is to use similarity or cost ratios estimation methods at the early stages of the research when low accuracy is accepted. Detailed cost ratios or detailed labor and materials estimates are generally developed prior to appropriation of funds to have a more accurate estimate for budgeting and cost control (Palluzi 1991).

The reduction of the time involved between the beginning of the pilot plant project and the data generation is always a concern. An average time of 6–18 months to progress through this process (3–12 months for design, 3–12 months for construction and 1–6 months for commissioning and start-up). This time can be decreased if careful and detailed planning is done.

41.5.1.2 Operational Cost

The costs for operating a pilot or a demo plant are a summary of the feedstock costs, product disposal, utilities, operating labor, spare parts, maintenance, and support services during the planned timeline for scaling. To have a forecast of the operation cost, some preliminary mass and energy balances must be done based on first assumptions and process basic design. Modeling tools using available commercial simulators or simple excel datasheets may be used to have a first figure of the mass and energy balances.

41.5.2 Assessing the Environmental Sustainability

The environmental sustainability of biochemicals is becoming increasingly important. During the stages of the technology development, environmental impacts can be preliminary assessed by tools such as Life Cycle Assessment (LCA). As the project advances, the performance indicators of the process are continually updated, and the initial environmental assessment tools should be periodically revised.

LCA is an import tool to compare environmental impacts of bio-based to traditional fossil products, and it is important to emphasize that the fact of using a renewable feedstock and a biotechnological process is not a guarantee that the product has less environmental impacts. Green routes use renewable feedstocks, but often generate very low product concentration, which needs to be purified. If the process design is not carefully done using heat thermal integration and water recycle, final process may not be more environmentally friendly when compared to the traditional route. This reinforces the need for LCA assessment during the research to guide design selection to have a good trade-off between economic and environmental aspects.

41.5.3 Managing Risks

The scale-up step is the most potentially risky of all phases of new process development. Some of the risks faced during this step are described here, as well as some recommendations of how to mitigate them:

- *Technical Risks*

  The use of unproven technology in scale-up is an unavoidable risk, as very often an innovative technology is required. Because of this inherent risk, the scale-up design should be conducted in a way to minimize the risk of using unproven technology or have a mitigation alternative. The designer should, whenever possible, use technology that has been proved through use in commercial facilities or should consider it as a possible mitigation plan.

  The integration of multiple new technologies tends the system to more complexity. If possible, the design of the process should be simple. The use of modular scale-up equipment and flexibility of having other candidates of unit operations that can substitute the main design is also recommended.

- *Operational Risks*

  It is highly recommended to have a plain for the scale-up program as well to set a training program for the operational team. Sometimes, if some disturbances of the process are expected, it should be investigated at lab scale to prepare a “what to do” plain to mitigate and inform the operation team. Biotechnological processes face risks of contamination, and the septic control is an important consideration for the design and for the elaboration of operation procedures.

- *Regulatory Risks*

  The scale-up must consider a variety of regulation standards related to govern workplace safety and waste disposal. Compliance with regulation must be thought from the earliest stages because of the potential costs involved. Waste disposal regulation, safety at workplace regulation, product regulation, GMO regulation must comply.

  Finally, to conclude this topic, it is worthwhile to stress that a successful scale-up does not guarantee successful commercial plant operation, however, it considerably decreases the risk.

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