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Inamuddin · Anish Khan *Editors*

Sustainable Bioconversion of Waste to Value Added Products

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Contents

Bioconversion of Biowastes for Energy Applications

Anil M. Palve, Ravi Arukula, and Ram K. Gupta

Abstract

The evolution from fossil energy to bioenergy economy demands the scientific breakthroughs and advancements in modern chemical manufacturing. For sustainability, the generation of chemicals and fuels must be originating from renewable resources. The white biotechnology, a technology that uses living cells such as bacteria, yeast, and fungi to produce degradable products, can deliver the essential enzymes for bioconversion of wastes into products that can be used for energy applications. Biowastes from various sources including industrial management (pulp, paper industry, and food industry), fruit and vegetable, animal (slaughterhouse waste), waste wood, and agriculture could be utilized as sustainable materials for nutrient-complete feedstock creation and biorefinery development. This chapter mainly emphasizes the possibility of utilizing biowastes from the existing waste management for the creation of chemicals, byproducts, and biofuels through various bioconversion processes. The first portion of the chapter deliberates the recent prominence and forecasts on feedstock creation of chemicals and biofuels. In the second part, the various sources of biowastes from existing waste management sectors and different bioconversion methods are systematically discussed. The third part presents the applications of biowastes for value-added products, chemicals, and biofuels. It is noticeable that the generation of compounds for chemical industries and biofuels for sustainable future via bioconversion of biowastes for energy applications is a significant research area with remarkable prospects for large-scale industrial production to meet the growing need for energy sustainably.

1 Introduction

The large-scale generation of biowastes from different sources is a global challenge for the human race. It is possible to transform this challenge into an opportunity by converting biomass into value-added products. By converting biowastes into energy, we can minimize our dependency on fossil fuels, a source of energy that takes several years to regenerate. The utilization of renewable biomaterials and biowastes for energy is another way to develop a nation sustainably without harming the planet. Currently, many possible alternatives to fossil fuels such as wind, hydro, and solar are being used. Biowastes generated via various sources have the potential to use for energy applications, however, the majority of biowastes are being used for landfills, burning in the open atmosphere, dumping on the ground, and releasing in the marine which causes detrimental effects to the environment (Mihai and Ingrao 2018). Even in developed countries, there are very few cities that use systematic disposal mechanisms of sewage and other biowastes.

Since ancient times, it has been observed that biowaste generation increases as the population grows. With the development of industrialization and an increase in the population, the biowastes produced from various sources, e.g., forest and wood industry, agriculture sector, agro-industry, municipal waste, animal waste, food processing, paper industry, etc. are increasing every year and creating challenges for waste management (Wang et al. 2018; Tan et al. 2018; Bhatia et al. 2018). Government, environment agencies, and scientists are looking for a better way to handle the wastes. Scientists and researchers are

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developing systematic processes for the conversion of biowaste into bioenergy (Farmanbordar et al. 2018; Cardoen et al. 2015). The conversion method is largely determined by the type of biowastes used for the production of bioenergy. Generally, biowastes are subdivided into two main types: (i) waste biomass and (ii) energy crops. The details of these biowastes are discussed in the following sections.

1.1 Waste Biomass

This type of biomass is generated through forest residues, agriculture, animals, food waste, and municipal waste (Bhatia et al. 2018). If all these bioresources are left to biodegrade in an uncontrolled way, it may be very harmful to the environment. This would lead to an increase in pollution, which transforms into contaminants and produces climate affecting gases. The ultimate effect of uncontrolled waste management is global warming (Idehai and Akujieze 2015; Wang et al. 2017). Conversion of these biowastes to commercial applications is necessary for sustainability in the present era. The biowastes can be transformed into high-value materials such as biogas, biodiesel, bioalcohols (methanol, ethanol, propanol, etc.), electricity, charcoal, syngas, and heat energy. In the conversion of biowastes to value-added products, different methodologies have been developed. The process of conversion of biowastes into value-added products can be divided into two groups: the biological and the physicochemical methods (Fig. 1).

The biological methods involve an anaerobic digestion, microbial enzymatic, fermentation and composting, microbial fuel cell, etc. The anaerobic digestion process is mostly used in the generation of methane and hydrogen gases (Wang et al. 2016; Borja et al. 2003). The anaerobic digestion process can be combined with other processes to produce biofuel as shown in Fig. 2.

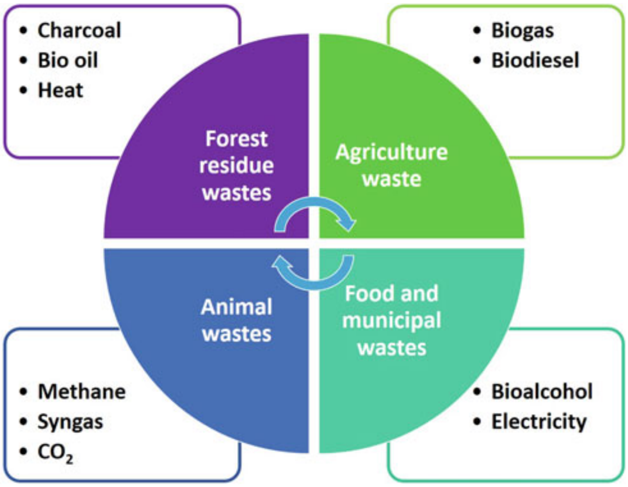


Fig. 1 Graphical illustration of the use of biowastes for bioenergy using biological and physicochemical processes

Liu et al. used zero-valent iron for improved methane generation by using wastewater sludge (Liu et al. 2015). It was observed that the chemical properties of iron have a significant effect on the production of methane. The production of methane was higher when either clean or rusty iron was used than iron powder. A few reports also suggested an improvement in methane production using different parameters and methods such as alkaline microwaving pretreatment (Yu et al. 2017), the effect of sonication (Aldin et al. 2010), solid concentration, and temperature (Paritosh et al. 2019). The transesterification method is the main method applied for the generation of biodiesel from various sources like jatropha oil (Lau et al. 2016), waste cooking oil (Degfie et al. 2019), frying oil (Vastano et al. 2019), etc. Also, a few innovative techniques such as a fluidic system (Yeh et al. 2016) and co-solvent method (Thanh et al. 2013) have been employed for the enhancement of bioenergy production. Nowadays, a few nanocatalysts are also employed for extensive and greener creation of biodiesel such as CaO (Degfie et al. 2019), carbon nanotubes with iron oxide (Fan et al. 2017), and iron-doped zinc oxide (Baskar and Soumiya 2016). Bioalcohols such as methanol, ethanol, and butanol are produced using the fermentation process (Bušić et al. 2018; Luque et al. 2008). The innovative organisms named electricigens offer the possibility of efficiently converting organic compounds into electricity (Liu et al. 2014; Lovley 2006). The assessment of the finest use of biomasses for heat, electricity, and transport purpose has been investigated in Europe (Steubing et al. 2012). An energy system model was proposed and various methodologies for the generation of energy using fossil and biomass were compared. It was observed that conversion efficiency was the key factor for the optimal use of biomass for these applications. It was further noted that woody biomass is the paramount material for energy generation if fossil fuels have to replace.

The physicochemical process involves pyrolysis, hydrothermal carbonization, gasification, landfill, and incineration. For example, biochar and charcoal are being mostly produced using the pyrolysis method (Santín et al. 2017). Biochar and activated carbon produced via pyrolysis are cost-effective and can be used for the removal of micropollutants in wastewater, however, their effectiveness as micropollutants removal depends on biochar production conditions and treatment capabilities (Thompson et al. 2016). The carbon and charcoal are also prepared using hydrothermal carbonization of different biowastes like biorefinery waste (Ho et al. 2018), human waste (Afolabi et al. 2017), carbohydrates, and organic molecules (Hu et al. 2010). Biomass can be used to generate syngas, methane, and hydrogen via the gasification method (Richardson et al.

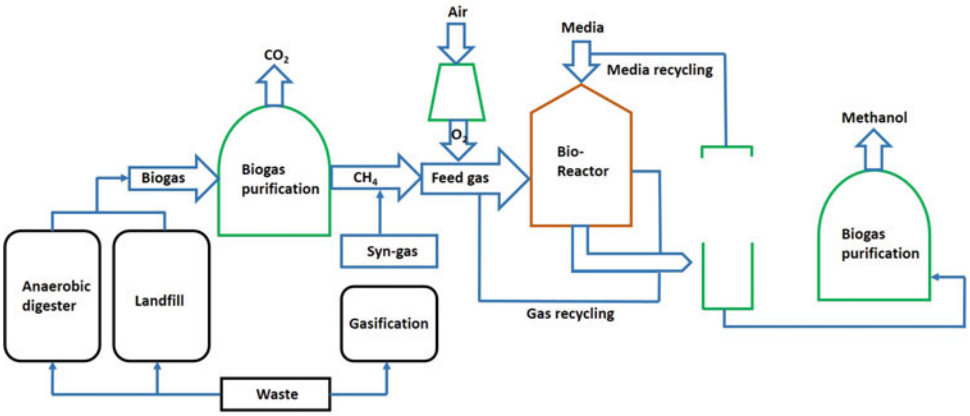


Fig. 2 Schematics for the biosynthesis of biomethanol. Adapted with permission (Paliwal et al. 2019). Copyright (2019), Springer, Singapore

2015; Terrell and Theegala 2019). Mostly, unmanaged biowastes are used for the landfill. Landfills generate mainly methane and carbon dioxide gases which leads to global warming. As the world is facing the problem of dumping of biowastes, systematic efforts toward the landfill in the production of biogas may become boon for human beings. Landfill gases have a promising potential as a sustainable supply of green energy (Powell et al. 2016; Jaramillo and Matthews 2005; Chen et al. 2015; Vrbová and Ciahotný 2017). Using these landfills, biogases can be generated through anaerobic, aerobic, or hybrid type (anaerobic-aerobic) bioreactors.

1.2 Energy Crops

Energy crops are defined as non-food crops useful for the generation of bioenergy and materials with higher market value. The presence of carbohydrates, oils, lipids, protein, and fiber in energy crops is important for the production of bioenergy for consumer and commercial applications. Generally, the yield of bioenergy depends on the amount of fibers in these crops; more fiber yields more bioenergy (Montross and Crofcheck 2010). Different types of bioenergy have been generated using diverse resources such as bio-oils from switchgrass forage and two sets of alfalfa stem (Mullen and Boateng 2008), short-rotation woody crops for woody biomass (Zalesny et al. 2011), solid biofuel from energy crops (Karampinis et al. 2012), bioenergy form ryegrass, sugarcane, willow, sugar beet, and Miscanthus Gigantes crops (Hattori and Morita 2010; Tonini et al. 2012). Agricultural waste is also used as energy crops material for the production of bioenergy (Ferronato and Torretta 2019). Bioenergy-generating crops are classified as biofuel crops, biomass crops, bioethanol crops, biodiesel crops, lignocellulosic crops, etc. Some countries, such as Mexico, have a relative abundance of agricultural land for the cultivation of energy crops because of the warm and sunny climate. With well-developed infrastructure facilities and easy availability of labor, it is possible to generate bioenergy from energy crops for commercial applications (Ruiz et al. 2016). Asian countries such as Japan, India, and a few more have paddy land for the cultivation of rice as energy crops (Hattori and Morita 2010). Energy crops are standalone as an alternative source for fossil fuels.

In the present situation, the world generates two billion tonnes of municipal waste every year. About 33% of the generated municipal solid waste are not utilized in an environmentally safe way. Worldwide, a person is responsible to produce about 0.74 kg of waste every day with high-income countries generating about 34% of the world's waste. As the population increases, the waste generated is anticipated to reach 3.40 billion tonnes by 2050. The projected waste generation, by region (millions of tonnes/year) by the World Bank, is given in Fig. 3 (Kaza et al. 2018). The conversion of biowaste into bioenergy is always a boon, but there are certain adverse effects of biowaste on the atmosphere and human life. Generally, countries follow the 3R rule: reduce, reuse, and recycle. If the wastes are disposed of in an uncontrolled way, there will be an impact on air quality and human life. Besides, uncontrolled disposing of wastes will increase emissions of greenhouse gases, pollute the marine system, pollute soil, and spread diseases (Ferronato and Torretta 2019). Various reports also mention the impact of biowastes on the environment, for example, air pollution due to the simple process of bioconversion such as the production of biochar from biowaste (Sparrevik et al. 2014). Biomedical waste dumping sites cause emissions of hazardous gases and an increase in heavy metal contents like chromium, zinc, nickel, lead, and copper (Manzoor and Sharma 2019; Chionyedua Theresa 2014). Municipal biowaste generates gases such as methane, carbon dioxide, carbon monoxide which lead to global warming issues (Vieira and Matheus 2019). Municipal waste also causes soil, water, and air pollution (Colón et al. 2012). Animal biowaste may impact the processing of other biowastes

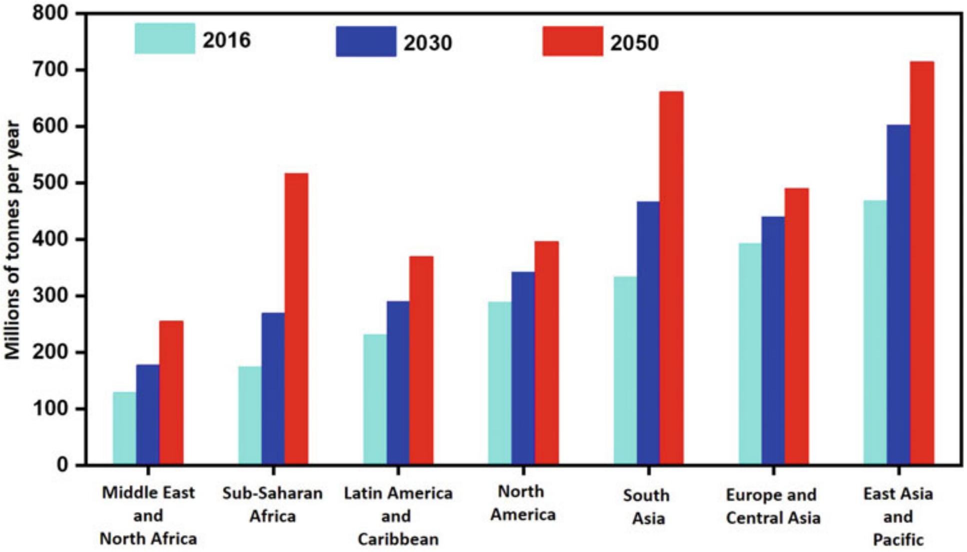


Fig. 3 Projected waste generation by region (millions of tonnes/year). Adapted from (Kaza et al. 2018)

(Huang et al. 2000). In the case study of Ningxia irrigation, China shows that the biochar adjustment decreases paddy soil nitrogen discharge but enhances the greenhouse gases (Wang et al. 2017). The issues such as waste generated in medical sectors need to be restructured (Datta et al. 2018). Industrial creation of biogas from lignocellulose has a significant role in the production of energy but needs to resolve technical issues that stem from poor understanding. It is also necessary to study the nature and number of microorganisms selected for the conversion of organic waste to biogas. Anaerobic digestion technology needs to upgrade its methodology and technology. All issues of biowaste and its effects on society and sustainability should be attempted in systematic planning and execution.

The World Health Organization (WHO) has suggested 17 sustainable development goals (SGDs) for all countries. They are mainly related to health and energy. Biowaste mismanagement is a worldwide concern in terms of environmental issues, social cohesion, and economic sustainability, which requires an integrated appraisal and comprehensive approaches for its solution. If not, then any country can face problems due to unregulated biowaste disposal. Many countries are making sincere efforts in the conversion of biowaste to bioenergy. Many countries are also encouraging their industries to create materials with high dollar values like biogas, biofuels, bioelectricity, etc. based on the waste generated by their own companies and nearby areas. Different studies were reported to overcome these issues by implementing novel technology and parallel methodology. A few initiatives in this area have been started such as the implementation of waste-to-energy plans and technologies (Ouda et al. 2016) and the use of biochar for phosphorous in agricultural soil (Glaser and Lehr 2019). Novel approaches can convert the biowaste or byproducts obtained during the conversion into value-added products more effectively. The following examples show that systematic efforts have been made by the scientific community. Some cost-effective strategies to recycle biowaste for green energy applications by converting them into high surface area carbon (Liu et al. 2020), conversion of eggshell waste to an adsorbent for contaminated water treatment (Mignardi et al. 2020), increasing efficiency of biogas production using nanoparticles (Shuttleworth et al. 2014), corn silk-derived carbon after activation for Na-ion storage applications (Vadivazhagan et al. 2018), application in sub- and super-critical water (Pavlovič et al. 2013), thermal hydrolysis (Allegue et al. 2020), etc. are reported.

2 Methods of Bioconversion

2.1 Bioconversion Process and Its Importance

Bioconversion is also referred to as *biotransformation*, which involves the transformation of organic materials (biowastes) into valuable materials or renewable energy resources via biological processes. This strategy signifies an auspicious and eco-friendly choice to substitute the traditional chemical methods applied presently for the generation of fuels and chemicals. Bioconversion processes mainly focus on sustainable resources such as biowastes and pollutants, which are considered foremost feedstocks. However, the feedstocks such as biomass (Periyasamy et al. 2018; Nghiem et al. 2018; Xiu et al. 2017), wastewater (Ben et al. 2016; Filho et al. 2017), waste gases (Iswmaw et al. 2019; Axelsson et al. 2012), solid waste (Scientific et al. 1981; Mahboubi et al. 2017; Chalima et al. 2017), sludge (Smoliński et al. 2019), glycerol, and other biorefinery byproducts were well scrutinized (Matsakas et al. 2018; Abghari and Chen 2017; Garlapati et al. 2016). Bioconversion processes are typically performed in bioreactors that might be governed in a batch, semi-continuous, or continuous approach. But definite bioreactor configurations might be chosen for specific bioconversion applications. This technology could be useful in the conversion of solid phase into the gas phase along with liquid bioprocesses. For any feedstock, bioreactor configuration, biocatalyst, and operating conditions should be optimized concerning chemical composition and pH range (Abghari and Chen 2017; Ginésy et al. 2017). The bioconversion process is ecologically friendly and is an alternative to both conventional chemical procedures and petroleum processing processes. Such a process also encourages the generation of a wide array of value-added end materials through low-cost biocatalysts with moderate reaction requirements.

2.2 Sources of Biowastes Generation

As mentioned above, “biowastes” refer to biodegradable materials, including vegetable wastes, fruits, domestic wastes, agriculture waste, animal and industrial wastes, etc. However, the biodegradability of these materials is mostly determined by the microbial strain and chemical structure of the components. Several types of biowastes and their corresponding bioconversion methods are discussed as follows (Fig. 4).

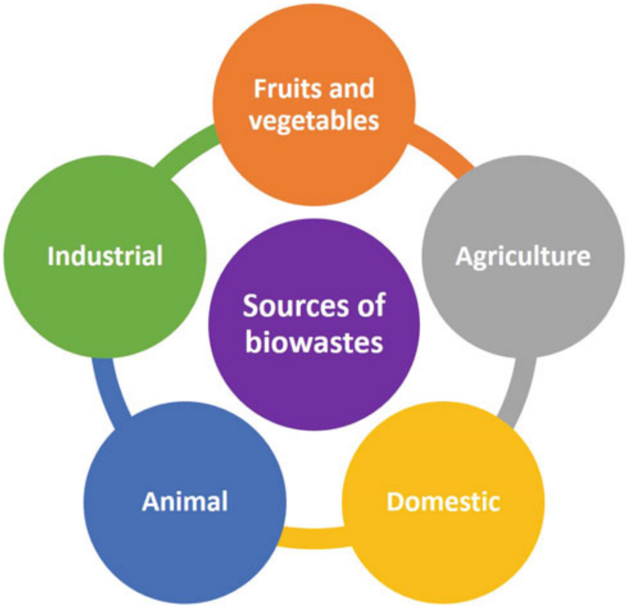


Fig. 4 Classification of various sources of biowastes for bioconversion processes

2.2.1 Fruits and Vegetable Wastes

As per the Food and Agriculture Organization (FAO) of the USA, 790 million tonnes of fruits along with 950 million tonnes of vegetables were produced in 2014. Both fruits and vegetables are high energy and nutritious food items containing solvable carbohydrates, minerals, vitamins, good fibers, and other bioactive components (Schieber 2017). From farm to fork, fruit and vegetable wastes are mostly produced from the following steps starting from cultivation, processing, boxing, and shipping (Ji et al. 2017). Sometimes these items are rejected from customers when they are subjected to wounding, staining, thermal exposure, and microbial attacks (tainted and unwanted surface growth). This leads to heavy fiscal damage of about US$ 484 million per annum because of the wastage of around 50 million tonnes of fruits and vegetable waste (Panda et al. 2016). As per the report obtained from FAO, in 2014, UK produced about 5.5 million tonnes of potatoes from which about 13% of the cultivated crops did not reach the consumer and were wasted due to the “low-grade” standard at supermarkets. In general, produced waste is managed through animal feeding, dumping on land, burning, and composting. These dumping methods induce serious ecological problems including emissions of greenhouse and toxic gases (Ji et al. 2017; Dessie et al. 2018). Such biomass must be used for value-added applications to avoid such problems.

2.2.2 Agriculture Waste

Agricultural waste is an organic and biodegradable material that possesses minerals, proteins, fibers, and vitamins. The agricultural sector generates mostly lignocellulosic wastes like straw (dry stalks of crops), molasses, spent grains, bagasse, husk (wheat, rice, and maize), shells (groundnut, walnut, and coconut), cotton stalks, and plant waste every year around the world (Madurwar et al. 2013; Dai et al. 2018). Lignocellulose wastes largely contain three main components including lignin, cellulose, and hemicellulose (Madurwar et al. 2013). As per 2013, FAO reports around 250 million tonnes of plant wastes were produced from various crop processing (Heredia-Guerrero et al. 2017). Typically, all these agricultural wastes are either burned or rotten in the fields, which cause serious air contamination (emissions of lethal gases, for instance, CH_4, N_2O, and SO_2, and soot, etc. into the atmosphere) as well as high soil and water contamination. However, agricultural biowaste is promising and resourceful material for the generation of wide-range materials including bioplastic and bioethanol using different portions of a plant (Heredia-Guerrero et al. 2017; Krishnan et al. 2010; Chandel et al. 2012). Some efforts are going on to properly utilize these wastes. For example, China is utilizing straw for bioenergy production. Zeng et al. observed that straw is the leading (over 70%) source of bioenergy from biowaste in China (Zeng et al. 2007).

2.2.3 Domestic (Household) Wastes

The increased urbanization, population, and fast economic growth resulted in increased food consumption, which leads to an increase in kitchen waste production (Zhao et al. 2017). Domestic wastes are typically generated from households, dining centers, public cafes, institute and factory canteens, etc. (Zhao et al. 2017; Liu et al. 2019). Usually, kitchen waste consists of vegetables, fruits, eggshells, meat, cooked food wastes, oil, and grease. Mainly, it contains polysaccharides (such as cellulose, hemicellulose, starch, etc.), lignin, protein, fats, inorganic salts, and a few organic acids (Chen et al. 2017). At present, China generates over 30 million tonnes of domestic remaining per annum. The European Union (EU) has been producing approximately 2.5 billion tonnes of food waste every year (Li et al. 2017). The conventional approaches to decompose kitchen waste including incineration, land-filling, composting, and discharge into the wastewater create harmful ecological health problems (Chen et al. 2019). Domestic wastes mostly contain biodegradable material which consists of high moistness and leads to the development of pathogenic microorganisms due to easy decomposition and breeding. This waste can be converted into valuable end-products including nutraceuticals, dietary fiber, antioxidants, fructose based syrup, single-cell protein, xanthan gum, etc. and are concurrently diminishing environmental pollution (Liu et al. 2019).

2.2.4 Animal Wastes

Animal waste is one of the most underutilized resources, especially the poultry and meat industries which are the leading sectors of a food chain system. As per statistics, the EU alone produces around 11 million tonnes of meat per annum. In 2006, Canada produced over 1500 metric tonnes of beef, which contributed about $26 billion to its total wealth. However, the production of such a large quantity of meat produced a huge amount of wastes such as abattoir and water (Ning et al. 2018). The animal waste mostly includes waste from poultry, pork, lambs, sheep, and cattle and is usually non-edible (Adhikari et al. 2018). Mostly, animal waste which comprises wool, feathers, skin, hoofs, horns, soft meat, bones, etc. is generating from the meat industries (slaughterhouse or abattoir). Owing to the nutritious composition, abattoir waste could be useful for numerous valued product yields including biomass for fish feeding (Yaakob et al. 2019), biogas produced from poultry, and animal litter (Adhikari et al. 2018), as well as methane gas generated through the anaerobic digestion of wastewater (Ning et al. 2018). Similarly, biodiesel was prepared from chicken manure and pork fatty waste using pseudo catalytic transesterification reactions (Marques et al. 2016). Besides that, animal waste also possesses versatile applications for cosmetic production development and the pharmaceutical industries. The conversion of animal waste into energy is a manure manage response for the ecosystem.

2.2.5 Industrial Wastes

A huge amount of waste and left-over cellulosic materials are being generated from industrial processing and other actions. The industrial waste mostly occurs in the form of pulp sludge from the production of paper, coffee grounds, cane sugar (bagasse pith), etc. Most of these materials comprise cellulose, hemicellulose, and lignin. This combination is known to be lignocellulose (Mathews et al. 2015). Nowadays, lignocellulose is used as a virtuous feedstock in many lignocellulosic industries for the advancement of numerous high-priced materials like pulp, paper, edible microbial protein, fuels, and chemicals using various bioconversion processes. On the other hand, India and other countries have been producing a huge quantity of cassava bagasse solid waste from sago industries. India has alone produced around 600 tonnes of cassava bagasse waste from the sago industry per day (Sugumaran et al. 2014). Owing to the minimal ash content, well nutritious composition (50% of starch), and high organic content, cassava bagasse works as an economical feedstock for a number of bioconversion procedures (Carta et al. 1999). Consequently, the bioconversion of these solid waste produces a variety of valued products like grain distiller, pullulan (polysaccharide polymer consisting of maltotriose), etc. and are useful to the society to diminish the environmental pollution (Sugumaran et al. 2014). The production of various biowastes and their possible usages in bio-industrial applications are presented in Table 1.

2.3 Various Bioconversion Processes

Compared to existing chemical and thermal pretreatment processes, the biological pretreatment process is green as well as energy-efficient. This part of the chapter focuses on the bioconversion technologies for converting biowaste to biofuels and chemicals, particularly the scientific models, possibilities, as well as future applications are discussed. The emergent advancements in bioconversion processes of four primary conversion pathways, including microbial, enzymatic, fermentation, and composting conversion techniques, are evaluated (Fig. 5).

2.3.1 Microbial Bioconversion Process

The microbial bioconversion technique gained huge attraction and has been progressively used to overcome the restrictions and environmental problems associated with the traditional chemical processes. This process involves a variety of microbes (microorganisms), for example, bacteria, yeasts, fungi, and microalgae (known as microbial enzymes)

Table 1 Biowastes from various sources and their potential usage

Type of product	Biowaste	Potential usage	References
Wood/paper industry	Sawdust or pulp	Biofuel and enzymes	Rathna et al. (2014)
Agriculture waste	Leaves, straw, husk, hull, stem, nutshell, and bagasse, etc.	Biogas, enzyme, and ethanol	Barakat et al. (2014)
Sugar industry	Molasses	Oligosaccharides and enzymes	Ghazi et al. (2006)
Oil industry	Fibers, sludge, husks, and shells	Bioethanol	Cerveró et al. (2010), Jørgensen et al. (2010)
Plant or animal waste	Fats, skin, fleshing wastage, horns, and bones	Biofuel and enzymes	Yazid et al. (2017)
Domestic food and municipal waste	Kitchen manure etc.	Biopesticides and organic acids	Ohkouchi and Inoue (2007), Zhang et al. (2015)
Industrial organic waste	Various slaughterhouse leftovers	Lubricants, surfactants, and fillers	Abraham et al. (2014), Yazid et al. (2016)
Fruits and vegetables wastes	Peels, fiber, seeds Kernel and stones	Biofuels, enzymes, and organic acids	Panda et al. (2016), Embaby et al. (2014), Botella et al. (2007)
Poultry processing waste	Feathers, skin, blood, fats, bones, liver, and intestines	Enzymes, and biofertilizers	Jayathilakan et al. (2012)
Nuts processing waste	Shells and pith	Bio-pulping, biochar, activated carbon	Mtui (2009)
Commercial and hotels waste	Coffee powder, waste tea leaves, outdated and waste diets	Biopesticides, bioethanol, and bioplastics	Jooste et al. (2013)

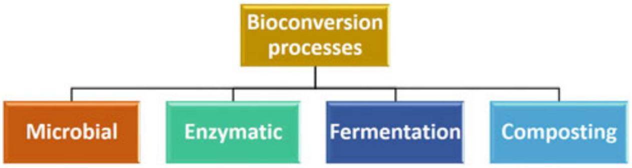


Fig. 5 Schematic illustration of various bioconversion techniques

for the conversion of biowaste to valued biofuels and chemicals (de Paula et al. 2019). As discussed in the aforementioned sections, the lignocellulosic biowaste conversion for biofuel production is a green substitute for fossil fuels due to the high availability of biowastes and less detrimental effect on the environment (Madurwar et al. 2013; Heredia-Guerrero et al. 2017; Krishnan et al. 2010; Chandel et al. 2012; Sarsaiya et al. 2019). The bioconversion of lignocellulosic biowastes to bioethanol is more difficult compared to the conversion of starch-based biowastes as it involves four steps: (i) the pretreatment, (ii) hydrolysis of cellulose and hemicelluloses to soluble monomers (pentoses and hexoses), (iii) bioconversion of these monomers to bioethanol through fermentation method, and (iv) purification of the final products. Bioethanol (biofuel) is one of the most significant materials which can substitute petroleum and is considered to be clean liquid fuel (Selim et al. 2018). The foremost challenge for biowaste conversion to bioethanol is attaining high yield which makes it cost-competitive with conventional fossil fuels. Cellulose is a main constituent of the lignocellulosic biowaste, however, cellulases (enzymatic hydrolysis) cannot be used effectively due to the low availability of crystalline cellulosic fibers and presence of hemicellulose and lignin on the cellulose surface (Dashtban et al. 2009). Hence, pretreatment is required to hydrolyze lignocellulosic biowaste using various approaches. Usually, in industries, acid and high thermal treatments are used for large-scale production. But, these approaches are very slow, expensive, and unproductive (Rubin 2008); however, those difficulties could be overcome by using microbes, including bacteria, fungi, and yeasts. For instance, the thermophilic fungal microbes, including *Thielavia terrestris* (Gilbert et al. 1993), *Thermoascus aurantiacus* (Gomes et al. 2000; Schuerg et al. 2017), *Sporotrichum thermophile* (Bhat and Maheshwari 1987; Singh 2016), etc., have thrived in literature as potential candidates for lignocellulosic waste bioconversion to sugars for large-scale industrial usage. The xylanases produced fungal microorganisms such as *Trichoderma*, *Penicillium,* and *Aspergillus* that possess elevated temperatures (approximately 60°C) in bio-industries. Similarly, the bacteria such as *Bacillus, Clostridium,* and *Pseudomonas* were used as promising hydrolytic microbial enzymes (Nigam 2013). The primary bottleneck problem is the conversion of biowaste into oligosaccharides. In this path, novel biological innovations are required to increase the productivity to reduce the bioethanol price. The enhancement in hydrolytic activity of microbes and inventing new suitable enzymes proficient for enduring acute environments has become of primary importance in several current reports.

In addition to this, a microbial fuel cell (MFC) device transforms the chemical energy from biowaste (e.g., wastewater) into electrical energy using microbes as biocatalysts under anaerobic environments (Sobieszuk et al. 2017; Mansoorian et al. 2013; Angosto et al. 2015). In a typical double (cathode and anode) compartment MFC, microbes are present in the anodic cell and oxidize biowaste (organic compounds) and produce electrons. The produced energy is then stockpiled in adenosine triphosphate (Sobieszuk et al. 2012). The generated protons from the anaerobic respiration process are moved through the proton permeable membrane to the cathode chamber and produce water by reacting with oxygen and electrons (Oliveira et al. 2013). Usually, the performance of MFC is specified based on obtained potential, which depends on the rate of the biowaste redox process by the microbes, the circuit impedance, the proton transportation towards cathodic cells through proton exchange membrane, reduction reactions at the cathode, etc. (Mardanpour et al. 2017; Zeng et al. 2010). A number of MFC configurations with different electrode materials, compartment numbers, and microbes were used as a biocatalyst (Hidalgo et al. 2015). Microbial fuel cells are potential candidates for wastewater and sewage treatment methods not only because of the producing electrical energy from biowastes but also due to a considerable reduction in the amount of sludge produced.

2.3.2 Enzymatic Bioconversion Process

After completion of pretreatment, polycarbohydrates (cellulose and hemicellulose) are hydrolyzed into soluble pentoses and hexoses using various enzymes. Scientists have discovered specific microbes from various biosources, with the perspective that those microbes would have an excellent ability to bioconversion as special enzymes. In many bioindustries, these enzymes act as biocatalysts to accomplish the reactions in an eco-friendly and economical method as conflicting to the usage of chemical reagents. Based on temperature, alkalinity, and acidity, the microbial enzymes are classified as thermophilic, alkalophilic, acidophilic, etc. A few enzymes with special characteristics are discussed as follows.

Amylase

Amylase enzymes are the most significant biocatalysts, and their main use in bioindustries is for starch-based conversion methods (Nigam 2013). An alpha-amylase enzyme, known to be endo-1, 4-α-D-glucan glucanohydrolase, randomly cleavage the α-1,4 bonding of contiguous glucose moieties in polycarbohydrates into small chain oligomeric sugars. The amylolytic and corresponding enzymes are considered as glycosidic hydrolases and were produced by a broad range of microbes (Singh et al. 1995; Sivaramakrishnan et al. 2006) and classified into exo, endo, and cyclodextrin producing enzymes. *Amyloglucosidase* is an exoamylase enzyme capable of breaking the α-1,4 bonding in starch to produce monomers. This amyloglucosidase cleaves the α-1,6 glyosidic bonds with sluggish rates and releasing β-D glucose (James and Lee 1997); however, the process can be efficient in an acidic environment and mild heat (Kumar and Satyanarayana 2009). The primary applications of these enzymes are in starch bio-liquefaction (for biofuels), sugar, paper, pulp, baking, and pharmaceutical industries (Nigam 2013). These enzymes possess large-scale production capabilities, including the production of commercial maltose syrup, glucose syrup, fructose corn syrups, decrease in turbidity to produce extended shelf-life for fruit juice, and starch saccharification in the brewing industry (Nigam 2013).

Protease

Among all the commercially available enzymes, the microbial protease enzymes are widely studied by the researchers (Vijayalakshmi et al. 2013; Mukherjee et al. 2008). In general, these proteases were prepared from three microbial environments which are alkaline, neutral, and acidic. Owing to the extraordinary activity and constancy in atypical circumstances of thrilling biological constraints, the basic serine proteases possess major applications in the bioindustry and are of specific attention being extra appropriate for a variety of bioconversion functions. These alkaline proteases show their ability to work even at a high pH range, elevated temperatures, as well as in the existence of constraint materials (Vijayalakshmi et al. 2013).

Ligninase or Laccase

Ligninase is a complex enzymatic system of three oxidative enzymes of manganese peroxidase, lignin peroxidase, and laccase. They are mainly used in bioconversion of lignocellulosic biowastes into monomers. Due to the combination of synergistic enzymes, these are extremely adaptable and are applied in a number of commercial progressions (Dahiya et al. 1998). Ligninolytic enzymes are mainly used in the pollution control system, bio-remediation process, and in the treatment of industrial wastes (sewage) comprising intractable and lethal chemicals like phenols, cloth colorants, etc. (Robinson and Nigam 2008).

Cellulose

Cellulose is the third most significant enzyme for the use of bioindustries and mainly used for the generation of glucose from cellulosic biowastes (Pandey et al. 1999). The primary

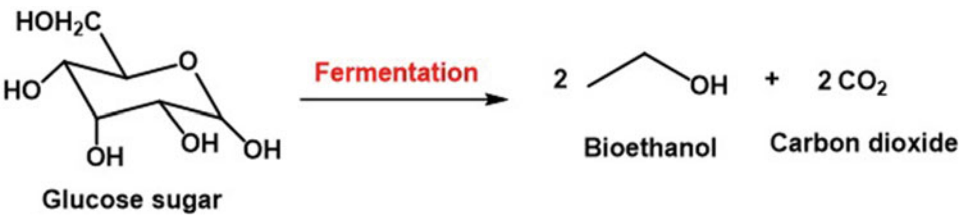


Fig. 6 The chemical process involved in the fermentation of sugar to produce bioethanol

importance of thermophilic cellulose hydrolyzing enzymes in manufacturing is the making of bioethanol as well as various valued end-products from agricultural wastes (Hardiman et al. 2010). Usually, cellulose is a complex of three main enzymes, which are endoglucanase, exoglucanase, and β-glucosidase. Owing to synergism, these enzymes efficiently hydrolyze the cellulose to glucose, cellobiose, and other oligosaccharides. The endoglucanase enzyme works on non-crystalline fibers of cellulose and converts them into small fibers comprising sugars. Finally, the exoglucanase enzyme produces cellobiose. Cellobiose hydrolyzes using the β-glucosidase enzyme and releases glucose. In addition to the aforementioned enzymes, other enzymes, namely hemicellulases, mannanase, inulinase, xylanase, lactase, invertase, pectinase, lipases, phytase, etc., have been used in industrial applications (Ravindran et al. 2018).

2.3.3 Fermentation Bioconversion Process

The fermentative production of biofuels, biopolymers, and value-added products through bioconversion of biowaste and byproducts is attractive for commercialization (Koutinas et al. 2014). Both biowaste and various byproduct sources from industrial segments including pulp, paper, and food industry could be used as sustainable possessions for biodiesel and bioethanol production using the fermentation bioconversion process. Bioethanol is a biofuel and platform chemical and an alternative to conventional energy sources. It is generated through the fermentation of various carbon resources, for example, lignocellulosic materials, starch content crops, and sucrose-based feedstocks. The process of the production of biofuel (bioethanol) thrived well in reports (Koutinas et al. 2014; Hamelinck et al. 2005). The cellulosic fragment of the lignocellulosic material is transformed into polysaccharides. The polysaccharides are converted to bioethanol upon the hydrolytic and the fermentation processes. Mostly, lignocellulose is hydrolyzed from an acid treatment, and the obtained sugars are then used to a bioethanol fermentation process using microbes like yeast. Since such hydrolysate sugars comprise not only glucose but also several monosaccharides including arabinose, mannose, xylose, galactose, etc., microbes need to proficiently ferment these carbohydrates for the fruitful industrial production of bioethanol (Katahira et al. 2006). The chemical process involved in the fermentation bioconversion is to convert glucose sugar ($C_6H_{12}O_6$) into bioethanol (C_2H_5OH) and carbon dioxide gas (CO_2) as given in Fig. 6.

2.3.4 Composting Bioconversion Process

Composting is a bioconversion of biowastes into materials that improve the earth's productivity, land strength, the capability to absorb water, and crop nutrients through the microbial process (Harindintwali et al. 2020). This process is mainly controlled through the microbiological, physiological, and physicochemical aspects. The composting process involves the degradation of organic waste, including sewage slop, food leftovers, and animal waste, to a manure-rich material that feeds plants and strengthens soil. Both fungi and actinomycetes are effective microorganisms in the composting bioconversion method. Bacteria such as burkholderia, pseudomonas, zymomonas, and xanthomonas, etc. are the most important decomposer microbes in the composting process (Sánchez et al. 2017). During the 1920 s, in Europe, the composting bioconversion process is being used to convert municipal waste and agricultural biowaste into an organic farming tool (Heckman 2006). Recently, the composting process attains additional interest and is accepted as a significant green process for salvaging biowastes. Five significant parameters greatly influence the composting process: (i) oxygen (aeration), (ii) nutrition (C/N ratio and the pH), (iii) moisture content (iv) temperature, and (v) microbial inoculation, which are deeply stimulated by the lignocellulosic biowaste composting (Vargas-García et al. 2007).

3 Application of Bioconversion Process for Energy

3.1 General Applications of Biowaste

Bioconversion processes are emerging industrial techniques with an innovative approach to realizing sustainability in the current generation. The main objective of the bioconversion

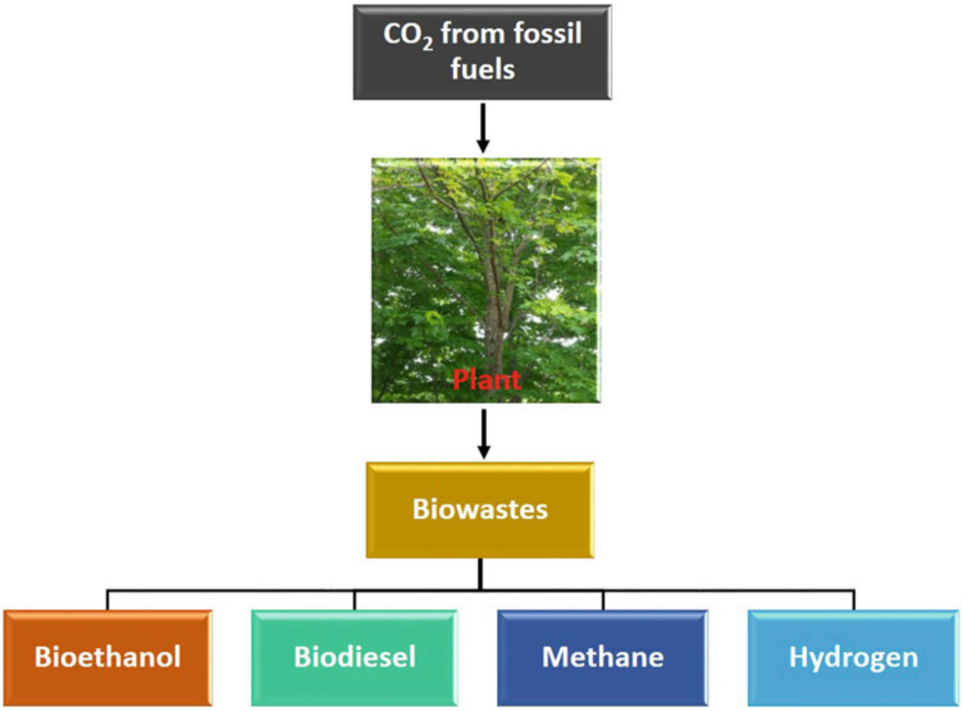


Fig. 7 Biofuels production from biowastes using various bioconversion techniques

process is to efficiently utilize biowaste in a cascading approach and produce several useful platform chemicals, bioproducts, and biofuels. Industrially, the value-added products or chemicals were mainly produced from the first-generation feedstocks (i.e., crops), and also from second-generation feedstocks (i.e., agricultural biowastes and lignocellulosic materials) (Srirangan et al. 2012). The first-generation feedstocks such as oilseed, corn, starch, and sugar crop often have a high content of carbohydrates, oil, and energy and are nowadays utilized for bioethanol (and also other bioalcohols), biodiesel (and also other bio-esters), and biogas production (Srirangan et al. 2012; Hein and Leemans 2012). Furthermore, agriculture waste acts as a promising, versatile material to synthesize a wide range of high-valued goods like bioplastic from plant shells (Heredia-Guerrero et al. 2017; Krishnan et al. 2010; Chandel et al. 2012). The application of lignocellulosic waste involves the production of drinks, food, textiles, paper, polymer products, biofertilizers, and chemical precursors of pharmaceutics (Deng et al. 2015). The domestic sewage could be useful to produce high-value end-products including nutraceuticals, dietary fiber, antioxidants, fructose-based syrup, single-cell protein, xanthan gum, etc. (Liu et al. 2019). Also, animal and industrial waste possess versatile applications for cosmetic production development, pharmaceutical industries, and valued products like pullulan (polysaccharide polymer consisting of maltotriose), biogas, etc. (Sugumaran et al. 2014).

3.2 Applications of Biowaste for Biofuels

In the present scenario, approximately 88% of the energy produced is based on fossil fuels (Wang et al. 2019). It is essential to meet global energy demand using renewable sources like solar power, wind energy, tidal, hydro, and biomass. The biowastes for energy conversion is the need of the present era. As mentioned, biowaste includes different sources including from crops. These biowastes can be used for the effective conversion of biofuels such as ethanol, methanol, methane, and biodiesel (Fig. 7). Initially, humans started using biowaste for heat and cooking of food. Presently, the application of biowaste for the generation of zero-emission fuel such as hydrogen gas is greener and a very popular approach.

3.2.1 Application of Biowaste for Ethanol

The bioalcohols include methanol, ethanol, and a minute quantity of propanol and butanol. These bioalcohols are formed by fermentation of sugars using different microorganisms. Bioethanol has higher flammability limits and a higher heat of vaporization than gasoline. This property of bioethanol allows shorter burn time. Therefore, bioethanol goes in front as compared to the gasoline internal combustion engine and can be utilized as a fuel or additives to fuel. The different feedstock sources such as corn (Wallington et al. 2012), potato (Widodo et al. 2015), sugarcane (Amorim et al. 2010), sugar beet (Tan et al. 2015), waste cake (Han et al. 2019), and any saccharide are used for the formation of alcohol using a fermentation process. Biowastes from corn, sugarcane molasses, wheat, etc. are mostly used as sources for the production of ethanol in several countries including developed and developing countries. The general biological process for the production of biofuel from lignocellulose biowaste was given by Canilha et al. (2012). During biofuel production, a pretreatment of lignocellulose, depolymerization of carbohydrate for making free saccharides, fermentation of saccharides to ethanol, and purification of ethanol are involved (Priyadarshan 2011). The ethanol production could be enhanced by attempting different methodologies. The enhancement in bioethanol production is reported using different methods such as the absence of lignin and prosperity of fermentable sugars and nitrogen (Sayed et al. 2018), pretreatment involving enzyme and basic solution (Bilal et al. 2017), high temperature (around 67 °C) in the absence of live yeast cells (Khattak et al. 2013), pretreatment with alkaline hydrogen peroxide (Karagöz et al. 2012), hydrolysis and fermentation (Guerfali et al. 2015; Gwak et al. 2017), etc. The detailed breakdown of the production of ethanol by countries is shown in Fig. 8.

While using ethanol as a source of fuel, it is necessary to study its impacts on air quality and health. Ethanol is the most widely produced fuel since it is produced crops which causes a less detrimental effect on the earth. But, CO_2 emissions by ethanol combustion is the most important concern of it as a source of fuel. The emission of carbon dioxide increases the level of global warming (Sadeghinezhad et al. 2014). This issue can be addressed by planting more trees. Different authors have reported the impact of the use of ethanol as biofuel. The use of ethanol as a biofuel has shown a surge in the amount of acetaldehyde in the surroundings which may affect air quality and human health (Millet et al. 2012; Hill et al. 2009). Traditionally, maize, as well as sugarcane stillage, were disposed of in rivers and ponds, and it became a considerable contaminant. Similarly, people burned the parts of plants such as leaves and tops before harvesting sugarcane (Wheals 1999). Another serious environmental concern is the degradation in soil that leads to erosion in intensive agriculture 10 to 30 times more rapidly in comparison to that in undisturbed soil (Pimentel 1991). Citrus waste has also great prospective for biofuel generation (Fig. 9) (Taghizadeh-Alisaraei et al. 2017).

3.2.2 Application of Biowaste for Methane

Biogas is green and sustainable energy as it is produced via the decomposition of biowaste under anaerobic conditions. The main sources of the biogas are food scraps, animal wastes, agricultural wastes, manure, municipal solid wastes, etc. (Pazera et al. 2015). The above sources decompose and produce a mixture of gases like CH_4 and CO_2. Production of biogas enlightens the major environmental problems such as dependence on fossil fuel energy to meet global energy demand, and the solid residue remains in the anaerobic digester are useful for the agriculture land (Das et al. 2019). Various studies are describing the generation of biogas through different resources such as household waste (Zamanzadeh et al. 2017), kitchen refuse (Singh et al. 2019), municipal biowaste in India (Breitenmoser et al. 2018) and Brazil (Moretti et al. 2020), cotton plant wastes (Ghasemian et al. 2016), rice straw (He et al. 2017), cattle manure with corn (Li et al. 2009), animal waste (Zhang and Ji 2015), etc.

Several studies are initiated to enhance the massive generation of biomethane gas using different resources, methods, and new technologies. Different methodologies such as mechanical, irradiation, thermal, chemical, and biological were studied for large yield production of methane gas (Dahadha et al. 2017). Also, the outcome of mixing sawdust-derived biochar into an anaerobic digester was studied for the enhancement of the generation of methane gas (Wang et al. 2019). Other methodologies such

Fig. 8 The details of the breakdown of ethanol production by country. Data adapted from (Alternative Fuels Data Center 2018)

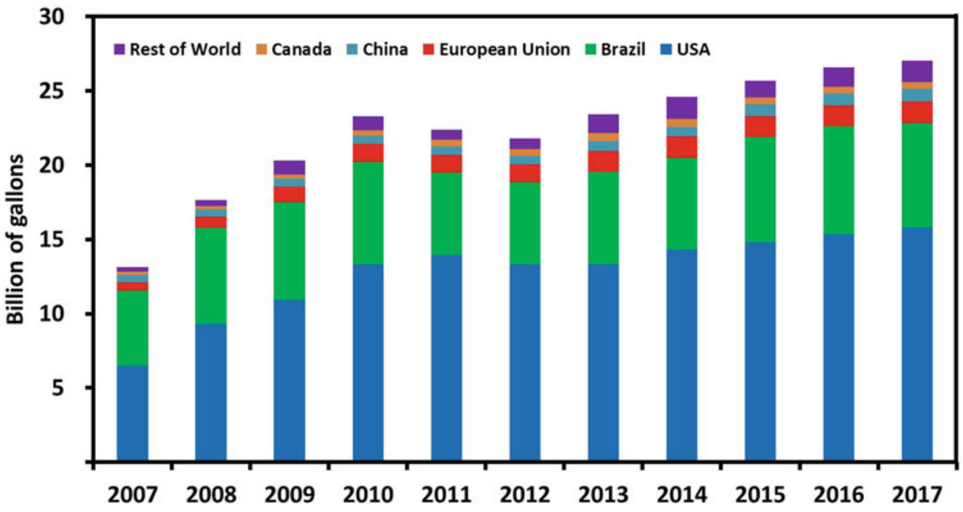
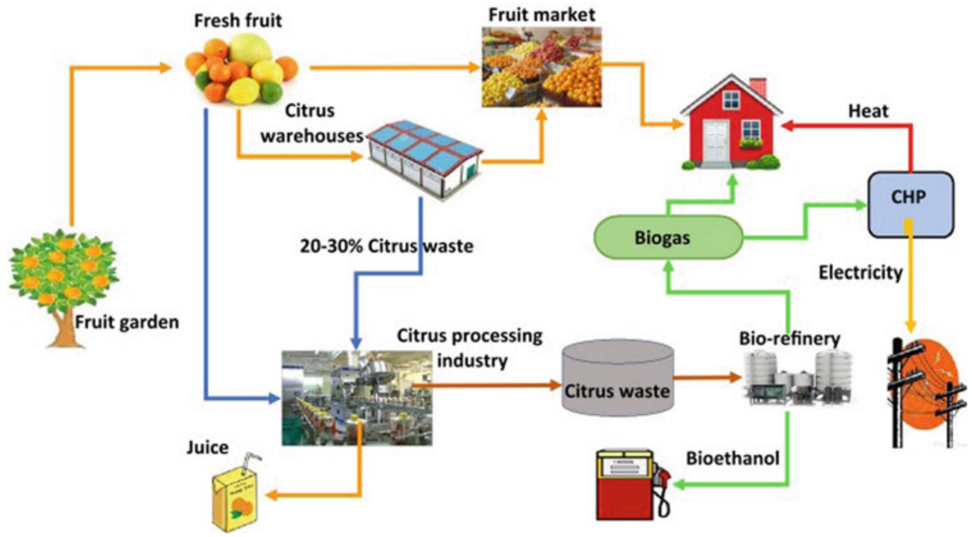


Fig. 9 Citrus waste for biofuels. Adapted from (Taghizadeh-Alisaraei et al. 2017), Copyright (2017), with permission from Elsevier.

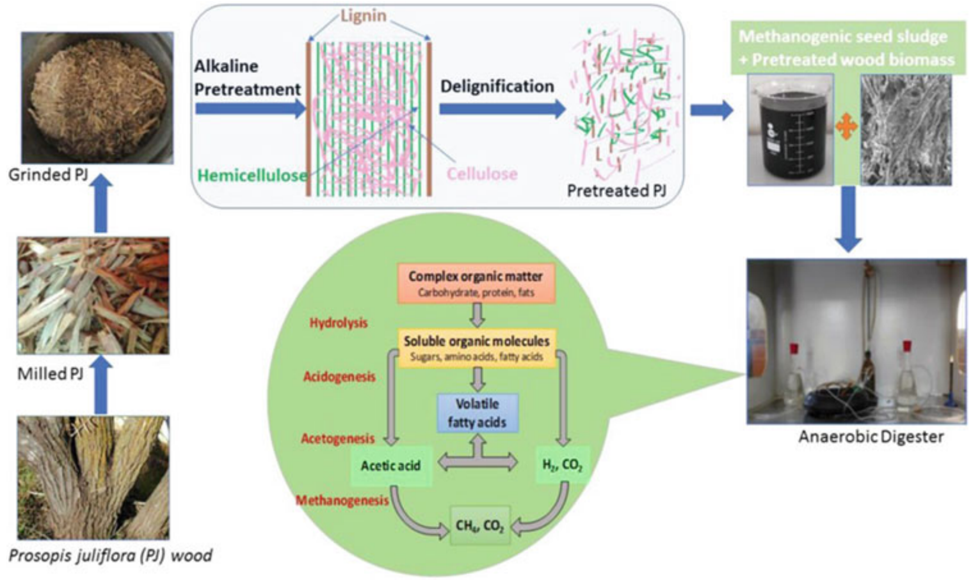


as a two-phase process (Cavinato et al. 2011), increasing the syntrophic interaction of different microorganisms for improved methanogenic reactions (Anukam et al. 2019), free nitrous acid, and Fenton technology (Karimi et al. 2020), microwave-assisted acid pretreatment (Liu and Cheng 2009), alkali-pretreatment (Thanarasu et al. 2019), etc. were studied. The process of anaerobic digestion for biomethane production is given in Fig. 10. During the production and utilization of the biomethane, it is obligatory to be aware of the public health risk and global regulations. A biowaste chamber includes a wide range of microorganisms which may lead to different contaminations and may be dangerous for humans (Liu et al. 2019). The growth of contamination is potentially harmful to sick animals as well as soil (Liu et al. 2019). The toxicity of combusted biogas in California is reported by Li et al. These results show that municipal waste biogas contained prominent levels of chemicals like aromatic hydrocarbons, siloxanes, and certain halogenated hydrocarbons (Li et al. 2019).

3.2.3 Application of Biowaste for Biodiesel

Different natural sources can be utilized to generate biodiesel, for example, rapeseed, soybean, flax, hemp, jatropha, and fresh as well as waste vegetable oils. The composition of biodiesel varies with the composition of the biowaste materials used. Certain limitation of the production of biodiesel has occurred due to lack of economically beneficial feedstocks. The outcome of the composition of waste materials on the production of biofuel was evaluated. The byproducts generated during these processes could also be

Fig. 10 The process of anaerobic digestion for biomethane production. Adapted with permission from (Thanarasu et al. 2019). Copyright (2019) American Chemical Society



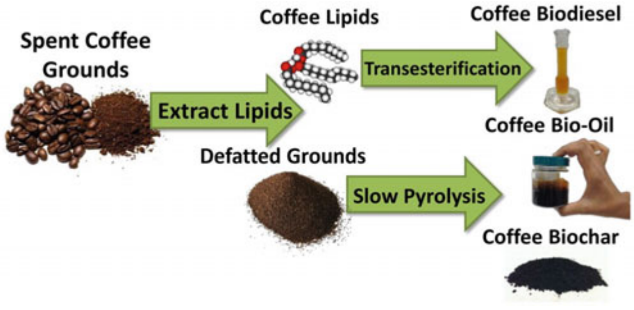


Fig. 11 Use of waste coffee for the production of biodiesel, bio-oil, and biochar. Adapted with permission (Vardon et al. 2013). Copyright (2013) American Chemical Society

used for bioenergy. For example, glycerol, a byproduct of biodiesel production, can be converted into green methanol as another value-added product (Haider et al. 2015). Coffee is another widely used beverage around the world leading to the generation of a great quantity of biowaste (Choi et al. 2019). Vadon et al. applied spent coffee grounds for the generation of biodiesel, oil, and char (Vardon et al. 2013). Lipids extracted from the spent coffee were used in the production of biodiesel (Fig. 11).

Various innovative approaches include Ru catalysts on Al_2O_3/AlF_3 tested in the reaction of glycerol hydrogenolysis to biodiesel production (Ahmed et al. 2016). Up-gradation of the crude oil into diesel blendstock using distillation combined with esterification is reported (Chen et al. 2018). In this report, the authors showed 90–100% engine output with less greenhouse gas emissions. In this process, the use of calcium oxide nanocatalyst offers an economic, sustainable development benefit production of biodiesel from used vegetable oil (Degfie et al. 2019). An economical method for the production of biodiesel utilizing used cooking oil was reported (Vastano et al. 2019). In this process, additional steps such as recycling of residual biomass after polymer extraction using pyrolysis were carried out for the zero-waste process (Vastano et al. 2019). In addition to this, some inventive advances such as immobilized lipase as a biocatalyst for biodiesel (Li et al. 2017), simultaneous production of vitamin K_2 achieved using crude glycerol (Zhang et al. 2020), jatropha to large-scale biodiesel (Prusty et al. 2008), etc. are reported in the literature. A study by Yan et al. suggests that the use of sugarcane molasses is a cost-effective material compared to used vegetable oil and glycerol for the generation of biodiesel (Yan et al. 2018). In addition, it is reported that waste glycerol generated in the biodiesel industry could be used for the production of green fuel like hydrogen and allotrope of carbon such as carbon nanotubes (Wu et al. 2013).

3.2.4 Application of Biowaste for Hydrogen

Hydrogen is a zero-emission fuel that reacts with oxygen to give water and energy. Since it gives energy, it is useful as a fuel source. It is rarely found in its pure form because it is light and rises in the atmosphere. Therefore, it is necessary to generate hydrogen fuel from different sources. Some of those different sources are forestry crops and residues, agriculture crops and residues, sewages, etc. The conversion of biomass to hydrogen involves a thermal process, electrolysis, solar-driven, and biological process. The thermal process is a high-temperature process that involves the reaction between steam and hydrocarbon. The electrolysis process involves breaking water electrochemically into oxygen and hydrogen. Water is a rich source of hydrogen, so hydrogen can be produced through water splitting. The Pt and other Pt-group metals are recognized as the best hydrogen evolution reaction (HER) catalysis. Due to the high cost of these metals, cheaper, easily available HER catalysis is needed for large-scale production (Zhao et al. 2019; Akram et al. 2020). Solar-driven energy generation involves a photobiological, photoelectrochemical, and solar thermochemical process. Here we are interested in the biological process which uses microbes to produce hydrogen gas.

The hydrogen from biomass is produced using different resources such as enzymatic decomposition of different types of sugars and alcohols (Li et al. 2019; Woodward et al. 2000; Waheed and Williams 2013; Cortright et al. 2002), steam-reforming of bio-oils (Román Galdámez et al. 2005; Valle et al. 2018), and gasification (Hu et al. 2015; Cay et al. 2019). Different microbes were used for the conversion of biomass to biogas such as the generation of hydrogen from cheese waste using lactic acid bacteria (Pandey et al. 2019). Sunflower stalks were used for the generation of hydrogen (Monlau et al. 2013). The effect of thermo-alkaline pretreatment, enzymatic pretreatment, and a combination of both processes was studied to understand the yield of bio-hydrogen (Fig. 12). It was observed that the combination process significantly enhanced the production of hydrogen.

Nanoparticles were found to enhance the fermentation process to generate hydrogen such as silver nanoparticles in anaerobic batch reactors (Zhao et al. 2013), gold particles in artificial wastewater (Zhang and Shen 2007), maghemite nanoparticles in starch wastewater (Nasr et al. 2015), metallic (Pd, Ag and Cu) or metallic oxide (Fe_xO_y) nanoparticles (Beckers et al. 2013), nanostructured iron, nickel, titanium oxide (Taherdanak et al. 2015; Kumar et al. 2019; Pandey et al. 2015; Dolly et al. 2015; Salem et al. 2017; Gadhe et al. 2015; Pugazhendhi et al. 2019). As compared to other fossil fuels, hydrogen is an environmental-friendly fuel that can be

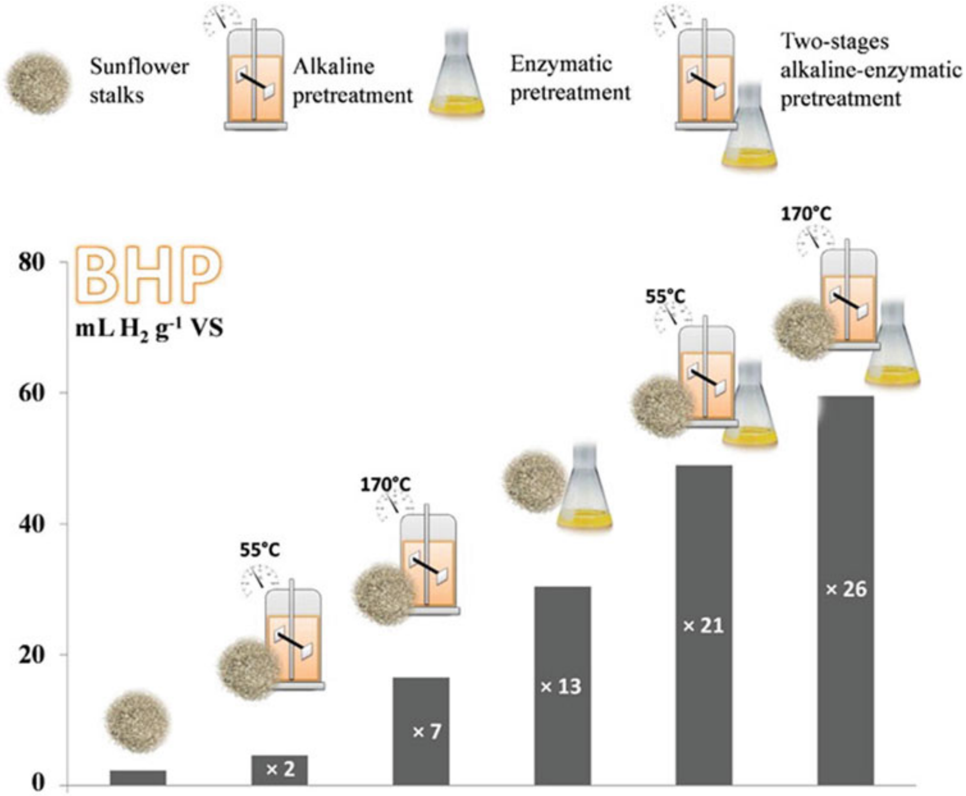


Fig. 12 Hydrogen production using sunflower stalks. Adapted with permission from (Monlau et al. 2013). Copyright (2013) American Chemical Society

produced very efficiently using renewable and sustainable sources. Other advantages include zero-emissions, reduces greenhouse gas emissions, etc.

4 Conclusion

The present global energy crisis requires strenuous efforts from the researchers to explore all probable energy solutions. There are increasing awareness and concern over the greenhouse effect caused by increased use of traditional energy sources. The universal heads are pushing to preserve energy use and to develop non-fossil energies (bioenergies). Ecofriendly biofuel and energy is the best option to replace fossil fuels/energies. The consumption of biowaste feedstock seems to be a perfect solution to the sustainable production of bioenergy in the forthcoming generation. Herein, we systematically discussed the foremost approaches that have been employed for the bioconversion of various biowaste management applications aiming to produce value-added chemicals, byproducts, and biofuels (e.g., bioethanol, biodiesel, hydrogen, and methane). The well-developed microbial, enzymatic, fermentative, and composting bioconversion systems could offer effective ways to produce well-defined chemicals and energy products with the least amount of pollutants and byproducts. To ensure its economic efficiency, the bioconversion process should be carefully optimized based on various factors, including a selection of feedstock, pretreatment approaches, separation process, water reprocessing, energy integration, and byproduct production. Despite the major advancements from the last decade, the bioconversion process is still facing significant challenges for broad-scale real industrial applications. The upcoming research should be focused on the development of inexpensive biocatalysts to produce large-scale industrial, high-yield value-added products and biofuels.

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Green and Sustainable Biomass Processing for Fuels and Chemicals

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Abstract

Among different carbon sources, biomass is the most abundant organic carbon source available for producing renewable bio-oils and the value-added chemicals. Hydrothermal liquefaction (HTL) is a green method for sustainable transformation of dry and wet waste biomass to bio-oils and chemical products that are potentially applicable as raw materials in chemical industries. Both sub- and supercritical water possess interesting physico-chemical properties, capable of dissolving a variety of waste materials for chemical synthesis and production of valuable liquid, gaseous and solid products. Under supercritical conditions, reactions like supercritical water gasification and supercritical water oxidation produce hydrolyzed and depolymerized products useful as synthetic intermediates in chemical industries. This chapter describes how hydrothermal conversion of waste biomass of different types containing both sugar and non-sugar derivatives leads to renewable biofuels and commodity chemicals by abiding green chemistry principles. Further, valorization of aqueous phase, obtained during hydrothermal processing, has also been discussed, including the chemical composition, reuse and applications for the chemical-enhanced recoveries. Therefore, the hydrothermal conversion of non-renewable waste biomass including agricultural waste, forest residue and organic (food) waste into valuable chemicals products can generate the wide opportunities for the development of sustainable chemical industries.

Keywords

Waste biomass • Sustainability • Green chemistry• Hydrothermal liquefaction • Sub- and supercritical water • Physical and chemical properties • Aqueous phase • Recirculation • Biorefinery • Biofuels• Chemicals

1 Introduction

Owing to globalization of automobile industries, the demand of energy is rapidly increasing. Globalization has not only increased the total consumption of fossil fuels but also enhanced significant environmental pollution. Because of high consumption of conventional fuels, associated potentially dangerous gases such as CO_2, CO, SO_x, CH_4, NO_x, linked to greenhouse gas (GHG) emission, have been evacuated directly into ecosystem. Biomass being an alternative source of energy is responsible for 10–14% of global energy requirement. By 2050, it is predicted that the global supply of fossil fuels would be debilitated and almost half of energy demand would be contributed by biomass (Tekin et al. 2014; McKendry 2002; Saxena et al. 2009). Extensive studies were carried out on the consumption of biomass as main source of energy; interest in waste biomass as feedstocks rises in an increasing order (Cortright et al. 2002; Román-Leshkov et al. 2007; Bond et al. 2010; Horne and Williams 1995; Collard et al. 2012).

The composition of biomass varies from components but generally includes a wide range of organic compounds, such as lignin, proteins, cellulose, starch, hemicellulose, and lipids. Among all the components, lignin, hemicellulose, and cellulose are the key components of woody biomass. Selection of a waste biomass feedstock as an energy carrier

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depends on the properties like fixed carbon, calorific value, moisture content, volatile matter and residual; ash and alkali contents play important roles (McKendry 2002). The energy produced from a selected biomass vary according to its properties and the conversion technology applied.

Two broad categories of techniques involved in the conversion process of biomass feedstock into biofuels and valuable chemicals are: (1) biochemical conversion technologies, including aerobic and anaerobic degradation, enzymatic hydrolysis and fermentation, performed by bacterial enzymes and microorganism; (2) thermochemical technologies, which depend on thermal conversion of waste biomass feedstocks into biofuels and commodity chemicals. The thermochemical process technology is the oldest one useful for different purposes, such as cooking, heating, and formation of coke, compared to the biochemical conversion technology. Combustion, gasification, pyrolysis, and hydrothermal liquefaction are the main thermochemical conversion technologies (Elliott 2011).

2 Hot Compressed Water as Green Process Medium

Water is benign, ecologically acceptable, readily available and is low-cost solvent. Recently, water in vicinity of its critical point attained significant research interest, particularly as a green medium with low polarity and much lower dielectric constant for reforming organic waste products and other by-products, being important from an ecological point (Bubalo et al. 2015). The principle of the sub- and supercritical water processes is to heat up wet biomass below and over critical points of water, respectively, to decompose organic wastes into valuable bio-based chemical compounds. Sub- and supercritical water treatment technologies are attaining importance as a way of high-valued materials recovery.

Both sub- and supercritical water methodologies are inexpensive, efficient and employ green solvent (water) for biomass processing; therefore, these techniques are considered as "green" processing techniques for economic transformation of biomass feedstocks to bio-oil and renewable chemicals (Vogel 2012). In addition to their "green," nature, they are also tunable solvents, so their physicochemical properties can be easily changed by changing the reaction conditions to control reaction kinetics and reaction products. Furthermore, the power of sub- and supercritical water can also be varied by varying the reaction pressure and temperature. This feature provides some benefits over the conventional solvents used under normal conditions.

2.1 Hot Compressed Water Chemistry/Properties

The term "hot compressed water" (HCW) refers to the water, heated over 200 °C temperatures at extreme pressure. The HCW is a general term for both super- and subcritical water when water is heated over 200 °C and sufficiently high pressure whose physical properties could be optimized and controlled by changing temperature, pressure and density in a broad range (Kruse and Dinjus 2007). The sub- and supercritical water possess different physical and chemical properties such as reduced densities, high compressibility (like gases) and catalytic activity around the critical point in comparison to their properties at normal conditions (Reddy et al. 2015). Tester et al. reported an enormous change in solvation behavior of water from highly polar to non-polar that occurs on increasing temperature from 25 to 350 °C at 30 MPa pressure (Fig. 1a) (Peterson et al. 2008). Specifically, the dielectric constant of water shows a sharp decrease from about 80 to less than 2 on increasing the temperature from 25 °C to 450 °C. However, the ionic ($K_w \equiv [H_3O^+][OH^-]$) by-products of water steadily increases first from 10^{-14} to 10^{-11} below 350 °C and then decreases to five-fold on rising the reaction temperature to 500 °C (Fig. 1a). Furthermore, the thermal conductance of sub- and supercritical water is apparently higher than one at ambient pressure steam (Cheng and Ye 2014). As the state of water changes from liquid to gas (steam), its thermal conductance also decreases significantly. Consequently, it is possible to gain most of energy from sub- and supercritical water by preheating incoming water, thereafter cooling the processed water. Additionally, the high compressibility (like gases) of HCW due to reduced densities in comparison to water at ambient conditions leads to a significant effect of solutes on the properties of HCW, which is of utmost importance for chemical reaction pathways. HCW also possesses high catalytic activity, attributed to the variations in ion dissociation constants with temperature. As shown in Fig. 1b, phase diagram of water at various temperature and pressure is referenced to highlight the different reaction pathways based on the co-existence behavior of liquid and vapor phases. The HTL pathways in general occur between about 200 and 370 °C temperature and 4–20 MPa pressure range. However, higher temperatures up to 500 °C or above favor hydrothermal gasification and thermolysis processes (Kruse 2008).

2.1.1 Properties of HCW in Subcritical Range

The term "subcritical water" denotes to water, which remains in liquid state at the temperature ranges from its boiling range and critical point. Subcritical water

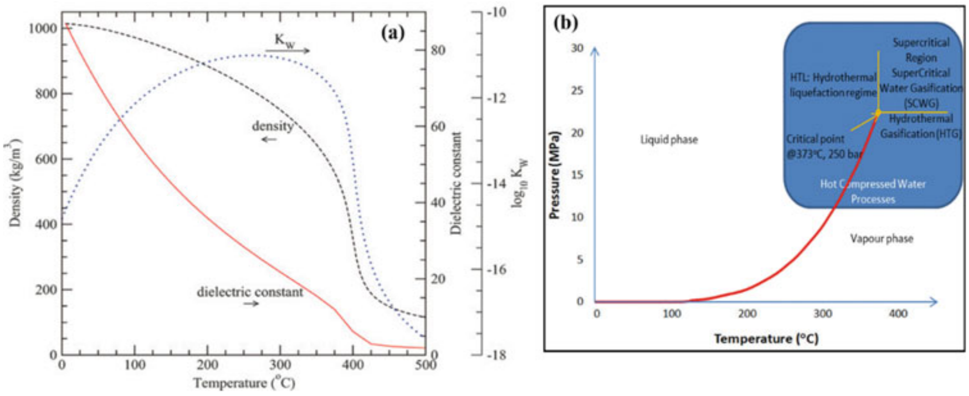


Fig. 1 **a** Physical properties of water as solvent at 30 MPa pressure and different temperatures. **b** Phase behavior of water (Adapted from Tester et al. 2008)

methodology is inexpensive, use non-toxic solvent (water), take short time, have good selectivity and is evaluated as environmental-friendly technology (Abdelmoez et al. 2014). Dissociation constant (K_W) of water increases with increasing temperature, and this reveals that the pH varies from higher to lower pH values. Because the hydronium (H_3O^+) and hydroxyl ions (OH^-) possess higher ionic strength than at ambient conditions, hydronium ions act as active catalyst in hydrothermal reactions (Möller et al. 2011). The high temperature water is most likely the source of hydroxide ions because subcritical water has greater tendency to dissociate into hydronium and hydroxide ions than normal water that makes subcritical water an effective Brønsted base and acid catalysts. Previous literature study reveals that both basic (Brønsted) and acidic catalytic properties of subcritical water in biochemical reactions follow the same pathway elucidated for the synthesis of lactic acid from sugar in both acidic and alkaline solutions (Jin et al. 2004).

Specifically, a three-fold change in dissociation constant of water is reported to increase with change in the experimental conditions from ambient to subcritical (Yang 2007). Due to its enhanced dissociate rate, subcritical water has been employed as acid/base catalyst in reactions for functionalization of chemical compounds (Chandler et al. 1997). In this case, the catalytic effects of bases and acids in subcritical conversion processes caused a further increase in hydronium/hydroxide (H_3O^+/OH^-) ions concentration and ionic strength. Moreover, the viscosity of hot water decreases with increasing temperature from room temperature to near critical point and becomes almost equal to the viscosity of water vapors (steam) at subcritical conditions (Toufiq Reza 2018). As a result, low viscosity of subcritical water offers a high diffusion coefficient and leads to high rates of reaction.

2.1.2 Properties of HCW in Supercritical Range

Supercritical water corresponds to the reaction conditions in which water is heated at temperature over its boiling range and critical point under varied pressures. In supercritical conversion processes, water shows tremendous physicochemical properties due to its low viscosity and extreme diffusion capability; a control reaction mechanism depends on physicochemical properties and new probability for oxidation and hydrolysis (Erkonak et al. 2008). In supercritical range, HCW exhibits the characteristics of non-polar molecules with solvation properties similar to the weakly polar solvents. At supercritical conditions, water exhibits two distinct features: first, its low dielectric constant (K) that makes it an efficient solvent for non-polar organic compounds, and secondly, high degree of self-ionization at high temperature. Further, hydrogen bonding plays a main role in dynamic, structural and solubility properties of supercritical water. Hydrogen bonding in supercritical water increases with the increase of densities but diminishes at high temperatures (Marcus 2014). The lower degree of hydrogen bond formation in supercritical water is attributed to the low polarity of water molecules in comparison to water at ambient condition.

At supercritical conditions, water changes its structure and most of the intermolecular associations are broken, causing the decrease of dielectric constant and changing polar interactions into dipole–dipole interactions (Franck 1987). Kamlet-Taft solvent parameter π^* (polarity/polarizability) for supercritical water up to 420 °C temperature measured from solvatochromic measurements showed a continuous decrease of polarity of water with increasing temperature (Minami et al. 2006). Therefore, the enhanced solubility of non-polar organic molecules in supercritical water is probably due to the high temperature, which helps in overcoming the phase boundaries for the mass transfer without any restrictions. Below the critical point, the HCW is not completely miscible, but an enhanced solubility of non-polar compounds (Lu et al. 2001) is noticed. Furthermore, the high mobility and high density of water molecules at supercritical conditions favor the energy transfer for the decomposition of activated complex; hence, this improves the reaction rates. Apart from the temperature, reaction pressure also affects the physicochemical properties of water. Equation 1 shows the substantial change in rate constants on increasing the reaction pressure in supercritical reactions, which is attributed to the change in volume of activation (Shaw et al. 1991).

$$\left(\frac{\partial ln k_x}{\partial P}\right)_{T,x_i} = \frac{-\Delta V^{\ddagger}}{RT} \tag{1}$$

where k_x, P, $\Delta V^{\ddagger}$, R and T are rate constant, pressure, molar volume of activation, gas constant and temperature, respectively. These results show that the reaction kinetics and physical characteristics of water can be controlled significantly by adjusting pressure and temperature. The resulting properties make supercritical water a tunable reaction solvent and medium for transformation of organic wastes to useful chemical compounds, which needs high reaction temperature and pressure to activate the reactants.

2.2 Sub- and Supercritical Water as an Efficient Solvent for Biomass Processing

Water is a green solvent that can be used as a reaction medium at both sub- and supercritical environment in different domains for the treatment of biomass and production of a variety of chemicals.

Subcritical environment in the biomass conversion reaction is very favorable, especially for the extraction of nutrients, photo-chemicals from various natural substances. Besides, for food and pharmaceutical industries, the subcritical water is an excellent source due to less toxic nature, and free organic solvent products are formed which lead to no or any expensive removal of organic solvent (Peterson et al. 2008).

In hydrothermal processing studies, especially for the liquefaction section, mostly subcritical water is recommended as a solvent for the enhancement of higher oil or bio-crude yields, and higher conversion rates as compared to other organic solvents. For example, Zhu et al. and Jindal et al. reported the HTL of barely straw and wood, respectively (lignocellulosic biomasses), and both reported high bio-crude yields with the lower amount of solids at subcritical conditions due to efficient transformation of cellulose and hemicellulose through alkali catalyst K_2CO_3 via hydrolysis (Zhu et al. 2014; Jindal and Jha 2016). Malins et al. employed subcritical water for the liquefaction of sewage sludge and observed an increase in energy recovery corresponding to higher ratio of weight fractions of sewage sludge and water (Malins et al. 2015). However, bio-crude showed a slight decrease in HHV values ranging from 35.95 to 31.35 MJ/kg, which is associated with the hydrolysis reactions of polysaccharides, lipids, and peptides that formed oxygenated compounds like acids and alcohols, etc. Moreover, it was also reported that subcritical water can also be utilized as an extractive medium for carbohydrate and protein. In one of the studies, microalgae was treated at (180–374 °C), which resulted in maximum carbohydrate and 14.2/100 and 31.2/100 (g/g) protein yields, respectively at 277 °C with 5% biomass loading (Awaluddin et al. 2016).

Besides the extraction of carbohydrate and protein, some publications focused on the isolation of phenolic compounds from the biomass. These phenolic compounds are associated with carbohydrates and proteins. By using subcritical water, the segregation and hydrolysis are carried out altogether and more active aglycones are formed in the product. These free aglycones are tended to be extreme antioxidant properties than bonded glycosides. Singh et al. studied the influence of subcritical water on potato peel, and noticed that the optimal temperature of 180 °C and 60 min for the extraction of phenolic acids like (hydroxyl benzoic, ferulic and coumaric acids) as listed in Table 1 (Singh and Saldaña 2011).

2.2.1 Supercritical Water as Reaction Medium

Water in supercritical environment is a sustainable solvent that possesses unique ability to dissolve a variety of organic substances and feedstocks for chemical synthesis and production of valuable products like oil, gas and char.

The feedstock includes cellulose, lignin, hemicellulose, plastics and other wastes, e.g., rubber tire, inorganics and wastewater. It has been found from the literature that the temperature above the critical point does not facilitate the liquefaction (Peterson et al. 2008). However, other technologies, like supercritical water gasification and supercritical water oxidation are strongly suggested at supercritical conditions. The supercritical water plays a crucial role in hydrolysis and pyrolysis reactions in supercritical water gasification. However, supercritical water oxidation holds reactions like depolymerization, defragmentation where water acts like: (1) a reactant or product for hydrolysis and hydration, hydrogen provider, (2) an acid/base catalyst or precursor, (3) responsible for intermolecular interactions, to enhance higher hydrophobicity, and (4) medium for energy transfer, diffusion and phase behavior (Knez et al. 2018).

Hydrolysis is a primary reaction in supercritical conditions, particularly for the destruction of non-polar organic waste. At supercritical state, higher temperature and pressure speed up the rate of hydrolysis reaction even when no catalyst is added. It is the breaking up of glycosidic, peptide, triglycerides, ester and amide bonds. Saski et al. observed the effect of supercritical water with cellulose decomposition in a detailed manner (Sasaki et al. 1998). Gasification is one of the most dominant hydrothermal processing methods in the supercritical region, and it has been extensively used worldwide to reform the organic matter and recover useful gaseous products like H_2, CO, CO_2 and CH_4. Cherad et al. had already optimized the aqueous phase produced from

Table 1 Applications of sub- and supercritical water in hydrothermal studies on different materials

S. no.	Feedstock	Processing method	Temperature (°C)	Catalyst	Key findings	References
1	Sewage sludge	Pyrolysis	300	Na_2CO_3, Raney nickel, $FeSO_4$, MoS_2	The highest energy recovery (69.84%) was reported with 5 wt%. $FeSO_4$, and sewage sludge to water in the ratio 1:5. Total conversion (70.64%) with the HHV of 35.22 MJ/kg	Malins et al. (2015)
2	Wood	HTL	280	K_2CO_3, KOH, Na_2CO_3, NaOH	K_2CO_3 improved the bio-crude yield (34.9 wt%) with lower amount of solid residue (6.8 wt%). The trend of reactivity with regard to liquid yields: K_2CO_3 > KOH > Na_2CO_3 > NaOH	Jindal and Jha (2016)
4	DDGS	HTL	350	K_2CO_3	The bio-crude yield increased relatively more with catalytic recycled aqueous phase as compared to non-catalytic recycled process water. The overall HHVs of bio-crudes from catalytic run lie in the range of 29.4 to 36.3 MJ/kg	Biller et al. (2016)
5	Barley straw	HTL	280–400	K_2CO_3	Lower temperature favored the production of bio-crude, and the highest yield of bio-crude (35.45 wt%) was obtained at 300 °C temperature. HHVs (26.75–35.48 MJ/kg) improved with rise in temperature. Bio-crude was composed of phenolics, carboxylic acid, aldehydes and ketones	Zhu et al. (2014)
6	Willow	HTL	400	None	At supercritical conditions, longer residence time decreased bio-crude yield and increased solid and gaseous products due to repolymerization and gasification reactions. However, alkaline pretreatment of feedstock improved the quality of bio-crude	Grigoras et al. (2017)
7	Algae	HTL	250–350	Na_2CO_3	Highest bio-crude yield was obtained from high carbohydrate-containing biomass with Na_2CO_3 at elevated temperatures (300–350 °C), while biomass feedstock with higher protein contents efficiently converted to bio-crude at 250 °C temperature with the help of alkali (Na_2CO_3) catalyst	Shakya et al. (2015)
8	Microalgae	HTL	100–400	None	Longer residence time ($t > 40$ min) and high reaction temperature (300 °C) reduced the bio-crude yield. Also, solid yield declined with longer reaction times due to the cracking of heavier fractions	Hietala et al. (2016)
9	Palm biomass	HTL	330–390	None	The supercritical conditions at 390 °C give maximum bio-crude yield due to increased rate of decomposition through radical mechanism. The bio-crude was composed of phenolic derivatives because of lignin degradation at high temperatures (390 °C)	Chan et al. (2014)
10	Swine manure	Pyrolysis	260–340	None	Bio-crude yield increased from 14.9 to 24.2% attributed to rise in temperature from 260 to 340 °C. The HHV 36.06 MJ/kg, with the viscosity of 853 (cp)	Xiu et al. (2010)
11	Microalgae and lignocellulosic	HTL	300	None	The optimal yield of bio-crude was observed at a weight ratio of (3:2) to microalgae/rice husk. Bio-crude comprised hydrocarbons, organic acids, straight chain and branched chain amides, and N and O containing heterocyclic	Gai et al. (2015)

(continued)

Table 1 (continued)

S. no.	Feedstock	Processing method	Temperature (°C)	Catalyst	Key findings	References
12	Micro-algae	Gasification	600	NaOH	The residual water from HTL process was optimized through gasification at supercritical environment. 30 mol H_2/kg algae was produced after the successful gasification of the 98% organics. The aqueous phase after the supercritical water gasification was still enriched with valuable nutrients that can be utilized for the algal growth	Cherad et al. (2016)
13	Crude glycerol and aspen wood	HTL	380–420	K_2CO_3	Composition of bio-crude and char as well as their yields was not affected by temperature changes	Pedersen et al. (2015)
	Microalgae	Liquefaction/ extraction	180–374	None	The results exhibited maximum total carbohydrate content and protein yields of 14.2/100 and 31.2/100 (g/g)	Awaluddin et al. (2016)
14	Potato peel (Red)	Extraction of phenolics	100–240	None	Phenolic compounds: gallic, chlorogenic, caffeic, protocatechuic, syringic, hydroxyl benzoic, coumaric acids and ferulic maxima at 180 °C and 60 min	Singh and Saldaña (2011)
15	Bitter melon (Momordica charantia)	Extraction of phenolics	130–200	None	Main polyphenols: gallic, catechin, gentisic and chlorogenic acids	Budrat and Shotipruk (2009)
16	Wastewater stream	Supercritical water oxidation	575–825	None	Above the temperature of 650 °C, the removal efficiency reached up to 99.95%, with reaction time lower than the 50 s and oxygen marginally greater compared to the stoichiometric value. The HHV in the feed stream for energy self-reliant operation is around 930 kJ/kg, which is comparable to a water stream holding 2% (w/w) n-hexane and 3.2% (w/w) hexanoic acid, and this depends upon the extent of oxidation	Cocero et al. (2002)

HTL via gasification at supercritical conditions (Cherad et al. 2016). It was reported that 30 mol H_2/kg algae was produced after the successful gasification of the 98% organics.

In supercritical water oxidation technology, the oxidative conditions are used at high temperatures to generate thermal energy and gas-phase containing a significant amount of CO_2. The principal objective of supercritical water oxidation is the decomposition of industrial waste products including toxic effluents and sludge, because of complete and rapid oxidation reactions in supercritical environment. Therefore, according to sustainable development, this process is termed as green chemistry technology. Cocero et al. used supercritical water oxidation for waste streams under the temperature range of 575–825 °C, and noticed 99.95% removal efficiency at 650 °C with residence time lower than the 50 s and excess oxygen slightly higher than the stoichiometric value (Cocero et al. 2002).

Since this chapter is more oriented in perspective of bio-crude production through HTL, therefore the majority of the HTL studies are based on sub-critical conditions (Biller et al. 2016; Hietala et al. 2016; Xiu et al. 2010; Gai et al. 2015; Budrat and Shotipruk 2009; Grigoras et al. 2017; Shakya et al. 2015). However, only limited references are there to support the supercritical region for the bio-crude production from different biomass, such as willow, barley straw, co-liquefaction of glycerol and aspen wood, which are listed in Table 1 (Pedersen et al. 2015; Chan et al. 2014; Maddi et al. 2016).

As discussed before higher temperature favors gasification reactions and sometimes cause repolymerization of reactive substance to form more char. In the context of the above literature, it can be summarized that water fulfills a comprehensive and promising role as a solvent and catalyst precursor in the treatment of biomass processing.

3 HTL Reaction Networks and Product Fractions

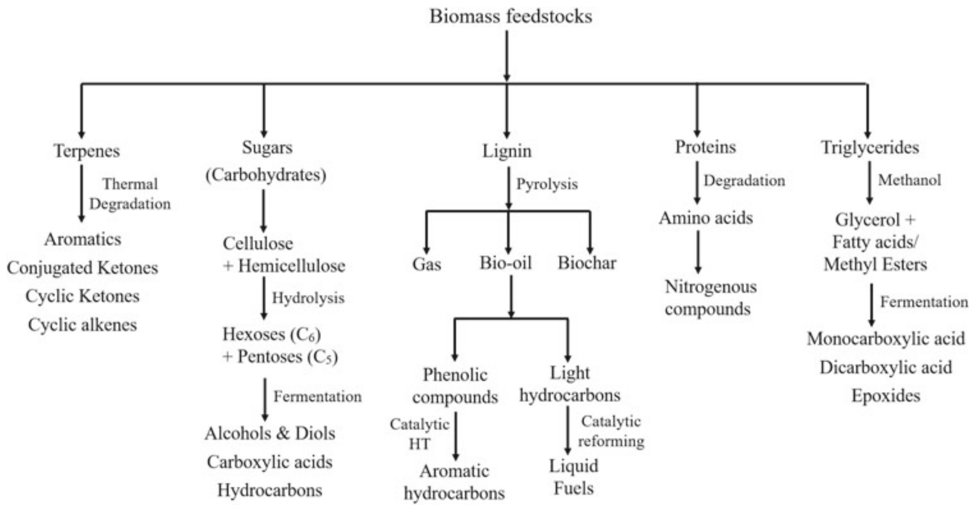
3.1 Biochemical Reaction Pathways

Synthesis of chemical compounds and bio-based materials through the conversion of organic waste biomass is the key challenge in chemistry, which requires the development of green and sustainable technologies, abiding the principles of green chemistry. Hydrothermal processes such as liquefaction, oxidation, carbonization, depolymerization and gasification have been discovered as green conversion technologies for the processing of biomass feedstocks into liquid, gaseous and solid chemical compounds (Maddi et al. 2016; Funke and Ziegler 2010; Hasegawa et al. 2011; Onwudili et al. 2013). Moreover, thermochemical conversion processes can also control intermediate materials and biomass feedstocks obtained from biological processes (Öhrman et al. 2013). Conversion of non-renewable agricultural and forest residues containing sugar, cellulose, hemicellulose, fibers, lignin, lignocellulose, proteins and triacylglycerides to valuable chemicals can generate the wide opportunities for the development of sustainable chemical industries (Besson et al. 2014). Figure 2 summarizes the strategies used in the literature for conversion of biomass feedstocks and its components to useful chemicals. The present section summarizes an outline of the biochemical reaction pathways for conversion of waste biomass feedstocks into valuable liquid and gaseous chemicals through different hydrothermal processes.

3.1.1 Conversion of Sugar Monomers

The term sugar refers to a wide class of monosaccharides (e.g. galactose, fructose and glucose) and the disaccharides (e.g. lactose, sucrose, maltose and trehalose). Both mono- and disaccharides are the simplest forms of carbohydrates. All categories of carbohydrates, including cellulose, chitin, glycogen, hemicellulose and starches, are basically the polymeric forms of monosaccharides. Degradation of polysaccharides under hydrothermal conditions showed that cellulose degrades into glucose and other products, while hemicellulose degrades into a number of simple monosaccharides units (Bobleter 1994). An understanding of successive reactions and chemical properties of monosaccharides is beneficial to mimic the conversion pathways of various complex carbohydrates for the formation of commodity chemicals. The isomeric forms and high value chemical products produced during the breakdown of D-glucose and D-fructose under hydrothermal reaction conditions were analyzed (Öhrman et al. 2013). Furthermore, the kinetics of degradation reaction and reactivity of glucose and fructose were also compared at different temperatures and pressure. It was observed that glucose possesses low reactivity for degradation than fructose at ambient conditions but the rate of degradation of glucose increased linearly on increasing the reaction temperature (Matsumura et al. 2006). Bobleter and Bonn examined the degradation of glucose and fructose under hydrothermal reaction conditions and separated the various fragmentation products using thin layer chromatography (Bonn and Bobleter 1983). According to their experimental results, glucose degraded mainly into glyceraldehyde, glycolaldehyde and pyruvaldehyde, while fructose was fractionated into dihydroxyacetone, methylglyoxal, 5-hydroxymethylfurfural (5-HMF) and simple furfural as the key reaction products. It was reported that 5-HMF produced as a degradation product could further be converted to 1,2,4-benzenetriol with an experimental yield of 46% (Luijkx et al. 1993). For a summary, various chemicals produced from the overall conversion of glucose and fructose under hydrothermal conditions are shown in Fig. 3. Furthermore, the effect of pH on degradation of glucose was also noted at different temperatures (180–230 °C) and it was

Fig. 2 Strategies for the primary conversion of biomass feedstock and its components to commodity chemicals



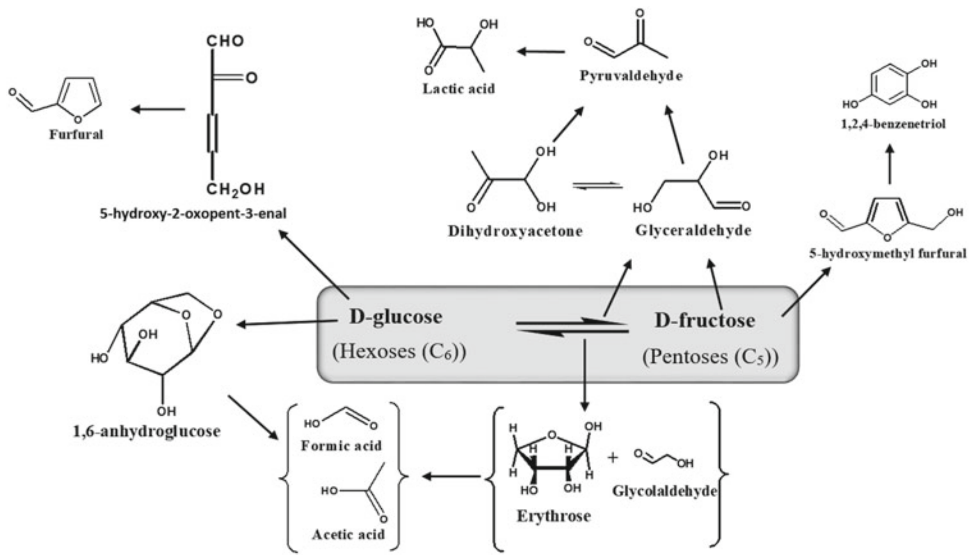


Fig. 3 General conversion pathway for the breakdown of glucose (hexoses) and fructose (pentoses) sugars under hydrothermal conditions

found, at 200 °C temperature, that the degradation of glucose increases with decreasing pH of the solution (Xiang et al. 2004). Addition of 2 mM sulfuric acid solution to the fructose significantly increased reaction yield of 5-HMF and furfural as well as reduced yields of pyruvaldehyde and lactic acid without affecting reverse isomerization of fructose to glucose (Antal et al. 1990).

After glucose, galactose and mannose are the next monosaccharides (hexoses) present in hemicellulose in high yield. Both galactose and mannose are important precursors for the production of 5-HMF and have been widely used for large-scale production. Mannose showed high reactivity in the presence of $CrCl_2$ in either DMA-LiBr and produced 5-HMF in 69% yield, while a low yield of around 40% of 5-HMF was obtained on reacting galactose under similar conditions (Binder et al. 2010). Like fructose, xylose is a pentose sugar and an important building block of hemicellulose, which is considered as a main source for the global production of furfural. The pyranose cyclic structure of xylose was found to produce furfural as a main product while open-chain structure produced pyruvaldehyde, glyceraldehyde, glycolaldehyde, lactic acid, acetol and formic acid as degradation by-products in high yield (Antal et al. 1990). The effect of pressure and temperature on the yield of furfural was noticed and observed that supercritical reaction conditions favor formation of by-products over the furfural (Qi and Xiuyang 2007).

3.1.2 Conversion of Non-sugar Monomers

Lignin is a complex organic compound with randomly-oriented phenyl derivatives and acts as a sustainable biomass for aromatic compounds. The most dominant monomers in lignin unit are all hydroxyl phenyl-alkane derivatives such as *p*-coumaryl alcohol, sinapyl alcohol and coniferyl alcohol (Fig. 4) (Joffres et al. 2013). Lignin derivatives can be easily converted into monomer units under sub- and supercritical conditions at varying pressure from 20 to 25 MPa, temperature from 280 to 400 °C and water-to-lignin ratio (2:50).

It was observed that with increase in density of water in a hydrothermal environment increases the degradation of lignin into lightweight chemicals (Saisu et al. 2003). Hydrothermal processing of lignin at 350 and 400 °C and 25–40 MPa pressure was studied by employing batch reactors in the absence of catalysts (Wahyudiono and Goto 2008). Under sub- and supercritical conditions, lignin was

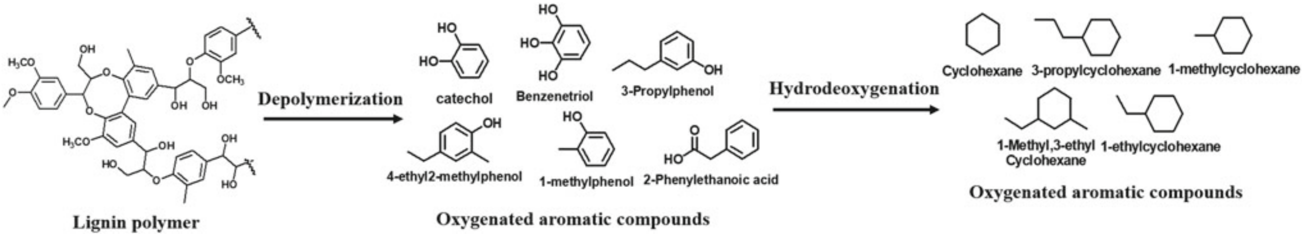


Fig. 4 Probable reaction for depolymerization of lignin and hydrodeoxygenation of aromatic oxygenated compounds pathways to cyclic structure hydrocarbons

successfully degraded at 400 °C temperature into phenol, catechol, *m,p*-cresol and *o*-cresol in 11.75, 26.18, 6.98 and 11.21 wt% yield, respectively. At 350 °C temperature, the yield of above chemicals was changed significantly to 3.31, 30.55, 8.76 and 3.65 wt%, respectively. Furthermore, the qualitative measurements for the production of 2,4-di-tert-butyl phenol and 1,3-di-tert-butyl benzene as the key chemical compounds from hydrothermal treatment of lignin using gas and mass spectroscopies were also performed (Quitain et al. 2003). Oasmaa and Jin evaluated hydrothermal degradation of lignin in the presence of catalysts and alkali and found that catalysts like K_2CO_3, NaOH and $Ca(OH)_2$ enhance yield of liquid product, while alkali facilitates the bond breakings in lignin and enhances the formation of formic or acetic acid (Oasmaa and Johansson 1993; Jin et al. 2012). Alkali lignin polymer was successfully converted through hydrothermal decomposition under alkaline conditions into guaiacol (11.23 wt%), catechol (11.21 wt%), phenol (4.21 wt%) and cresol (7.00 wt%) at temperatures approximately 280, 380, 390 and 390 °C, respectively (Pinkowska et al. 2012).

Natural oils and fats containing triglycerides and fatty acids are potential renewable feedstocks for synthesis of fuels and commodity chemicals. Selective hydrothermal deoxygenation of saturated and unsaturated triglycerides to C_{n-1} hydrocarbons was carried out by using Pd/C catalyst (Hollak et al. 2014). Deoxygenation was performed in HCW at 250 °C temperature, which resulted in the formation of linear paraffin and olefins as the main products. Catalytic hydrothermolysis at 21 MPa pressure and temperatures varying from 450 to 475 °C using zinc acetate as catalyst was performed using water as a solvent (Li et al. 2010). The resulting reaction produced non-ester biofuels in 40–52% yield. The factors like temperature, pressure, heating oil rate, catalyst and oil to water ratio were identified as main factors in catalytic hydrothermolysis reaction to control the selectivity of the product.

Amino acids, the important precursor of all kinds of proteins, have high market value due to their great demand in food, pharmaceutical and cosmetic industries. Previously, a large number of efforts have been made to explore hydrothermal techniques for the synthesis of amino acids from protein-rich biomass feedstocks (Quitain et al. 2001, 2006; Rogalinski et al. 2005). Earlier, hydrothermal treatment of shrimp shells was performed at different pressure and temperature for production of different amino acids (Quitain et al. 2001). Amino acids were produced in highest yield at temperature of 250 °C for 60 min residence time that was 2.5 times longer in comparison to that produced at 90 °C. The amount of alanine and glycine amino acids first raised with enhancing temperature to 250 °C and declined afterward. To enhance recovery of tyrosine amino acid through the degradation of silk protein, microwave-assisted hydrothermal technique was employed (Quitain et al. 2006). Addition of alkali and acid to the reaction mixture significantly enhanced the yield and NaOH favored the hydrolysis of protein. Bovine serum albumin protein was treated in continuous-flow reactor at different temperature and residence time for production of amino acids (Rogalinski et al. 2005). At subcritical conditions, the highest yield of amino acid was formed at 290 °C temperature for 65 s residence time, while 310 °C was the optimum temperature for 30 s residence time.

Thermal degradation of a variety of terpene derivatives at different residence time temperatures was studied (McGraw et al. 1999). The percent degradation of the terpenes at heating temperature of 120 °C was 100% for R-terpinene in 4 h, 38% for camphene in 72 h, 50% for limonene in 24 h and 36% for Δ^3-carene in 72 h. Later, hydrothermal degradation of pinene, camphor, carvacrol, limonene and citronellol terpenes was studied in subcritical water (Yang et al. 2007). Among all terpenes, pinene and limonene showed highest degradation of 25–31% at 100–150 °C after 30 min heating, which reached to 64% at 250 °C temperature. However, the camphor, carvacrol and citronellol terpenes showed lower degradation (10%) and better stability at subcritical conditions.

3.2 Reaction Mechanism and Potential Reaction Pathways for HTL

Hydrothermal liquefaction is a complicated process due to involvement of various kinds of chemical reactions. Some work has been done to predict yield of HTL bio-crude using both model compounds and kinetic modeling based on chemical composition of biomass (Biller and Ross 2011; Teri et al. 2014; Leow et al. 2015; Sheng et al. 2018; Hietala et al. 2016, 2017; Li et al. 2017; Déniel et al. 2017; Sheehan and Savage et al. 2017). Transformation of biomass feedstocks during the HTL process is a combined reaction of hydrolysis of biopolymers, degradation of feedstock and several other secondary processes involving the synthesis of hydrolyzed products (Yang et al. 2018; Arturi et al. 2016). Hydrolysis is the first degradation step, resulting in monomers and oligomers intermediates. Monosaccharides can be obtained from cellulose and hemicellulose, while methoxyphenol derivatives can be obtained from lignin, lipid, protein fatty acids and amino acids, respectively (Déniel et al. 2016, 2017; Peterson et al. 2008; Sasaki et al. 2000; Mok and Antal 1992; Garrote et al. 1999; Gao et al. 2011). The secondary reactions like dehydrogenation, dehydration, Cannizzaro reaction, retro-aldol condensation, rearrangements, polymerization and cyclization depend upon

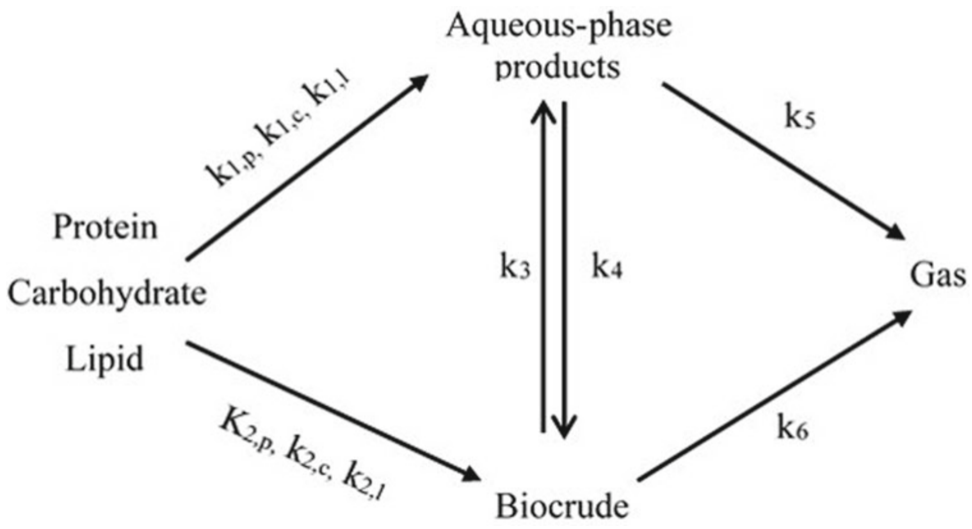


Fig. 5 HTL reaction network (adapted from Vo et al. 2016)

process conditions (Srokol et al. 2004; Brunner 2009, 2009; Kabyemela et al. 1997; Chornet and Overend 1985; Russell et al. 1983).

Biller and Ross used compounds additive approach to obtain a linear prediction model for the bio-crude yield (Biller and Ross 2011). This proposed model was only limited to microalgae species like Chlorella and Nannochloropsis to accurately predict their bio-crude yield. However, it did not work well for other biomass species. Teri et al. obtained a quantitative approach by incorporating interaction terms and studied liquefaction of binary components (Teri et al. 2014). The model constituents with interaction terms showed less accuracy for the investigation of bio-crude yield than linear model. Ky Vo et al. examined HTL of high-lipid microalgal at varied temperatures ranging from 250 to 400 °C and retention times (10–60 min) (Vo et al. 2016). In this study, they used HTL mechanism for kinetic modeling developed (Valdez et al. 2014). In this model, lipid, protein and carbohydrate fractions reacted independently to yield aqueous phase and bio-crude products. Consequently, reversible interconversion between these products resulted in further transformation to gaseous products (Fig. 5).

They suggested ten reaction rate constants and assumed all reactions follow first-order kinetics. By following rate law equation, they proposed rate of each reaction according to the following pathways:

$$\text{Proteins: } \frac{dx_{1,p}}{dt} = -\left(k_{1,p} + k_{2,p}\right)x_{1,p}$$

$$\text{Lipids: } \frac{dx_{1,l}}{dt} = -\left(k_{1,l} + k_{2,l}\right)x_{1,l}$$

$$\text{Carbohydrates: } \frac{dx_{1,c}}{dt} = -\left(k_{1,c} + k_{2,c}\right)x_{1,c}$$

$$\text{Aqueous} - \text{phase product: } \frac{dx_2}{dt} = -(k_4 + k_5)x_2 + k_{1,p}x_{1,p} + k_{1,l}x_{1,l} + k_{1,c}x_{1,c} + k_3x_3$$

$$\text{Biocrude product: } \frac{dx_3}{dt} = -(k_3 + k_6)x_3 + k_{2,p}x_{2,p} + k_{2,l}x_{2,l} + k_{2,c}x_{2,c} + k_4x_2$$

$$\text{Gaseous product: } \frac{dx_4}{dt} = k_5x_2 + k_6x_3$$

Gai et al. and Chen et al. examined the results produced from HTL of microalgae with low-lipid contents under subcritical condition (Gai et al. 2015; Chen et al. 2014). The general reaction pathways for complete HTL process were inferred from experimental outcomes of previous studies reported in the literature (Fig. 6).

Chen et al. proposed a potential HTL reaction scheme based on possible reaction pathways and GC-MS data (Fig. 7) (Chen et al. 2014). The thickness of the arrow shows relative amount of product distribution into different phases. Currently linear additive models are available by assuming that each component behaved independently during the HTL process. Thus, it is crucial to design prediction models by using more illustrative model compounds and considering the influence of interaction between them. Such model derivatives can be more advantageous to predict product yields accurately and assess the viability of co-liquefaction for use of various biomass sources to enhance energy production. Additionally, the chemical reactions among the biomass components can also be explored to mimic their conversion pathways. It would provide the basic information for significant alteration of product supply and enhanced knowledge of synergistic phenomenon, when different biomass feedstocks are mixed.

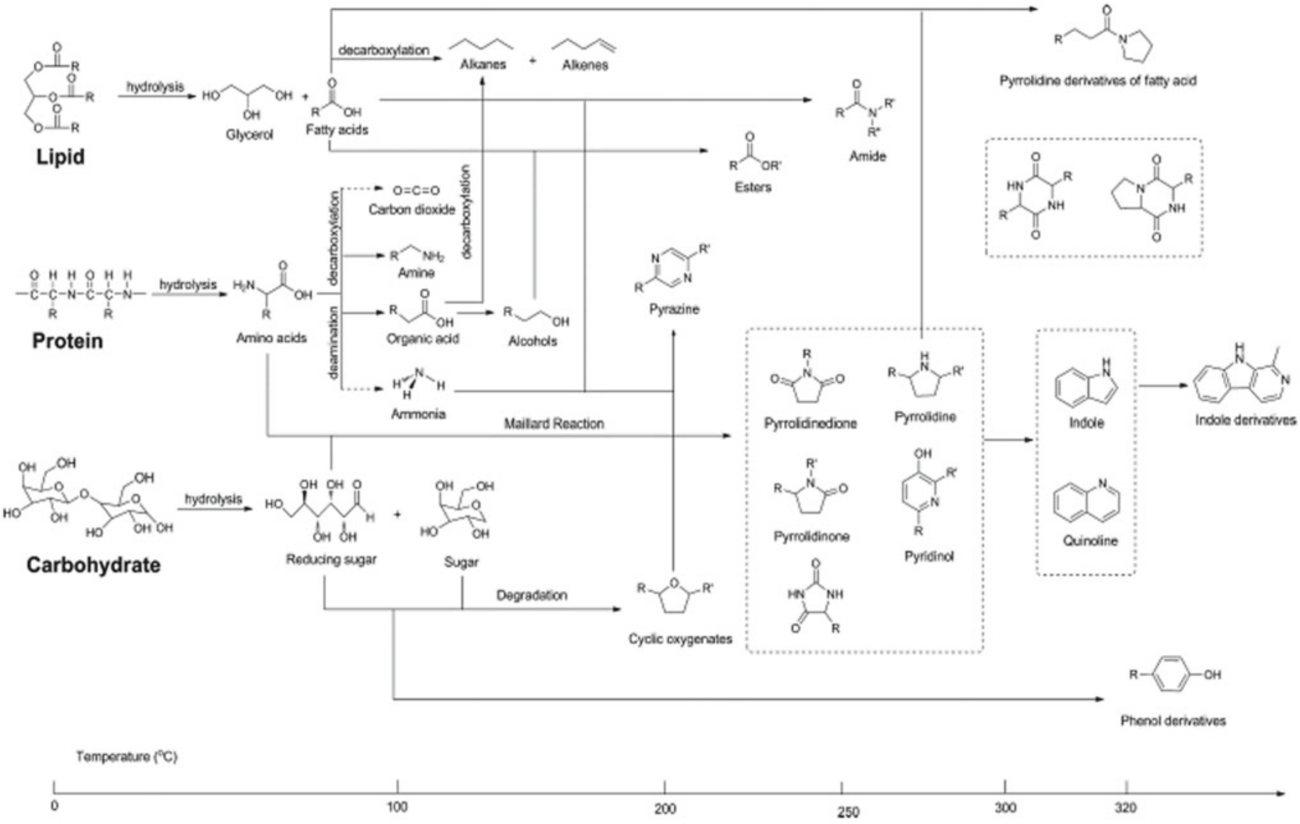


Fig. 6 General reaction pathways for HTL of low-lipid microalgae (adapted from Gai et al. 2015)

3.3 Biorefinery and Value-Added Chemicals

Comparatively low energy and carbon recovery as well as geographically discrete availability of biomass have been renowned as main hurdles for the sustainable production of biofuels. However, chemical synthesis requires comparatively lower amount of biomass to fulfil the demand. The concept of biorefinery will continuously gain importance due to evolving research outcomes in the synthesis of bio-based intermediates and products (FitzPatrick et al. 2010; Lipinsky 1981).

Biorefining of bio-crudes and bio-oils is equally important to petroleum refinery that generates multiple fuels and products from fossil crudes. The overall goal is to produce a variety of products from different biomass feeds in biorefinery by combining various technologies. An ideal biorefinery should combine thermochemical conversion techniques to obtain a variety of biofuels, power and commodity materials (Fernando et al. 2006; Kaparaju et al. 2009; Laser et al. 2009; Lynd et al. 2009). This allows the system development that ideally try to reduce all kinds of wastes during biomass feedstock processing. In future, the biorefineries would be capable of mimicking the energy efficiency of bio-oils refining through the development of sustainable bio-products and heat integration. Within the biorefinery, the amount of heat released during the various processes could be used to encounter the heat necessities for hydrothermal processes.

The classification of biorefinery depends mostly on existing biomass transformation technologies to obtain a broad range of bio-products through various stages. Mostly hydrothermal conversion techniques are established because of particular chemical properties of the biomass feedstock. Thus, individually integrated biorefineries are estimated to be designed based on composition of biomass feedstocks. Therefore, biorefinery is divided into three main categories depending on contents and chemical composition of biomass feeds: lignocellulosic biorefinery, triglyceride biorefinery and sugar/starch biorefinery, as shown in Figs. 8, 9 and 10, respectively. The current biorefinery classification covers the complete range of feedstocks and depends on identified conversion techniques. Nevertheless, these techniques and valuable compounds are estimated to be extended in coming future in terms of scientific developments and finding of new feedstocks. Individually integrated biorefineries will be established based on contents of different feedstock with aims to obtain various products by implementing precise

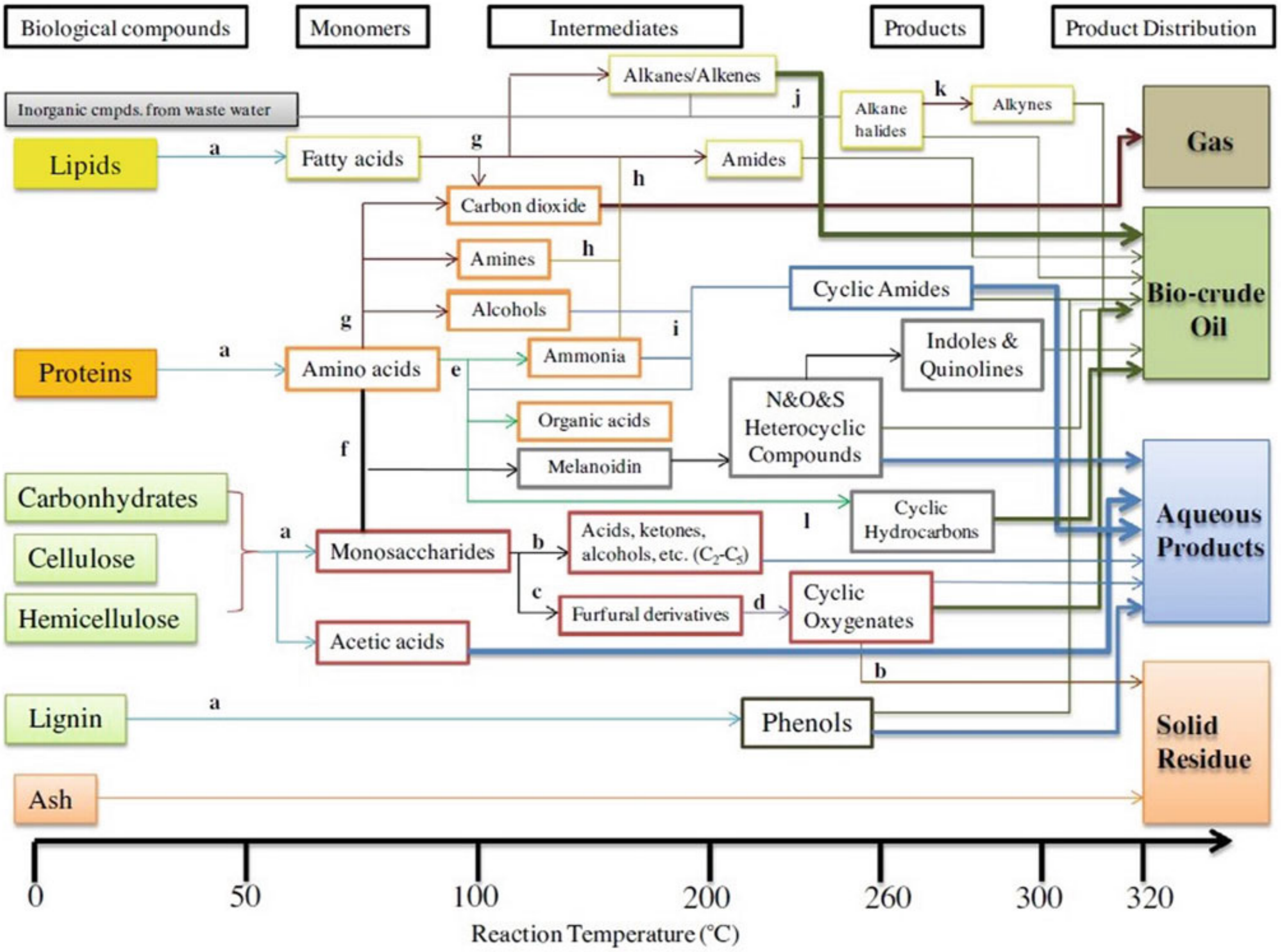


Fig. 7 Different HTL conversion processes: **a** hydrolysis of proteins, lignin, lipids and sugars, **b** decomposition of sugars and cyclic oxygenates, **c** dehydration of sugars, **d** polymerization of oxygenates, **e** deamination of N-derivatives, **f** Maillard reaction between sugars and amino acids, **g** decarboxylation of lipids, **h** aminolysis, **i** cyclization of N-derivatives, **j** halogenation, **k** dehydrohalogenation and **l** pyrolysis (adapted from Chen et al. 2014)

conversion processes (Maity 2015; Alonso et al. 2010; Octave and Thomas 2009).

For operation and commercialization of biorefinery, there are lot of obstacles and gaps. By using energy crops, the current technical barriers are related to the production cost, complications during harvesting and sorting the material produced, particularly for annual or other crops, harvested within a narrow time. While calculating the overall costs of biomass, transportation costs are of principal importance; hence local synthesis of biomass feedstock is most favorable and encouraging. Distribution of nutrients is another technical problem allied with energy crops. The major non-technical obstacles are restrictions on use of land as well as ecological effects of large areas of monoculture. The main non-technical barriers for the industrialization of biofuels in transport sector relate to costs of production, taxation policies, legislation and available markets as well as distribution and blending (Demirbas 2009).

4 HTL Aqueous Phase as a Precursor

4.1 Aqueous Phase Recirculation in HTL

HTL at laboratory level has been broadly studied for assessing the operational parameters. However, the commercial-scale implementation is being delayed due to unsolved challenges, which include the utilization and management of the aqueous phase stream produced along with the bio-crude (Déniel et al. 2016). Generally, the majority of feedstocks contain 50% water content, which can be used as reaction solvent in HTL processing. Thereby an excessive amount of water is produced, which requires water handling management (Biller et al. 2016).

Depending upon the composition of biomass, the aqueous effluent often carries water-soluble organics and nutrients. For the overall process economics of HTL, the management

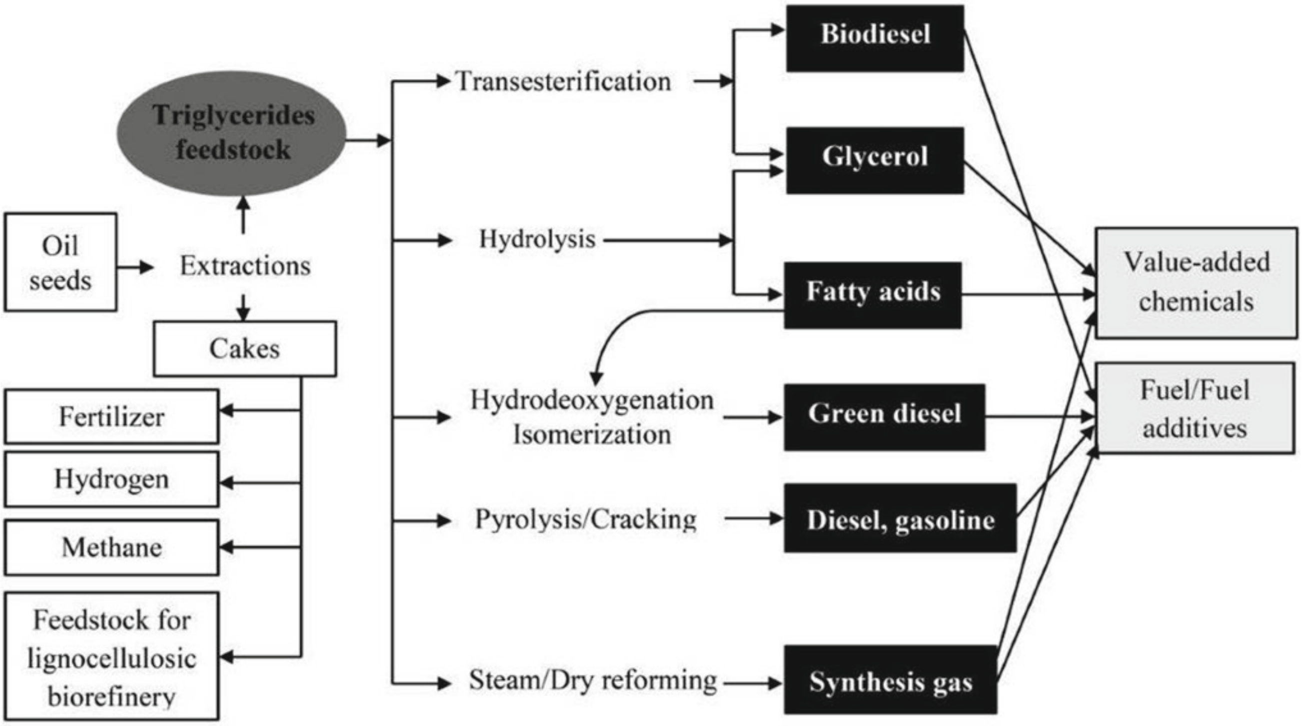
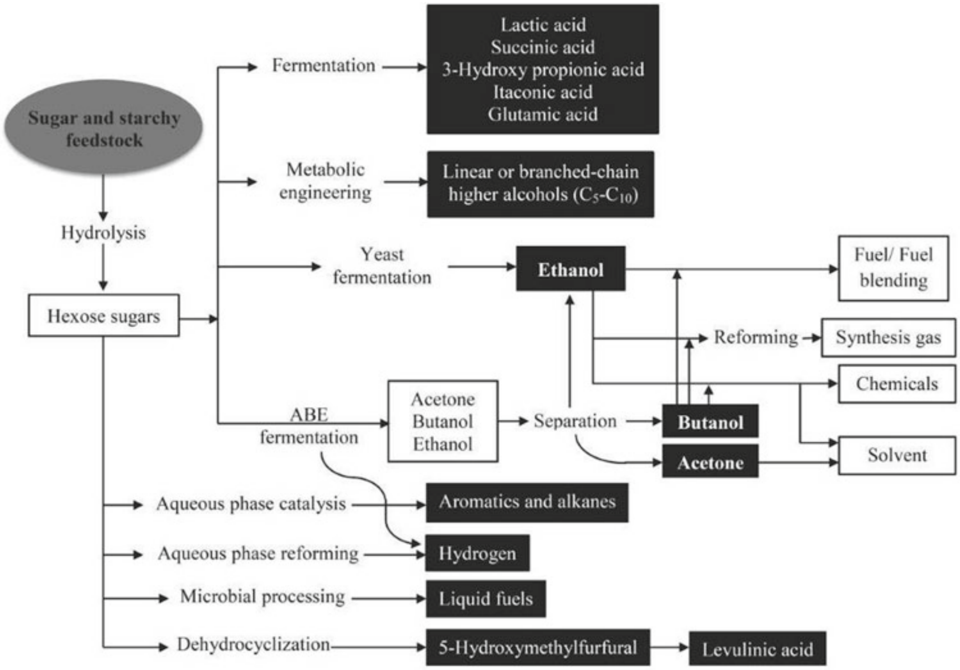


Fig. 8 Potential avenues of triglyceride biorefinery (adapted from Maity et al. 2015)

Fig. 9 Potential of starch and sugar biorefinery (adapted from Maity et al. 2015)



of the aqueous phase is extremely important to be considered. However, the treatment of aqueous effluent is costly and diminishes the process economy of the HTL process. Thus, it is essential to explore the ways for recovering non-polar organic fractions micro- and macronutrients that existed in aqueous phase (Madsen et al. 2016).

There are some alternate ways for the valorization of aqueous phase that are widely discussed in many publications, like catalytic hydrothermal gasification (CHG), anaerobic digestion and recirculation of residual water to HTL system. Elliott et al. suggested the CHG to recover the methane gas for process integration (Elliott et al. 2015).

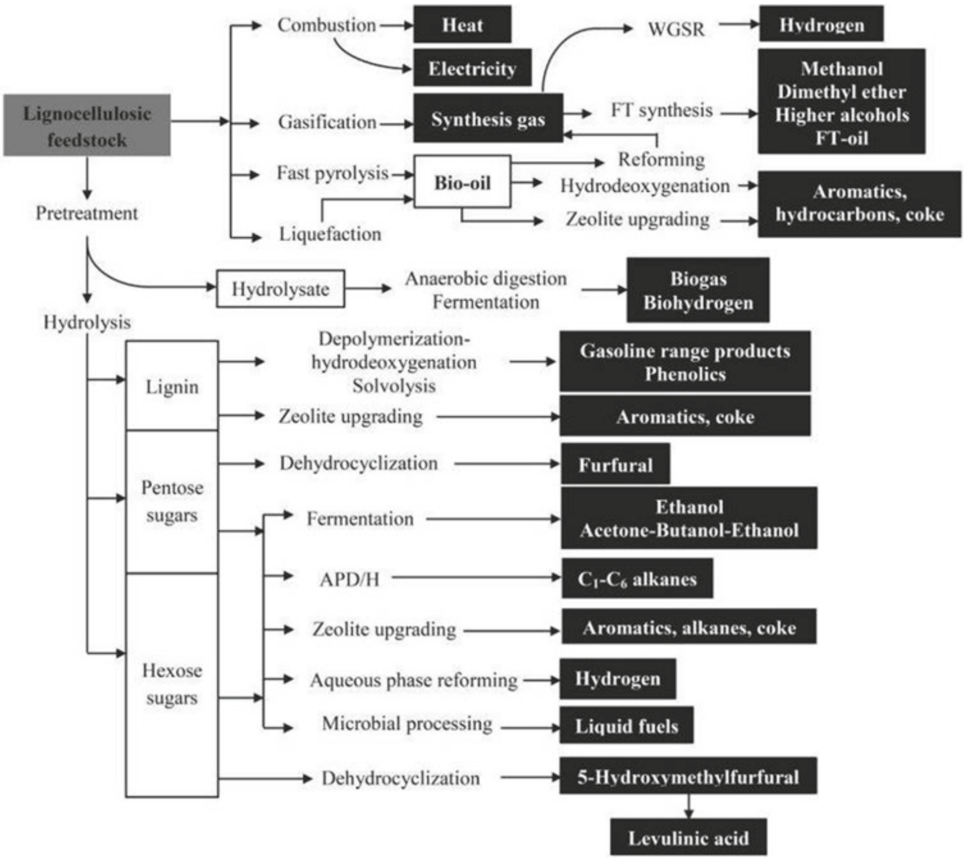


Fig. 10 Potential avenues of lignocellulosic biorefinery (adapted from Maity et al. 2015)

Similarly, Tommaso et al. had used the HTL aqueous phase for anaerobic digestion to produce methane gas with 61% of removal of COD and 84% of an anaerobic biodegradability (Tommaso et al. 2015).

Among all these ways, the recirculation of residual water from the HTL system has received much attention recently. In the literature almost all the studies reported enhanced bio-crude quantity according to the number of recirculation (Déniel et al. 2016; Biller et al. 2016; Li et al. 2013; Ramos-Tercero et al. 2015; Zhu et al. 2015). Pedersen et al. could not notice a trend in the yield of bio-crude because of complicated extraction procedure from the continuous plant, while H/C was observed to increase slightly with three recirculations. Pacific Northwest National Laboratory (PNNL, USA) also noticed enhanced bio-crude quality and quantity with recycling residual water produced from the HTL of corn stover and pine (Elliott et al. 2015). From the available literature, the major studies found related to recycling of aqueous phase from different biomasses are described in Table 1.

Zhu et al. studied the effect of residual water recycling from lignocellulosic feedstock straw at 300 °C with a catalyst (K_2CO_3) (Zhu et al. 2015). It was reported that after three successive cycles, bio-crude production yield was raised from 34.9 to 38.4 wt% (db) as demonstrated in Fig. 11a.

The presence of organic components in residual water accelerated the decomposition reaction rate of barley straw and portioned into bio-crude. Secondly, solid residue increased due to repolymerization of reactive compounds present in bio-crude. From the quality point of view, a smaller gain in HHV (from 27.29 to 29.4 MJ/kg) unwraps the new possibility of usage of residual water in liquefaction of straw at subcritical condition. Recirculation of Chlorella vulgaris was performed at 240 °C for 30 min residence time. The bio-oil yield raised up to (42.2 wt%, daf) after six cycles, almost three times more as compared to the reference run (14.3 wt%, daf) as shown in Fig. 11b (Ramos-Tercero et al. 2015). This increase in bio-crude was due to saturation of light polar organic in the aqueous phase. The interesting point to be noticed here is that HHVs bio-crude slightly decreased. This decrease in HHV is related to increasing concentration of nitrogen due to repolymerization of nitrogen-rich organic molecules of aqueous phase, which ended up in bio-crude. Biller et al. also found increased concentration of nitrogen from 5 to 8.3% after nine recirculations (Biller et al. 2016).

Previous studies observed that the acetic acid is the most essential and responsible compound in aqueous phase for increasing the bio-crude yield (Li et al. 2013; Ramos-Tercero et al. 2015; Zhu et al. 2015). Ross et al.

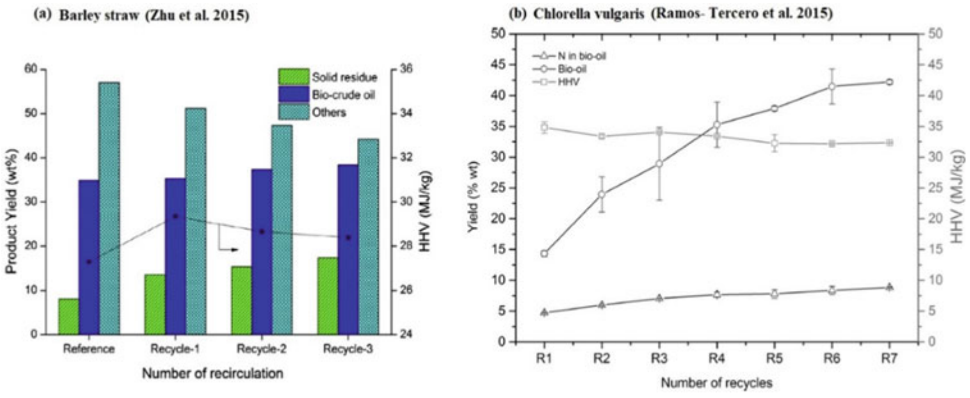


Fig. 11 Effect of recirculation of residual water on bio-crude quality and yield, **a** Barley straw (adapted from Zhu et al. 2015), **b** Chlorella vulgaris (adapted from Ramos-Tercero et al. 2015)

investigated the catalytic effect of acetic acid at subcritical conditions for two microalgae species with different amount of lipid content (Ross et al. 2010). It was found that acetic acid was comparatively more favorable than alkali catalyst to enhance bio-crude yield. In biomass liquefaction, the decomposition of organic acids form in-situ carbon monoxide and hydrogen; subsequently, the in situ hydrogen could work as a hydrogen (H) donor to boost the bio-crude quantity and quality. Hu et al. further validated this finding by reporting maximum energy recovery up to 65% via recycling one-time aqueous phase with formic acid as catalyst (Hu et al. 2017). However, the HHV of resulting bio-crude also slightly improved from 33.87 to 34.95 mJ/kg. Li et al. liquefied desert shrubs (Salix psammophila) with acetic acid and found the same increment in bio-crude yield as it was in the second cycle (Li et al. 2013).

4.2 Chemical Composition and Applications

The composition of residual water is highly dependent on the chemical components of the feedstocks. The most significant indicators of assessing the quality of aqueous phase are total nitrogen, total organic carbon, and the composition of organic and inorganic elements. The comprehensive characterization of the aqueous phase is very complex, because of the presence of a variety of light-weight organic compounds, which require specific columns for the detection through gas chromatography-mass spectrometry (GCMS). However, there are few studies in which characterization of aqueous phase has been specifically investigated (Gai et al. 2015; Maddi et al. 2016, 2017; Villadsen et al. 2012).

Hu et al. characterized aqueous phase from Chlorella vulgaris, and observed that with the successive recycling, the dark color was developed in residual water, which indicates saturation of organic matter in aqueous phase (Hu et al. 2017). Figure 11a illustrates that N-containing compounds accompanied with amides covered the majority of the area due to the decomposition of protein in hydrolytic environment (Shuping et al. 2010). The N-containing compounds are generated from the Maillard reaction between amino acids and sugars. These could serve as scavengers of highly reactive fractions, and prevent conversion of bio-crude into char (Déniel et al. 2016). This point was proved by Hu et al. in the same study, who found a minor reduction in solid residue afterward three recirculations (Hu et al. 2017). Lower organic acids were produced via recycling, as shown in Fig. 12a. The recycling increases in the concentration of organic compounds that reduce solubility of carboxylic acids in residual water, and leads to bio-crude formation. Various studies reported previously related to the recycling of aqueous phase during HTL have been discussed in

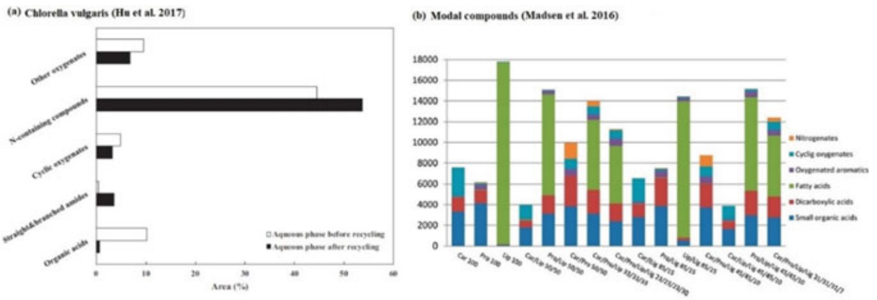


Fig. 12 Characterization of aqueous phase, **a** Chlorella vulgaris, adapted from Hu et al. (2017), **b** Modal compounds, adapted from Madsen et al. (2016)

Table 2. In one of the studies, Madsen et al. investigated the residual water produced from the model compounds in different amounts of carbohydrate, lipid, lignin and protein at 335 °C (Madsen et al. 2016). The author quantified the percentages of different compounds in aqueous phase by preparing the calibration curves. A total of 67 compounds were quantified, which include short-chain cyclic oxygenates, carboxylic acids, fatty acids, nitrogenates and oxygenated aromatics as reflected in Fig. 12b.

The fatty acids containing ($\geq$C14) were found in higher concentration due to the addition of alkali catalyst, while cyclic oxygenates were probably derived from carbohydrates. Organic acids in the range of C12 are formed specifically from the hydrolysis of proteins and carbohydrates; however, the oxygen containing aromatics mainly originated from lignin. Surprisingly, the maximum concentration of acetic acid was formed from the proteins sample that is probably due to deamination of glycine (Gai et al. 2015). Earlier studies from HTL of microalgae has indicated a high concentration of acetamide, which is formed between the reaction of acetic acid and ammonia (Maddi et al. 2016). From nitrogenated compounds, especially pyrazines were mainly formed from protein. The pyrazine is formed by the secondary reactions of ammonia produced from deamination reaction of amino acids. However, in sample 6 in Fig. 12b, pyrazine increases 20-fold with the mixing of carbohydrates. Moreover, the addition of slight quantity of lipid or lignin significantly decreases the quantity of pyrazines that is due to production of amides derivatives with carboxylic acids.

Gai et al. determined the presence of nitrogenous compounds in residual water from protein-rich feedstocks (Gai et al. 2015a, b, c). The observed concentration of total nitrogen (TN) contents in residual water was in the range of 11000 ± 306 to 31700 ± 1350 mg/l. The degradation of triglycerides formed fatty acids. It is important to discuss that dicarboxylic acids like succinic acid and glutaric acid existed in higher amount in the mixtures of biomass that contain 45% protein than in mixtures with lower protein. Villadsen et al. had used HPLC-TOF-MS spectroscopic technique to detect fatty acids in carbon number range (C14−C22) in residual water from "Dried Distillers Grains with Solubles" (DDGS) (Villadsen et al. 2012). The major fatty acids detected are octadecanoic acid, tetradecanoic acid, hexadecanoic acid, icosanoic acid (C20) and docosanoic acid (C22).

Besides the quantification of organic compounds, in one of the studies from the literature Maddi et al. detected the inorganic elements from aqueous phase produced from industry-based food residues, biomass affiliated to wastewater, municipal wastes and through ICP-OES (Maddi et al. 2017). The selected inorganic elements detected through ICP-OES from different feedstocks are mentioned in Table 3. For food waste four types of materials were used: Montepulciano grape pomace, Cabernet Sauvignon grape pomace, sugar beet tailings, and grains. They are designated as F1W01, F1W02, F1W03 and F1W04, respectively (Table 3).

From Table 1, Na and K showed the highest concentration. These elements existed in the form of chlorides, sulfates, nitrates, phosphates, etc. This is further validated by the presence of high amounts of chlorides (57, 103, 73 ppm), sulfates (100, 231, 236 ppm), nitrates (65, 50, 67 ppm) and phosphates (24, 765, 62 ppm) for primary, secondary and digested sludge, respectively. Sulfur was detected in all aqueous phase streams of feedstock, which could have originated from the hydrolysis and cleavage of protein-containing sulfur. Similarly, phosphorus was found in substantial amount in municipal organic and solid wastes as well as other biomass derived from lignins (corn stover).

The higher concentration of phosphorus was detected in the streams of residual water obtained from HTL of municipal organic and solid waste residues. Intrinsically, these wastes often carry phosphorus through industrial run-offs, sewage, fertilizers etc. (Fytili and Zabaniotou 2008). However, for biological agents, the phosphorus salts are used as feed on the media for fermentation of sugars derived from corn stover. However, the global supply of phosphorus is limited, and it is necessary to reuse phosphorus recovered from residual water generated from HTL of municipal residual wastes (Neset and Cordell 2012).

The valorization of the aqueous phase as a precursor for hydrothermal processing is an environmentally friendly concept. Valorization of aqueous phase not only improves the energy recoveries but also avoids the treatment cost of the aqueous phase. This enormously decreases the process cost and make the continuous HTL commercially viable for large scale. Since HTL has not been used on a commercial scale due to several complexities, therefore a new concept has emerged as an integration of HTL unit with other technologies, which are commercially available like gasification and anaerobic digestion. Thus, the option of integrated HTL with gasification plant has been suggested, where aqueous phase from HTL could be utilized to produce hydrogen gas that fulfills the hydrotreating requirement for the bio-crude (Cherad et al. 2016). Few studies suggest the integration of HTL with anaerobic digestion, which could form the methane gas (Tommaso et al. 2015). Moreover, apart from organic fractions, the aqueous phase is mostly enriched with valuable elements like Na, K and Mg, which paves another alternate way of utilizing aqueous phase as a fertilizer for soil amendment and cultivating biomasses like algae after the necessary treatment.

Table 2 Studies related to recycling of aqueous phase in HTL unit

Feedstock	Temperature (°C)	Catalyst	RT (min)	Cycles	Key findings	References
Barely straw	300	K_2CO_3	15	3	In recirculation, acidic acid played a vital role in the improvement of bio-crude quantity from 34.9 to 38.4 db, due to efficient decomposition of barley straw. On the contrary, solid residue increased and higher carbon content was noticed in solid residue with the recycling of aqueous phase	Zhu et al. (2015)
Micro algae (Chlorella vulgaris)	240	None	30	7	The bio-crude yield increased three times to its original yield (14.3 to 42.2 daf). HHV decreased due to increase in N content in the bio-crude	Ramos-Tercero et al. (2015)
Black current (Ribes nigrum L)	310	None	10	5	Recycling of aqueous phase increased bio-crude yield (26 to 31 db) and energy recovery (48–57%)	Déniel et al. (2016)
(DDGS)	350	None/ K_2CO_3	20	9/10	Recycling of aqueous phase with catalyst showed higher increase in bio-crude as compared to non-catalytic samples. Higher accumulation of total organic carbon and total nitrogen was noticed in the aqueous phase via recirculation	Biller et al. (2016)
Desert shrub Salix psammophila	340	None	50	3	Substantial increase in bio-crude was found (30–46.9 db), whereas bio-crude with recycling aqueous phase had lower HHVs due to lower carbon. Acetic acid was employed as catalyst and increased bio-crude yield equivalent to the second recycle	Li et al. (2013)
Micro algae (Chlorella vulgaris)	275	None	50	3	Bio-crude yield was increased from 29.39 to 38.87 db, with recycling of aqueous phase. Catalytic recycling of aqueous phase with Na_2CO_3 and formic acid yielded more bio-crude. HHV was not affected by recycling with fresh water, but slightly increased with Na_2CO_3	Hu et al. (2017)
Aspen Wood/ Glycerol	400	K_2CO_3	15	3	No clear trend was observed in bio-crude yield, but high quality of bio-crude was obtained with 34.3 MJ/kg. However, total organic carbon in aqueous phase was increased up to 136.2 g/l after three recirculations	Pedersen et al. (2016)

Table 3 Inorganics in residual water, adapted from Maddi et al. (2017)

	Industrial food waste				Municipal waste water treatment plant (MWWTP)			Biomass grown on waste streams	
	F1W01	F1W02	F1W03	F1W04	Primary sludge	Secondary sludge	Digested sludge	Oleaginous yeast grown on corn stover lignin residue	Mixed algae culture grown on MWWTP
Al	BDL	BDL	BDL	BDL	2.12	2.17	2.13	3.15	BDL
Ba	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Ca	BDL	8.06	BDL	BDL	BDL	BDL	BDL	5.74	2,58
Fe	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
K	3342	3883	1165	53.64	83.1	386.3	102.7	5034	323,5
Mg	2.55	3.26	47.12	BDL	4.15	BDL	BDL	12.89	3.42
Mn	BDL	BDL	9.2	BDL	BDL	BDL	BDL	BDL	BDL
Na	5341	4205	3579	953	56.7	84.76	53.27	108.3	441.8
P	BDL	BDL	BDL	202.7	11.96	306.6	30.74	441.6	BDL
Sr	BDL	BDL	23.91	BDL	BDL	BDL	BDL	BDL	BDL
Si	38.65	50.92	54.08	56.96	97.27	120.3	207.9	63.04	61.32
S	66.78	39.65	29.55	44.94	75.89	211.3	166	1224	198.4

5 Conclusions

Hydrothermal liquefaction is a green and sustainable technology for transformation of waste biomass from biological processes, agricultural waste, forest residue and municipal organic waste materials to biofuels and valuable commodity chemicals. The utilization of organic biomass wastes, agricultural and forest residue could be an important substitute renewable energy and chemical source. Both sub- and supercritical techniques employ water as a sustainable and green solvent for biomass processing under high pressure and temperature conditions and it is important from environmental and economic point of view that worldwide waste biomass is evaluated as precursors for biofuels and commodity chemicals. Supercritical water, being a single-phase component, acts as sustainable medium for dissolving a variety of substances and organic wastes for chemical synthesis and production of bio-oil. Furthermore, recirculation of aqueous phase obtained during hydrothermal liquefaction process improves the yield of organic chemical compounds and hydrocarbons in the bio-crude oil. Nevertheless, future of synthesis of chemicals and biofuels from the organic waste materials employing sub- and supercritical water treatment technologies is promising, which can lead to low production cost, high yield, high efficiency and quality products.

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Bioconversion of Food Waste into Ethanol: A Review

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Abstract

The development of sustainable sources of energy brings forth the idea of exploration of different renewable sources for the production of biofuels. Globally, the contribution of the biofuel industry in reducing fossil-fuel dependency, mainly in the transportation sector, is rising. With the development of alternative sources of energy, biofuels like ethanol and butanol are becoming progressively comparable to the petrochemical-derived fossil fuels in terms of their technical and environmental performance. First-(1G) and second-generation (2G) biofuels are derived from food-competent substrates and non-food-competent substrates, respectively. This chapter demonstrates the feedstocks available from different food wastes for biologically-derived ethanol and how they help in ensuring sustainability. Biochemically, ethanol is produced from microbial-fermentation reactions. This article brings out an in-depth comparison of thermochemical and biochemical routes for ethanol production. It aims to provide a basis and understanding of the plausible shift toward the development of microbially-derived fuels. There are, however, many technological challenges for the commercial production of biofuels. Different pretreatment techniques adopted for structural modification of biomass have been discussed. Also, different fermentation strategies based on the degree of integration of intermediate steps involved have been described. The selection of the pretreatment techniques, fermentation strategies, and other intermediary steps in the biological process synchronously determine the overall economic competitiveness and the level of technological readiness of the process. The technology-readiness levels (TRL) of 1G and 2G bioethanol-production technologies are at commercialization and pilot-plant demonstration stages, respectively.

Keywords

Bioethanol • Lignocellulosic-based biomass • Pectin-based biomass • Pretreatment techniques • Microbial fermentation • Ethanol recovery

1 Introduction

The global-energy dependency is the key concern of the twenty-first century. 90% of the world's energy requirement is met through fossil-fuel consumption (coal, petroleum, and natural gas) (Sivakumar et al. 2010; Singh et al. 2016; Dale 2008). The conventional energy sources (coal, petroleum, and natural gas) have limited reserves and their utilization has adverse effects on the environment, which include greenhouse-gas emissions like that of carbon monoxide, NO_x, SO_x, and drastic changes in climatic conditions (Stephen and Periyasamy 2018). Petroleum oil contributes to 40% of our energy demands. There is, therefore, a surge in the price of petroleum oil and soon we would reach the tipping point, the peak-oil point. The peak-oil point is considered to be a theoretical stage where the exploration of newer oil fields will not suffice to compensate for the depletion of the existing oil reservoirs. It is predicted vaguely when the peak-oil point will occur, but the consumption trends depict that the oil reserves would be depleted soon. Besides, of the existing oil reserves, some are located in the areas of political agitation which make them inaccessible, and thus the fluctuations in the oil supply and price are well expected (Sivakumar et al. 2010). The fossil-fuel dependency along with an increase in pollution levels worldwide creates the need for the development of renewable fuels.

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Liquid biofuels are suitable for use as an alternative to fossil fuels. Renewable biofuels can be used as a replacement of fossil fuels only if: (a) the global food-supply chain is not compromised, (b) the carbon-energy balance is neutral (C-neutral fuel) or negative (C-negative fuel), and (c) these are environment-friendly. C-negative fuels are expected to decrease the atmospheric carbon concentration and C-neutral fuels are the ones that have no effect on the atmospheric carbon concentration (Johnson et al. 2007). Among the biofuels, bioethanol is considered a potential transportation biofuel. Bioethanol is known to have an 80% lower emission profile when compared to the conventional petro-gasoline (Akbas and Stark 2016).

Choice of substrate: The choice of substrate for bioethanol production plays a significant role in the overall economics of the process. Among agricultural biomasses, different food wastes for bioethanol production are being explored worldwide, some of which are potato peels, potato-processing wastes, pineapple peels, whey, rice husks, coffee-bean husks, corn-processing wastes, and fruit-processing wastes. Food-waste utilization for bioethanol production provides sustainability as well as reduces solid-disposal liability (Gonzales et al. 2005; Pires et al. 2011).

1G biofuels are considered to be the ones that are derived from energy-intensive substrates like starch-based crops, sugarcane molasses, and many other crops. The dependency on starch-based crops for biofuels production creates food competency and stress on farmlands. 2G biofuels are those which are produced from lignocellulosic-based substrates, mainly from agricultural wastes. Other lignocellulosic biomasses include organic wastes from municipalities and industries (Akbas and Stark 2016). The utilization of organic wastes for biofuel production is one of the strategies to ensure food security, and waste management along with minimizing environmental pollution (Stephen and Periyasamy 2018).

2 Utilization of Food Wastes for Bioethanol Production

As the population is increasing steadily, the demand for food production is expected to rise as well. Solid wastes from the food industries are either dumped into landfills causing environmental pollution or fed as an animal fodder. For example, out of the wastes generated from the Indian-grain processing industries, 90% is discarded and only 10% is utilized as an animal fodder (Akbas and Stark 2016). Data indicate that 55% of food wastage comes from fresh fruits and vegetables, dairy products, and the rest is due to wastage of grain products and fats and oils [U.S. Department of Agriculture]. Different food wastes are generated by the industries which have the scope of utilization for biofuel production, like sugarcane residues, citrus wastes, molasses, residues from starch-based foods, and so on. Their utilization thus provides dual benefits, concerning economics and waste management with zero or low cost of substrate (waste) procurement. The food wastes are a supplement to the biologically derived ethanol. Table 1 indicates different food wastes, fermenting organisms, and fermentation strategies involved in bioethanol production.

3 Whey and Lignocellulosic-Based Biomass

The main difference between lignocellulosic and pectin-based biomasses lies in the availability of predominant lignin content present in the former while being absent in the latter. The wastes from fruits industries have a negligible amount of lignin content in them; for example, the lignin content is less than 2% (dry wt. basis) in citrus wastes and sugar-beet pulp when compared against 26% (dry wt. basis) present in Monterey pine (Edwards and Doran-Peterson 2012). Lignin present in lignocellulosic biomasses hinders the pretreatment step, and thus affects the efficiency of the enzymatic degradation process (Chang and Holtzapple 2000; Guo et al. 2009). The compositional analysis of lignocellulosic biomasses suggests that cellulose present is 25–55%, hemicellulose 24–50%, and lignin is present in the range of 10–35% (all on dry wt. basis) (Sun and Cheng 2002). Linkage of cellulose with hemicellulose is just a physical association, whereas there is a chemical linkage of cellulose with lignin (Mussatto et al. 2008). Cellulose is bonded with hemicellulose as microfibrils to form a matrix layered with lignin fractions over it (Rubin 2008). The lignocellulosic biomasses need pretreatment (physical, chemical, or biological) prior to fermentation for lignin separation and/or its effective particle size reduction. Economics of the process show that more than 50% of the total operating cost arises because of the pretreatment for lignin degradation. The choice of the pretreatment technique has a pervasive influence on all factors concerning the degradation of cellulosic materials (Yang and Wyman 2008).

Pectin-rich biomass, as the name suggests, is predominant in pectin content, varying from 12 to 35% (dry wt. basis) of the biomass. The main advantage of using pectin-rich biomasses lies in the ease of hydrolysis, as these biomasses are a processed residue discarded from the processing of fruits or vegetables for sugar or juice production. A study on this class of biomasses by different research groups revealed that these do not require harsh pretreatment techniques, as required otherwise by lignocellulosic-rich biomasses. Citrus wastes, one of the abundant pectin-rich biomasses, require pretreatment for limonene separation which is inhibitory toward fermentation and also for the biomass-structure

Table 1 List of different food wastes utilized for bioethanol production

	Substrate	Hydrolysis technique	Fermenting organism	Fermentation strategy	Ethanol titer value	Ethanol yield	References
Pectin-based biomass	Orange peel	Enzymatic	*S. cerevisiae*	SHF	15 g/L	0.495 g/g	Santi et al. (2014), John et al. (2017)
	Apple pomace	Enzymatic	*S. cerevisiae*	Batch fermentation (5L)	190 g/kg	0.393 g/g	Parmar and Rupasinghe (2013)
	Grape pomace	no data	*S. cerevisiae*	SSF	53.2 g/kg	81%	Hang et al. (1986)
	Banana peel	Enzymatic	*S. cerevisiae, Pachysolen tannophilus*	SSCF	26.84 g/L	0.426 g/g	Sharma et al. (2007), Mamma and Christakopoulos (2014)
Lignocellulosic-based biomasses and whey	Potato-processing waste	Enzymatic	*S. cerevisiae*	Batch fermentation (2.5L)	35 g/L	no data	Izmirlioglu and Demirci (2012), Dos Santos et al. (2016)
	Coffee-processing pulp	no data	*S. cerevisiae*	Batch fermentation	13.6 g/L	75.04%	Gouvea et al. (2009)
	Cheese whey	no data	*Kluyveromyces marxianus*	Batch fermentation	23 g/L	no data	Sansonetti et al. (2009), Panesar and Kennedy (2012)
	Rice husk	Enzymatic	*E. coli* (Recombinant)	SHF	9.8 g/L	0.49 g/g	Saha and Cotta (2008)

SHF: Separate hydrolysis and fermentation
SSF: Simultaneous saccharification and fermentation
SSCF: Simultaneous saccharification and co-fermentation

degradation to bring it to a hydrolyzable form (Kennedy et al. 1999; Zhou et al. 2008; Grohmann et al. 1994; Wilkins et al. 2007).

A few examples of whey and lignocellulosic-based biomasses are given below.

3.1 Whey: A Cheese Processing Waste

The major by-product of cheese-manufacturing industries is cheese whey which is produced in significant amounts, resulting in waste-management problems as their disposal is a serious issue. Studies depict that environmental pollution arising from discarding 4000L of whey is equivalent to feces discharge of 1900 humans (Akbas and Stark 2016; Tunick 2008). Currently, the production rate of cheese whey is 10^8 ton/year (Zotta et al. 2020), most of which is utilized as a food ingredient. The unutilized portion is either disposed off or utilized as a fertilizer.

Whey is composed of 5–6% lactose, 1% protein, 0.06% fat, and 0.1–0.8% lactic acid (Akbas and Stark 2016). Based on the pH value, whey is classified into two categories: sweet whey (pH $\geq$ 5.6) and acid whey (pH $\leq$ 5.1). The compositional analysis shows that acid whey has a higher content of calcium, phosphate, lactic acid, and lactate than sweet whey.

Comparative studies between different yeasts and bacteria show that low ethanol titer value at the end of fermentation is a common problem that researchers are continually trying to find solutions for (Porro et al. 1992; Guimaraes et al. 1992; Leite et al. 2000). On using cheese whey as the carbon source for ethanol production, the major limitation for *Saccharomyces cerevisiae* (*S. cerevisiae*) is its inability to utilize lactose, which comprises glucose and galactose, and lacks the β-galactosidase enzyme and thus lactose cannot be transported into the cell (Domingues et al. 2010). Unlike *S. cerevisiae*, yeasts like *Kluyveromyces fragilis* are capable of utilizing lactose, up to a concentration of 20%, but experience inhibition by the presence of sugar and salt in whey and have a negligible ethanol tolerance.

Researchers have adopted techniques like mutagenesis for the simultaneous utilization of glucose and galactose by *S. cerevisiae* (Bailey et al. 1982). Treating the cheese whey with β-galactosidase for easy conversion of lactose to glucose and galactose is yet another approach other than hydrolysis of cheese whey before its fermentation by the yeast. However, this method has its limitations of carbon catabolite repression (CCR) because of which galactose utilization by the yeast takes place only after glucose utilization (Gancedo 1998; Mehaia and Cheryan 1990).

Economics of the process show that production of 2–3% (v/v) ethanol from whey comprising 5–6% lactose are not favorable due to the very high distillation costs involved in ethanol recovery from the fermentation broths (Guimarães et al. 2010).

3.2 Coffee Pulp and Husk

The by-products generated during coffee-beans production include pulp, wastewater, and husk, all of which are rich carbon sources for ethanol fermentation. These are, otherwise, dumped into water sources polluting them extensively, and making water highly acidic.

Processing yields one-tonne pulp per two tonnes of coffee beans (Roussos et al. 1995). The compositional analysis (dry weight basis) of coffee pulps suggests that these are mainly made up of 23–27% fermentable sugars and 8.25% protein. The pretreatment of coffee pulp using dilute sulfuric acid results in a hydrolysate of composition: xylose (up to 3.23 g/L), arabinose (up to 11.26 g/L), fructose (up to 3 g/L), glucose (up to 6.31 g/L), sucrose (up to 96 g/L), and maltose (up to 3.50 g/L) (Urbaneja et al. 1996).

Apart from sulfuric-acid treatment, even distilled water is used to pretreat the coffee pulp prior to fermentation. This treatment had been adopted and carried out for 4 h by Kefale (2011) prior to fermentation by *S. cerevisiae*, which was performed for 24 h at 30 °C to yield ethanol of 7.4 g/L.

In addition, many other by-products of coffee-bean industries, for example, coffee husk, can be used for ethanol production. For every 1 kg of coffee beans produced, an equivalent amount of 1 kg of coffee husks is produced. Coffee husks provide other uses, for example, as a fuel, as an animal feed, and many others (Franca and Oliveira 2009). Ethanol concentration up to a titer value of 13.6 g/L was achieved by Gouvea et al. (2009) by fermenting whole and ground coffee husks by *S. cerevisiae*.

3.3 Potato-processing Waste

Potatoes are considered a significant food crop that is made up of starch molecules. Starch, a polymer of glucose molecules, serves as the main source of energy in plants. It is the main carbohydrate source from which energy is derived for all the metabolic functions of the plant (Fonseca et al. 2008). A large fraction of potatoes is wasted during its production as well as in the potato-chips industries (Fadel 2000). Glucose recovered from the wastewater, produced during the manufacturing of the potato chips, can be used as the carbon source for bioethanol production. Optimization studies on hydrolysis had been conducted by **Izmirlioglu and Dermicri** for the potato-processing wastes to be fermented by *S. cerevisiae* for bioethanol production (Izmirlioglu and Demirci 2012).

3.4 Rice Husk

Rice is an important food crop in most of the Asian countries. Rice processing produces rice husks, which contribute to 22% of the processing waste, whereas the rest 78% comprises rice, broken rice, and bran (Nagrale et al. 2012). Rice husk could be used as a fermentable carbon source for ethanol fermentation, instead of dumping it as such creating environmental pollution.

Many fermentation techniques have been adopted for ethanol production from rice husks, which include separate hydrolysis prior to fermentation, simultaneous saccharification and fermentation, and many others. Rice husk is composed of 50% cellulose, 25–30% lignin, and 15–20% silica (Akbas and Stark 2016). The presence of lignin in rice husk makes the availability of cellular enzymes to cellulose very cumbersome and hence provides resistance during hydrolysis (Rostagno et al. 2015). It is, therefore, preferred that the addition of the rice husk to the fermentation medium takes place after pretreating the rice husk to form fermentable sugars, else the overall efficiency of the process goes down. **Saha and Cotta** had done lime treatment followed by enzymatic treatment using enzymes like cellulase, hemicellulase, and β-galactosidase to produce a fermentable hydrolysate of monomeric sugars which yielded 9.8 g/L ethanol after 19 h of fermentation at 35 °C by *Escherichia coli (E. coli)* FBR5 (Saha and Cotta 2008). An ethanol titer value of 11 g/L was produced by simultaneous saccharification and fermentation carried out for 53 h at 35 °C.

Other fermentation techniques have been investigated too. Acid pretreatment of the rice husk prior to fermentation by Moon et al. (2012) gave an ethanol yield which is 4% lesser than the theoretical maximum. The cell growth is slightly compromised because of the presence of inhibitors produced during the acid pretreatment.

4 Pectin-Rich Biomass

Pectin is a polysaccharide which is in plenty in cell walls of plants and is an important source for the overall growth of the plant (e.g. morphogenesis, defense, wall porosity, seed hydration, and fruit development). The uses of pectin include a gelling and stabilizing agent, production of adhesives, plasticizers, and in drug delivery systems. The study on the structure of pectin suggests that it is covalently bonded by galacturonic acids (70%) (Mohnen 2008). Many other constituents are also expected in pectin, like rhamnose, xylose, arabinose, and galactose (Edwards and Doran-Peterson 2012). The four pectic polysaccharides comprising pectin are homogalacturonan (HG), xylogalacturonan (XGA), rhamnogalacturonan I (RG-I), and rhamnogalacturonan II (RG-II) (Scheller et al. 2007).

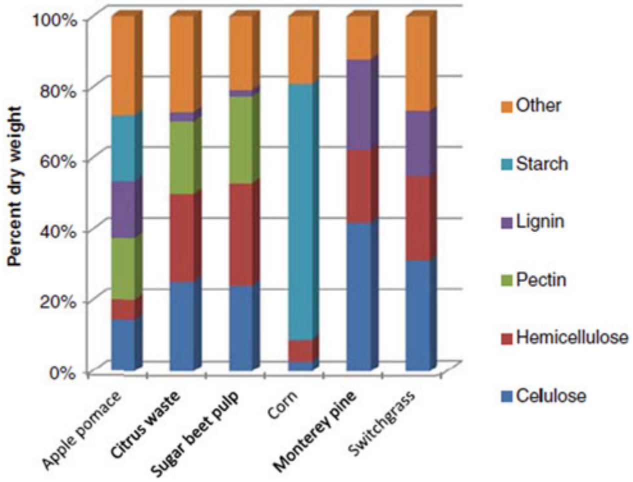


Fig. 1 A compositional analysis (dry weight) of pectin-based (apple pomace, citrus waste, sugar-beet pulp), lignocellulosic-based (Monterey pine, switchgrass), and starch-based (corn) biomasses. (Illustration adapted from Edwards and Doran-Peterson (2012) with permission from Springer)

Pectin is found to be present in enormous quantities in the fruits processing industries wastes like apple pomace, citrus waste, and sugar-beet pulp. Figure 1 depicts the dry weight compositional analysis of pectin-rich and lignocellulosic-rich biomasses. Research on pectin-rich biomasses suggests that, instead of utilizing as an animal fodder, these under-utilized biomasses can serve as a rich and potential source of ethanol production. This class of biomasses comprises pectin, which is roughly around 20% of its total dry weight. Some examples of this class of biomasses are mentioned below.

4.1 Apple Pomace

Apple processing involves several intermediate stages. The apples, when subjected to squeezing and pressing for juice extraction, simultaneously produce a residue called apple pomace, which constitutes ~30% of the fruit. The compositional analysis of apple pomace shows that the major components present in it are cellulose, hemicellulose, pectin, lignin, and lower levels of vitamins and proteins. The soluble polysaccharide of the pectin in apple pomace is called protopectin (Vendruscolo et al. 2008; Shin et al. 2005). Solid-state fermentations were carried out for ethanol production by Hang and group (Hang et al. 1981) at 30 °C for 96 h and by Khosravi's group (Khosravi and Shoja 2003) with an initial sugar content of 26 w/w% to yield 2.5 w/w% ethanol without saccharification and 8 w/w% with saccharification.

4.2 Waste Orange-peels Biomass

Orange peels usage for bioethanol production imparts value addition to the orange-producing industries. The orange peel is rich in soluble sugars (glucose, fructose, sucrose) and fibers like cellulose, hemicellulose, pectin, and lignin. They are also a good source of components like organic acids, and essential oils (Rivas et al. 2008; Plessas et al. 2007). Essential oils have applications in food industries as flavoring agents (Hull et al. 1953). Succinic acid finds its application as a green-platform chemical for the production of value-added products like polyamides, polyesters (Ángel Siles López et al. 2010; Bechthold et al. 2008). Enzymatically treated orange peels are acted upon by *S. cerevisiae* in a fermentation reaction to give ethanol. A study on threshold D-limonene concentration, one of the inhibitory products toward ethanol production, was performed by Wilkins and group (Wilkins et al. 2007). They performed their experiments using *S. cerevisiae* and *Kluyveromyces marxianus* and concluded the threshold concentrations at 24, 48, and 72 h to be 0.05%, 0.10%, and 0.15%, respectively. The steam-explosion method was adopted as the pretreatment technique for D-limonene separation. Cell-immobilization technique, with operational stability of the immobilized cells over a temperature range of 30–15 °C, was adopted for ethanol production with productivity close to 150.6 g/l-d (Plessas et al. 2007).

4.3 Banana-peels Biomass

Bioconversion of banana-peels biomass into ethanol can contribute to solid-waste management with respect to the heavy-disposal liability of the dry banana peels which make up ~30% (w/w) of the total weight. Lower ethanol productivity and concentration are technological barriers faced during this conversion process (Hammond et al. 1996). Banana-peels biomass, rich in fibers like hemicellulose and pectin, were enzymatically treated followed by simultaneous saccharification and fermentation (SSF) by Oberoi and group (Oberoi et al. 2011) for optimization of different fermentation parameters involved. The banana-peels biomass, before and after pretreatment, had different concentrations of cellulose and pectin. Two enzymes, cellulase and pectinase, were therefore added into the pretreated banana-peels biomass. Of the two, pectinase was more effective in hydrolyzing the biomass. However, the addition of both the enzymes in an optimum ratio was necessary for achieving optimal ethanol concentration. Fermentation beyond 14 h resulted in CCR due to the aggregation of glucose molecules in the fermentation broth. A study on the utilization of kinnow waste and banana peels for ethanol production was performed by Sharma et al. (2007). Effects of different fermentation parameters were studied to find out the ethanol yield (0.426 g/g) and fermentation efficiency (83.52%) under the optimized conditions (Sharma et al. 2007).

4.4 Ethanologens for Ethanol Production from Pectin-rich Substrates

S. cerevisiae: *S. cerevisiae* is the most widely used microorganism when it comes to ethanol production. It is considered a very robust microorganism due to its high threshold toward both substrate and ethanol concentrations as well as its tolerance toward comparatively lower levels of oxygen and pH (Gujjari et al. 2009). The metabolic pathway of *S. cerevisiae* is such that the product channeling using sugar as a substrate is mainly toward ethanol, thus lesser by-products are formed. This yeast strain can also break down sucrose without any hindrance during the degradation process to form ethanol. However, *S. cerevisiae* cannot effectively metabolize pentose sugars and galacturonic acid, the prominent constituents of pectin-rich biomass (Edwards and Doran-Peterson 2012). Out of the four pectic polysaccharides present in pectin, rhamnogalacturonan I (RG I) contributes to 20–35% of the pectin structure and contains arabinose and arabinan linkages (Mohnen 2008). On that account, researchers have developed xylose and arabinose fermenting strains of *S. cerevisiae*. Detailed research has also gone into the development of galacturonic-acid fermenting strains of *S. cerevisiae* (Sedlak and Ho 2001; Van Maris et al. 2006).

E. coli: *E. coli*, in contrast to *S. cerevisiae*, has very limited tolerance toward both ethanol as well as *S. cerevisiae*. It has, however, a very low pH requirement (Gujjari et al. 2009). This remains the primary reason for the inefficient performance of *E. coli* during fermentations involving break down of biomass structure in acidic medium. Nevertheless, the metabolic pathway of *E. coli* is such that it is competent enough to utilize different carbohydrate sources, including arabinose and galacturonic acid. Galacturonic-acid utilization by *E. coli* has been widely studied by different research groups (Richard and Hilditch 2009). The varied product distributions for sugar fermentation by *E. coli* interferes with its fermentation efficiency. The products formed, other than ethanol, during sugar catabolism include acids, acetates, formates, succinates, and lactates (Jarboe et al. 2007). The production of these bio-based chemicals can lessen the dependency on petroleum-based products. Different research groups have adopted bioengineering of *E. coli* in order to modify its metabolic pathway so as to limit the product distribution more toward ethanol. The major issues regarding fermentation of pectin-rich biomasses are acetate formation along with ethanol and the presence of inhibitors, for example, limonene in citrus wastes (Shaw 1979).

The chemistry involving the fermentation reaction for ethanol production suggests that ratio wise, 1 mol of galacturonic acid forms 1 mol of ethanol and acetate each. The reason behind this lies in the existence of galacturonic acid in higher oxidation states which is why consecutively the requirement for NAD(P)H molecules increases. The need for NAD(P)H molecules is met through pyruvate formate lyase pathway, which gives both ethanol and acetate (Grohmann et al. 1994).

As mentioned earlier, the presence of inhibitory compounds in the biomass is yet another problem. For example, the industrial processing of citrus fruits results in a residue rich in limonene, which constitutes 86–95% of essential oils of this biomass (Shaw 1979). Limonene comprises monoterpenes, an aromatic compound, which are said to disintegrate membrane integrity of cells resulting in movement of cellular components in and out of the cells along with the loss of driving forces which include proton movement and K^+ gradient (Koroch et al. 2007). Limonene offers inhibition toward fermentation even at concentrations of 1.4% (v/v).

Food waste has a varied range of carbohydrate sources. Their structural degradation gives different groups of monomeric units, namely pentoses and hexoses. The ethanologenic organism, therefore, must be able to maximally ferment the mixture of the substrates. This enhances the viability of using the biochemical route with respect to the economic competitiveness of the whole process (Kumar et al. 2009). In this regard, many approaches have been adopted for engineering the fermenting organism in order to expand its metabolizing capability for different carbohydrate sources.

5 Physico-Chemical Characteristics of Food Wastes

The food waste composed of biodegradable constituents can be categorized into solid, liquid, or semi-solid waste. The uniformity in the product composition ensures lesser variations in the composition of the corresponding food waste generated (Zhang et al. 2014). A few examples of solid and liquid food wastes are given below.

Solid food waste: Wastes like tomato waste, apple pomace, grape pomace produced during wine production are mainly characterized by starch, cellulose, hemicellulose, and lignin.

Liquid food waste: Residues from cheese-and yogurt-processing industries, brewery industries, characterized by nitrogen content, fats and oils, and other suspended solids.

The nutrients distribution in the food waste is based on their respective sizes and are broadly classified as a macronutrients (carbohydrates, proteins, and lipids) and micronutrients (sodium Na^+, potassium K^+, calcium Ca^{2+}, magnesium Mg^{2+}, to name a few). Some of the characteristics are as follows (Hegde et al. 2018):

- pH: The pH value of the biomass is suggestive of the period over which it has been stored. The lesser the value, the fresher is the biomass.
- Chemical oxygen demand (COD): It gives a quantitative estimation of the organic compounds present in the biomass. Biomass COD values are proportional to the nutritional values of the same.
- Total solids: The quantifiable constant weight solid fraction produced by the heat treatment (at 100 °C) of the waste.
- Ash content: The measurement of this parameter tells about the inorganic fraction present in the biomass.
- Metal ions: They are the cofactors of enzymes involved in alcohol synthesis. A balanced metal-ion requirement is required for optimum cell growth (van Vliet et al. 2001).
- Carbohydrate content: Higher the carbohydrate content of the substrate (food waste), higher will be the probability toward conversion to alcohol.
- Lipid content: Lipid molecules with a high content of free fatty acids (FFA) enhance tolerance limits of the fermenting organism (yeast) toward ethanol produced in the fermentation broth (van Vliet et al. 2001).
- Protein content: Proteins are a source of nitrogen content and need to be present in an optimum carbon to nitrogen ratio. Protein limitation or excessive overloading can affect the hydrolysis process and ultimately hinder substrate utilization (Hegde et al. 2018; Zhao 2008).

6 Comparison of Conversion Strategies for Ethanol Production

Feedstock utilization for 2G bioethanol production is carried out worldwide using collateral conversion routes, namely thermochemical and biochemical (as mentioned in Sects. 3 and 4) routes. A detailed comparative study of both these routes has been reported by Mu et al. (2010).

Thermochemical process: The entire process can be broken down into 6–7 stages. It starts with feedstock production followed by an assemblage of the same and further transportation to the thermochemical-conversion facility. At the facility, the substrate undergoes initial drying using flue gas produced from the gasification of the substrate in the presence of steam, olivine, magnesium oxide, and air. Gasification results in the synthesis of carbon monoxide, hydrogen, and some sulfur content. The gaseous mixture is then subjected to oxidation, with the addition of some oxidizing agent and catalyst, along with the simultaneous removal of the sulfur produced. The alcohol synthesis takes place in the presence of a catalyst immediately after syngas conditioning. The later stages of this process include alcohol separation into ethanol and other higher alcohols produced.

Biochemical process: The first stage of this process remains the same as that of the previous one which is biomass cultivation and further carrying it to the required biorefinery facility. Since this process involves a biochemical route for ethanol production, the biomass undergoes pretreatment which can be physical, biological, and chemical depending on the structural complexity of the biomass. The pretreatment is done to break down the complex structure of the substrate into an easily hydrolyzable one consisting of monomeric sugars. Pretreatment of the substrate is followed by hydrolysis using calcium oxide, or acid, water, and steam to form a fermentable mixture (selection of the fermentation medium components may vary depending on the substrate) which then undergoes fermentation and/or co-fermentation using the chosen yeast or bacterial strain to then form a fermentation broth containing ethanol and other by-products. Ethanol is then usually recovered by steam distillation. The lignin in the lignocellulosic biomass may, however, not disintegrate effectively. It is therefore subjected to combustion resulting in heat and electricity production which in turn are used during the conversion process.

7 Pretreatment Technologies Involved in Biochemical Conversion Route

Food waste is one class of lignocellulosic biomass. The structural composition of the lignocellulosic biomass is mainly by cellulose, hemicellulose, lignin, and some amount of pectin. These four components may be present in varied fractions in different biomasses (Pérez et al. 2002). An overview of the lignocellulosic structure of this class of biomass (i.e. food waste) depicts that of all the components present, the accessibility for hydrolysis by the cellulose pretreatment techniques is hindered by the presence of hemicellulose and lignin (Mcmillan 1994). Lignin separation ensures the removal of non-productive adsorption sites. The pretreatment techniques are intended for disruption of the structural configuration of the components and thus removal of any steric hindrance toward the accessibility of the cellulosic fibers (Fig. 2). Most commonly, acid (dilute acid at high temperature and pressure or concentrated acid treatment at low temperature and atmospheric pressure) and enzymatic pretreatments (using an enzyme called cellulase) are adopted (Kumar et al. 2009; Iranmahboob et al. 2002). The structural breakdown of cellulose gives its glucose (hexose)

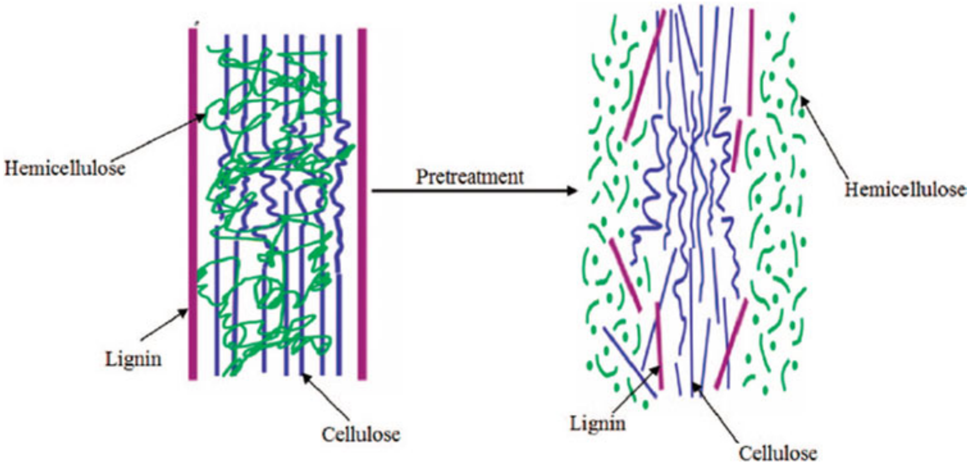


Fig. 2 Effect of pretreatment on minimizing the structural complexity of the lignocellulosic-based biomass prior to fermentation (Illustration reprinted (adapted from Kumar et al. (2009) with permission from American Chemical Society)

monomers, whereas hemicellulose degradation gives pentoses and hexoses (Kuhad et al. 1997). The effectiveness of the pretreatment technique depends on a number of factors like substrate porosity (indicative of the accessible surface area) for low digestibility substrates (Ishizawa et al. 2007), cellulose crystallinity (cellulose breakdown is more easily achievable when it is present in its amorphous form than crystalline form) (Mosier et al. 2005; Béguin and Aubert 1994), and hemicellulose and lignin percentages present. The celluloses have different degrees of crystallinity ranging from 30 to 70%.

An efficient pretreatment technique is characterised by of the following factors:

- Maximum degradation of the carbohydrate sources into their respective monomeric units.
- Formation of inhibitory products should be less probable.
- The overall technique should be economically feasible.

The most commonly practised methods are:

Acid hydrolysis: This chemical pretreatment technique can be subdivided into two categories:

- Dilute-acid hydrolysis: The operating conditions of this process are high temperature in the range of 160–230 °C for effective cellular hydrolysis, and high pressure around 10 atm (Kumar et al. 2009). This technique takes comparatively lesser time (1-5 min) than the concentrated-acid hydrolysis technique. The ethanol yield at the end is low. Moreover, the probability of the formation of inhibitory compounds is very high in this process. The concentration range of acid (generally sulfuric acid) in this technique varies between 2 and 5 wt% (Lee et al. 1997).
- Concentrated-acid hydrolysis: The required conditions for carrying out this process are temperatures less than 50 °C and ambient pressure of ~1 atm. This technique yields very high ethanol concentration, but is carried out for a longer time duration (1 h to 8 h, for 60–80% and 20–30% acid concentration, respectively) (Janga et al. 2012; Farone et al. 1996). Sulfuric acid or hydrochloric acid is generally used, within a concentration range of 10–30% (Kumar et al. 2009; Broder et al. 1995). Recovery of the concentrated acid is of utmost importance considering the economics of the overall process (Sun and Cheng 2002).

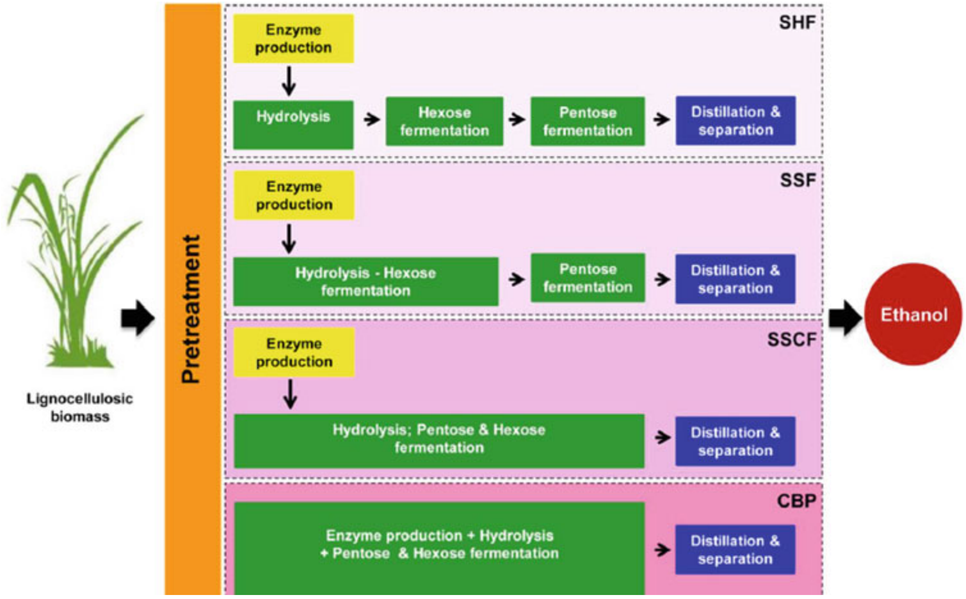
Alkaline hydrolysis: Alkaline pretreatment is comparable to the concentrated-acid hydrolysis technique with respect to the process operating conditions of low temperature and pressure (Kumar et al. 2009), except for the longer time duration for which the process is to be carried out (may extend up to weeks) and lower levels of carbohydrates digestibility. It is done mainly using sodium hydroxide (Fox et al. 1989; MacDonald et al. 1983) and the effectiveness of the technique is dependent on lignin-percentage present in the biomass (Mcmillan 1994).

Enzymatic hydrolysis: The main advantage of this biological pretreatment technique is the absence of harmful and toxic by-products, formed otherwise by chemical treatments. The carbohydrate chains of the fruit waste are catalyzed by cellulase enzymes at ~50 °C and pH ~ 5 to reducible fermentable monomeric units. The synthesis of cellulase can be found in fungi, bacteria, and some protozoans. Also, some animals like cows and sheep are a source of cellulase.

8 Fermentation Strategies for Ethanol Production

Bioethanol production from food wastes (biomass feedstocks) can be achieved using either direct or indirect fermentation. Direct fermentation involves the administration of the feed into the bioreactor without a change in the physical state, whereas indirect fermentation involves the substrate gasification into syngas which is followed by its

Fig. 3 A schematic diagram of ethanol production from lignocellulosic-based biomass (Illustration adapted from Devarapalli and Atiyeh (2015) with permission from Biofuel Research Team)



conditioning prior to its addition to the bioreactor for fermentation in mineral-defined aqueous fermentation medium (Devarapalli and Atiyeh 2015; Phillips et al. 2017). Fermentation-strategies development has taken place over the years with respect to the degree of consolidation of various steps involved in bioethanol production. A schematic diagram of the same is shown in Fig. 3.

Separate hydrolysis and fermentation (SHF): Enzyme production (if present), hydrolysis, and fermentation (hexose and pentose fermentation) all take place in different bioreactors with different operating conditions and, thus, increasing the processing time for each. Since pretreatment and hydrolysis of the biomass are carried out separately, enzyme inhibition due to the fermentable-components accumulation in the hydrolysate prior to hydrolysis may take place (Margeot et al. 2009).

Simultaneous saccharification and fermentation (SSF): The process modification adopted in SSF was to avoid enzyme inhibition as faced in SHF. That is why hydrolysis and hexose fermentation take place in a single bioreactor and the sugar monomers are, therefore, concomitantly hydrolyzed along with their formation. SSF thus helps in efficiency enhancement of the enzymatic process. The problems faced in SSF are with respect to the inability of the fermenting organisms to utilize both hexoses and pentoses and different requirements of the operating conditions for the enzymatic and hydrolysis processes (Devarapalli and Atiyeh 2015; Lin and Tanaka 2006). The operating cost of the overall process with respect to the energy investment is lesser due to the process intensification, i.e. the merging of two intermediate stages (hydrolysis and fermentation) into one. Temperature monitoring and control is an important factor pertaining to SSF due to the difference between temperature required for enzyme activity for hydrolysis (45–60 °C) and ethanol fermentation (30-35°C). Moreover, the heat released during the fermentation reaction also contributes to the temperature increase in the system (Mejía-Barajas et al. 2018). A trade-off between the inefficiencies of activities of enzyme(s) for hydrolysis and of organism(s) for fermentation would therefore seem inevitable for the best possible choice of temperature in such a scenario, for example, Liu et al. (2014) had chosen 39°C as the best possible temperature.

Simultaneous saccharification and co-fermentation (SSCF): To overcome the issues faced in SSF, fermentation of both sugars (hexoses and pentoses) is carried out in the same fermentor by bioengineered fermenting organisms with the ability to utilize different classes of sugars simultaneously (Devarapalli and Atiyeh 2015; Öhgren et al. 2006). This allows for maintaining a steady rate of glucose release ensuring a high xylose to glucose ratio. This facilitates higher rates of xylose utilization (Mejía-Barajas et al. 2018).

Consolidated bioprocessing (CBP): This is a biorefinery where all the bioprocessing steps of enzyme production, and hexose and pentose fermentations are integrated into a single operation in a single fermentor at the same time. The selection of the fermenting organism or of a microbial consortium, with the capability of participating in all the enzymatic as well as fermentation reactions, is very crucial. Moreover, the existence of compatibility between co-cultures, if used, is necessary for increasing the overall process effectiveness (Ibrahim et al. 2018).

9 Bioethanol Production: Technological Feasibility

Although the entire world is focusing on the paradigm shift in the production of 2G and third-generation (3G) biofuels, there are certain technological challenges (Kumar et al. 2019) in this regard which are explained below.

Feedstock availability: Since the choice of substrate for bioethanol production in the scope of this book chapter is limited to food wastes (i.e. agro-based), the availability and supply of these at all times is a serious concern. Biofuels generation should not compete for land with agricultural activity. Higher rates of biofuel generation would also mean a continuous substrate availability. And, in order to increase the accessibility to more wastes, a higher rate of agricultural land conversion would be necessary, causing deforestation. Hence, in wastes-conversion processes, feedstock availability is a major bottleneck.

Pretreatment design: The choice of a pretreatment technique is always substrate-dependent. Since food waste encompasses a wide range of substrates within, for example, pectin-based biomasses (citrus wastes), lignocellulosic-based biomasses (coffee pulp), the pretreatment method for each substrate would vary too. A poor pretreatment technique with respect to its associated energy consumption, lignin heterogeneity, or inhibitory-components formation would largely affect the overall economic or technical competitiveness of the bioethanol-production process (Kumar et al. 2019).

Sugar concentration: Each class of biomass within food wastes is structurally different from another and therefore, each one leads to a different sugar concentration in the fermentable hydrolysate. Hydrolysates with lower levels of sugar concentration can add to the overall downstream-processing cost for ethanol recovery.

Product inhibition: Ethanol production through the bioconversion route, unlike the thermochemical route, is greatly affected by product inhibition. In microbial fermentation, the product concentration in the fermentation broth should be maintained well within a range. The products formed, start affecting the cell membranes by disrupting their integrity if present beyond the range (Kumar et al. 2019).

Lack of resources: Biofuels (1G, 2G, or 3G) production from biomass has high levels of water requirement, in all the stages of the processes like pretreatment and hydrolysis, microbial fermentation, and so on. Moreover, the production of food crops like rice, wheat, and maize, which are mostly utilized for 1G and 2G biofuels production, has high levels of water requirement. Process water economy is, therefore, an important factor directly affecting the economic competitiveness of the biofuel so produced (Kumar et al. 2019).

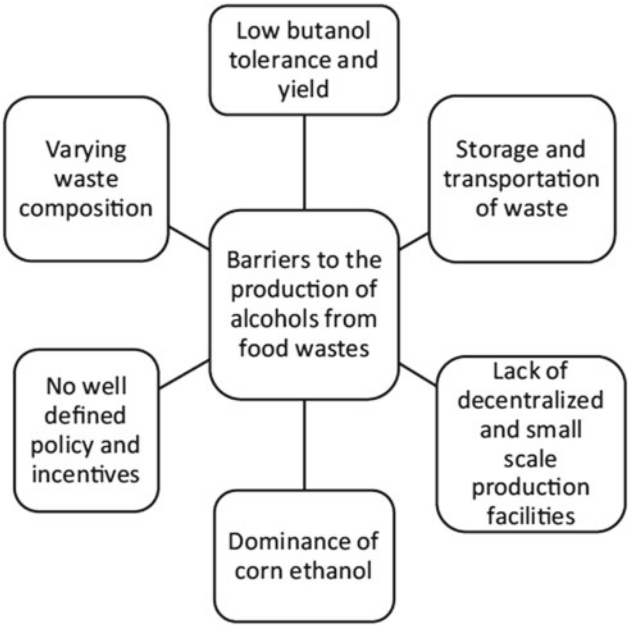


Fig. 4 Potential barriers that come in the way of commercialization of bioalcohols production (Illustration reprinted from Hegde et al. (2018) with permission from Elsevier)

Growth inhibition and toxic compound: The formation of inhibitory compounds during bioconversion of most of the lignocellulosic-based biomasses is yet another problem. Toxic compounds like acetate, furfural, 5-hydroxymethylfurfural (HMF), and phenolic compounds are formed as by-products of the pretreatment processes and they affect the growth rate of the fermenting organisms such that the growth is arrested and thus the overall ethanol yield is affected (Sakai et al. 2007).

Enzyme cost and reusability: The enzymatic pretreatments of lignocellulosic biomasses using enzymes called cellulases and hemicellulases are expensive processes as these use purified enzyme extracts which account for 20–40% of the total cost. Also, due to the complexity in the structural configuration of the biomass, it is highly recalcitrant (Maitan-Alfenas et al. 2015). Enzyme recyclability enhances its productivity (product yield per quantity of enzyme applied) (Weiss et al. 2013). Therefore, it is highly recommended to focus on enzyme reusability to make the process economically feasible.

Storage: The high levels of organic content present in the food wastes pose an operational problem of decay/degradation of the biomass if moisture removal is not done effectively prior to storage. Drying is yet another mechanical operation which would add to the overall cost of the process (Hegde et al. 2018).

Standardization: Due to inconsistency and non-uniformity in the nature of the food wastes in different sectors across the globe, the feasibility of standardization of an ethanol-production process is a bit cumbersome.

Figure 4 presents the major barriers in the commercialization of bioalcohols production (Hegde et al. 2018).

10 Ethanol Recovery

Ethanol is formed as a dilute component (10–15% (w/w)) in the fermentation broth due to the presence of other by-products in the mixture. It is, therefore, subjected to various degrees of purification to obtain ethanol with a purity of about ~99% or more.

The steps involved in the most widely used recovery technique are fractional distillation followed by dehydration (Cheng and Timilsina 2010).

Fractional distillation: This unit operation is based on the principle of vapor–liquid equilibria (VLE) of the components present in a mixture to be distilled, with a difference in their boiling points. Ethanol and water form a non-ideal solution with a positive deviation from Raoult's law. Ethanol recovery takes place in a fractionating column with a choice of packings or plates. Depending on the azeotropic characteristics of the mixture, the ethanol concentration range can be divided into two categories for maximum theoretically achievable ethanol concentration during fractional distillation, the first concentration range of 0–93% (w/w) and the other range of 93–100% (w/w). The higher the number of theoretical plates in the column, the better will be the mass transfer between the components, and thus it signifies that with a count of enough number N of theoretical plates, the vapor-rich mixture at the top of the fractionator can have 93% (w/w) ethanol concentration and the liquid-rich mixture at the bottom of the column can be approximately 0% (w/w) in ethanol. Therefore, the theoretical maximum for ethanol concentration in fractional distillation is 93% (w/w).

Dehydration: Further enrichment of the fractionally distilled ethanol to a concentration of ~99% calls for the dehydration mechanism using molecular-sieve adsorption with the size of pores of around 0.3–0.35 nm. The difference in the sizes of the ethanol (0.40 nm) and water (0.28 nm) molecules allows for the water molecules adsorption, thus resulting in concentrated ethanol of ~99% (w/w).

11 Concluding Remarks

- Bioethanol produced using food competitive and energy-intensive crops like starch and sugarcane using conventional technology (1G) is at its early stages of commercialization. The scope of the present work was limited to the study of food wastes for bioethanol production (2G). The maturity status of this 2G technology is contained still at the pilot-plant setup and demonstration stage, due to the hassles in the incorporation of many desirable yet incompatible characteristics in the technology. The development of the 2G technology from pilot to commercial scale is in progress still and is expected to be achieved in the next few years (Stephen and Periyasamy 2018).
- This chapter is suggestive of the fact that pectin-rich biomasses have significant benefits when utilized for bioethanol production. The notable ones include the high degree of hydrolysis and the number of fermentable sugars achieved (John et al. 2017; Parmar and Rupasinghe 2013; Mamma and Christakopoulos 2014). It has also been mentioned that the most commonly adopted pretreatment techniques are acid hydrolysis, alkaline hydrolysis, and enzymatic hydrolysis. However, depending upon the physical complexity of the biomass used, many hybrid pretreatment techniques have been designed based on the level of interlinkages of different fundamental principles of conventional pretreatment techniques (Kumar et al. 2019).
- Commercializable bioethanol (1G) finds its way through the regional storage centers to the retail fueling stations. It is then blended with gasoline as per the government norms of the respective geographical areas of fuel distribution (Singh et al. 2016). However, the evolution of the conventional processes (1G) into advanced processes (2G and 3G) is still ongoing and their commercialization is expected in a few years to come.
- The production of 3G biofuels is based on the usability of algae or cyanobacteria, an undervalued substrate source. The algal biomass is mainly composed of lipids, proteins, and sugars, and its cultivation does not demand huge water-or farmable-land requirements (Stephen and Periyasamy 2018; Ibrahim et al. 2018). It, therefore, has the potential to produce sustainable competitive bioethanol using valorization of low-valued algal biomass. The advancement toward the green-design approaches, with a need for further intensified research toward bioethanol and other biofuels production because of their advantages, marks the beginning of an energy-secure habitat.

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Bioconversion of Lignocellulosic Residues into Hydrogen

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Abstract

The development of a clean energy alternative is a crucial aspect of current scientific research concerning the ever-growing surge in demand for energy. The use of traditional sources (fossil sources) for energy generation has raised critical climate issues that are threatening human life on the planet earth. In order to sustain energy demand, hydrogen has emerged as an assuring energy alternative. Recently, biohydrogen gas production from renewable sources has received significant attention. Lignocellulose biomass is one such potential renewable source that can be employed to generate energy, fuel, and value-added chemicals. Biohydrogen generated from lignocellulosic biomass is a clean, efficient, environment-friendly fuel and has no harmful emissions. However, the utilization of lignocellulose is still challenging due to their complex structures. Researchers around the globe are exploring various aspects affecting the process of biohydrogen production using lignocellulosic biomass while making the process sustainable. The current chapter presents an overview of bioconversion of lignocellulosic residue to hydrogen along with potential pretreatments. A systematic approach for efficient H_2 production and factors affecting the hydrogen generation are comprehensively discussed. Further, the current challenges and opportunities concerning hydrogen production via lignocellulosic biomass bioconversion are also discussed.

Keywords

Pretreatment • Biomass • Lignin • Cellulose • Lignocellulosic residues • Lignocellulose bioconversion • Biohydrogen • Lignocelluloses-to-H_2

1 Introduction

An overgrowing demand for energy and mounting concern over climate change has begun a quest for clean alternative energy sources. Lignocellulosic biomass is one such promising candidate that could be used as an efficient and environment-friendly source. Lignocellulose is the main constituent of biomass, comprising half of it produced by photosynthesis and mainly contains lignin, hemicellulose, and cellulose (Ren et al. 2009). The stockpile of agricultural or agro-industrial waste accumulates lignocellulose in massive amounts creating a disposal issue while deteriorating the surrounding environment. The abundant availability of raw material from hard and softwood, grasses (e.g., switchgrass), forest (e.g., sawdust, thinning, and mill waste), and agro-wastes (e.g., corn stover, and wheat straw) makes it a desirable source for the production of biofuel, valued industrial products, paper manufacturing, composting, and for feeding livestock (Elgharbawy et al. 2016; Ren et al. 2009; Gawade et al. 2016; Molleti et al. 2018; Tiwari et al. 2017, 2020). In order to strengthen energy security and lower dependency on fossil fuels, hydrogen has emerged and proved to be an assuring energy alternative. In recent, significant attention has been focused on biohydrogen gas production from renewable sources. Hydrogen is an energy-dense alternative, which is an established transport

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fuel and acknowledged as a feasible option to fossil fuels. Hydrogen is the future ideal fuel that extends environmental, social, and economic advantages. The global dependency on imported oil and the transportation sector emissions can be reduced by switching to hydrogen (Meher Kotay and Das 2008). Moreover, the higher net calorific value of H_2 than other fuels and its broad applicability in the conversion of industrially valuable products (synthetic gas, plastics, olefins, ammonia, methane, methyl alcohol, etc.) make it more versatile raw material (Ladanai and Vinterbäck 2009). The demand for hydrogen, around the globe, has been continuously increasing, with a growth rate of approximately 10% per year (Winter 2005). Currently, more than 90% of the hydrogen is produced from fossil fuels comprising 18, 30, and 48% production from coal, oil/naphtha, and methane feedstock, respectively (Łukajtis et al. 2018). Steam methane reforming is a popular method of producing hydrogen, along with thermochemical (gasification), and electrolysis of water. However, these methods increase the carbon footprint of hydrogen production and release high levels of CO_2 (Nagarajan et al. 2019). Therefore, biological hydrogen production is one such promising alternative to these conventional methods, which is energy-efficient compared to those of chemical and electrochemical processes (Das and Veziroğlu 2001). Moreover, the utilization of low-value renewable feedstocks is an efficient means to lower the overall cost of hydrogen production (Lay et al. 2012). The global biomass residue yield passes 220 billion t yearly, capable of generating energy equal to the energy generated by crude oil of 60–80 billion tons (Fan et al. 2006). Therefore, its abundance and low-cost make lignocellulosic biomass a promising resource for biofuel production, such as hydrogen and ethanol (Ladisch et al. 1983; Lechner and Papinutti 2006). The general pathway of the transformation of lignocellulose into biohydrogen is shown in Fig. 1.

Lignocellulosic biomass is primarily generated from plants such as trees, grass, bushes, etc. Also, it is produced in the form of biomass waste from the forestry and agriculture industry (Ren et al. 2016). Lignocellulosic biomass mainly comprises 70–80% of carbohydrates in the form of cellulose and hemicellulose, which are firmly linked together with the help of lignin (Fig. 2). Lignin furnishes strength and rigidity to the plant material as a shield against external environmental factors (Bhange et al. 2019). However, it also hinders smooth biotransformation to hydrogen. Therefore, in the case of hydrogen production from fermentation, biomass must be subjected to some pretreatment methods to attain their delignification, succeeding liberation, and uptake of sugars. The transformation of lignocellulose biomass into bio H_2 is a multi-step process, including (a) size reduction (physical pretreatment, (b) lignin/hemicellulose removal (chemical, physicochemical, or biological pretreatment), (c) hydrolysis of biomass to produce readily metabolizable molecules (simple or complex sugars), (d) conversion of simple or complex sugars into organic acids along with CO_2 and H_2 as by-products through dark fermentation and (e) conversion of organic acids into H_2 along with carbon compounds and CO_2 through photo fermentation. Several biological processes are employed in hydrogen productions, such as photo/dark fermentation, integrated system, and direct/indirect bio photolysis. Typically, in photo fermentation, light energy is utilized by photosynthetic bacteria from several organic acids, along with agricultural and food processing wastes. On the contrary, in dark fermentation, anaerobic bacteria are used in the absence of light to produce hydrogen using substrates (carbohydrate-rich) (Bharathiraja et al. 2016; Hallenbeck et al. 2002). In an integrated system, dark fermentation and photo fermentation are utilized sequentially. Further, in direct bio-photolysis, algae and cyanobacteria are employed that utilize solar energy for the conversion of water into biohydrogen and oxygen. On the contrary, in indirect bio-photolysis, separate biohydrogen and oxygen evolution reactions are carried out linked via CO_2 fixation (Hallenbeck et al. 2002). The results of H_2 production through dark fermentation look promising with a significant production rate. However, the commercialization of the process has several significant barriers, such as low efficiency of H_2 production compared to other conventional methods and high production costs (Ren et al. 2016). The development of clean alternative energy sources is critical concerning rising interest over environmental changes. Hydrogen production employing lignocellulosic biomass is a promising process that is efficient, environment-friendly, and does not emit any toxic gases in the environment. Moreover,

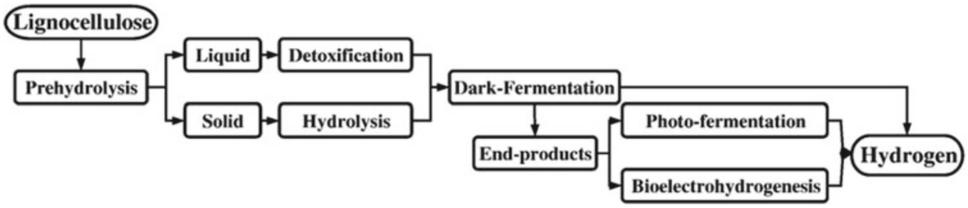

Fig. 1 General scheme for converting lignocellulose to biohydrogen (Copyright © 2009 Elsevier B.V. All rights reserved, reprinted with permission) (Ren et al. 2009)

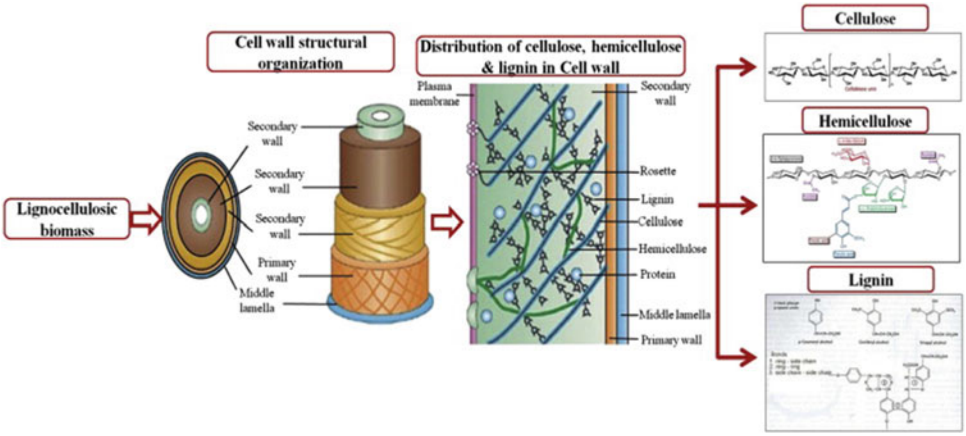

Fig. 2 Diagrammatic illustration of the framework of lignocellulose; cellulose; hemicellulose, and lignin (Copyright © 2012 Elsevier B.V. All rights reserved, reprinted with permission) (Menon and Rao 2012)

hydrogen has no greenhouse gas (GHG) emissions during combustion (da Silva Veras et al. 2017).

2 Pretreatment of Lignocellulosic Biomass

The lignocelluloses are complex in structure and cannot be utilized directly by microorganisms for the production of useful products. The pretreatment of lignocellulose is required to overcome these structural resistances, followed by the hydrolysis to convert the lignocellulosic residues into simple sugars. The pretreatment improves the efficiency of the hydrolysis of lignocellulose and thus enhances the overall production of hydrogen. The pretreatment results in the breaking of complex structures into simple sugars via lignin removal from the residue (Patil and Yadav 2018). It also decreases the lignocellulose crystallinity while reducing the cellulose's polymerization degree and ultimately enhances the available area of lignocellulose residue to microorganisms (Ren et al. 2016; Chundawat et al. 2010). The various pretreatment methods have been primarily categorized based on the mode of action, such as biological, chemical, physical, and physicochemical. An ideal pretreatment should attain a high yield of sugars, avoid the loss or degradation of carbohydrates, minimize the inhibitor formation, and must be cost-effective. The following section highlights these methods, along with their advantages and disadvantages.

2.1 Physical Pretreatments

Physical pretreatment involves the breaking of crystalline structures or reducing particle size, which enhances the overall availability of lignocellulose's surface area for the enzymes. The most widely used physical methods include chipping, grinding, and milling, along with some modern techniques such as ultrasonication and microwave irradiation.

Chipping, Grinding, and Milling Method

A typical application of chipping and grinding is to reduce the size of lignocellulose materials into chips or in small pieces. However, the chipping and grinding alone are not efficient, and it is generally followed by milling to reduce the residue's size further. The milling results in a significant reduction in the structure's crystallinity and forms very fine particles, thus increasing the accessible area (Ren et al. 2009). Milling offers several advantages since it obtains uniform particle size, provides convenient operations, requires less water, and enhances enzymatic hydrolysis. However, milling is an energy-intensive technique that limits its wider adoption (Salakkam et al. 2019). The category of biomass, duration of the process, and kind of milling employed determines the final degree of polymerization, decrease in the cellulose crystallinity, and increment in the surface area (Kumar and Sharma 2017). Yu and Wu have reported a significant decrease in cellulose crystallinity after the ball milling of α-cellulose (2011). Similarly, Liu et al. reported wet milling of corn stover biomass after dilute-acid pretreatment. The optimized milling conditions were found to be as follows; the power of 1.1 kW, current of 2.6 A, rotation speed of 1800 rpm with varying residence times, giving enhanced enzyme accessibility to cellulose and pore volume of biomass (Liu et al. 2016).

Microwave Irradiation and Ultrasonication Method

Microwave irradiation and ultrasonication are alternate physical methods that result in the structural disintegration of cellulosic fraction and bulging of the lignocellulosic biomass (Patil and Yadav 2018). These methods are capable of altering the chemical and physical properties of lignocellulose while disintegrating the aromatic and carbohydrate polymer by splitting the ether and ester linkages (Kumar and Sharma 2017). Microwave irradiation is a direct application of the electromagnetic field to the molecular structure that causes the fragmentation and swelling of lignocellulosic biomass. The use of microwave helps to breakdown the lignocellulosic material through the molecular collision produced by dielectric polarization (Aguilar-Reynosa et al. 2017). The advantages of the microwave irradiation method include (a) reduced reaction time, (b) enhanced digestibility, (c) reduced energy consumption, (d) convenient operations, and (e) minimal inhibitor formation in the process (Salakkam et al. 2019; Kumar and Sharma 2017). However, the method suffers a few drawbacks, including an uneven radiation distribution in the heterogeneous mixture or bulk materials that ultimately affects the process's overall efficiency (Salakkam et al. 2019). The combination of chemical reagents with microwave irradiation has shown a substantial increase in the yield of sugar while decreasing the biomass's lignin content (Kumar and Sharma 2017). Hu and Wen have reported the use of alkali reagents along with microwave irradiation to yield 70–90% sugars from the switchgrass (2008). Cheng et al. described the maximum reducing sugar yield of 69.3 g/100 g TVS (total volatile solid) under microwave heating of 50 g/L rice straw at 140 °C for 15 min in 0.5% sodium hydroxide (NaOH) solution (2011).

Ultrasonication is a relatively new technology and has been used on a lab scale for lignocellulose pretreatment. Ultrasound treatment forms small cavitation bubbles, which is responsible for the breaking of hemicellulose and cellulose fraction and hence increase the accessible area for further hydrolysis (Patil et al. 2020). Various studies have shown that the reactor type, its geometry, solvent, and biomass characteristics, along with ultrasonic frequency, are critical aspects of this pretreatment method (Kumar and Sharma 2017; Kumar et al. 2009). Montalbo-Lomboy et al. have shown five to six times increase in the sugar yield from corn starch slurry by using ultrasonication compared to the control method (2010). Although these modern techniques have proved their potential in lignocellulose pretreatment, the process's overall cost is very high, making the process less desirable. Moreover, such pretreatments require a piece of corresponding equipment that adds up the total energy consumption. Therefore, the use of these methods is relatively limited. However, a novel approach to integrate chemical and physical processes can make these methods economically feasible.

2.2 Chemical Pretreatments

Chemical methods include the use of various chemicals, such as alkali, acid, organosolv, and ionic liquid for the pretreatment. The acid and alkali pretreatment is the most commonly used method that can be further employed with ionic liquids concerning their significant chemical properties.

Acid Treatment

The acid method generally employs acid in dilute or strong concentration. The dilute acid pretreatment occurs at an elevated temperature, while the strong acid requires mild temperature conditions. Dilute acid pretreatment can obtain lignocellulosic material with improved porosity and enhanced enzymatic hydrolysis. Strong acid pretreatments have a flexible choice of feedstock and can boost the yield of monomeric sugar. However, both methods have a few shortcomings, including concerns over corrosion of the instruments, high cost, and requirement of the neutralization reaction that forms salts (solid waste) (Harmsen et al. 2010). Several acids, such as nitric acid, sulfuric acid, hydrochloric acid, and carboxylic acids (maleic and oxalic acid), have been used for the pretreatment of a variety of lignocellulose (Kumar and Sharma 2017). Using diluted sulfuric acid at 121 °C for pretreatment of corn stover showed a substantial increase in the breaking of hemicellulose and lignin from the lignocellulosic structure (Cao et al. 2014). Zhang et al. reported acid pretreatment of cornstalks with dilute hydrochloric acid (0.2% HCL), which resulted in a 46-fold increase in the hydrogen production compared to that of raw corn stalk with a cumulative maximum H_2 yield of 149.69 mL/g of TVS (2007). Fan et al. reported a 136-fold rise in the amount of hydrogen production from the wheat straw waste when treated with acid (2% HCl) under microwave heating compared to raw wheat straw waste (2006). The use of concentrated acid, i.e., strong acid, causes the synthesis of highly concentrated inhibitors during the degradation of cellulose. On the contrary, diluted acid helps to hydrolyze both cellulose and hemicellulose while producing a minimum concentration of inhibitors (Kumar and Sharma 2017).

Alkaline Treatment

Alkaline pretreatment methods are generally used to degrade lignin present in biomass and usually performed at ambient conditions. Typically, alkaline reagents break the ester and glycoside bonds between lignin and hemicellulose, leading to a change in the lignin structure, decrystallization of cellulose, and an increase in the solvation of hemicellulose (Salakkam et al. 2019; Kumar and Sharma 2017). Among various alkaline reagents (calcium hydroxide, potassium hydroxide, sodium hydroxide, and ammonium salts), sodium hydroxide was found to be the most active reagent for alkali pretreatment of lignocellulose (Kumar and Sharma 2017). Alkaline pretreatment can be carried out at moderate temperature and pressure. It requires non-corrosive and non-polluting chemicals that help to make the process environment friendly. Moreover, suppression of toxins and inhibitors by alkaline pretreatment results in an enhanced fermentation process (Seok et al. 2015). However, the high operational cost and requirement of an excess amount of energy (varies with reagent) make the process less desirable (Badiei et al. 2014; Brodeur et al. 2011). Cui et al. pretreated 1 g of dry grass with 20 mL of dilute NaOH (0.5, 1, 2, 4, and 8% (w/v)) at 35 °C for 30 min resulting in a maximum total reducing sugars (TRS) of 330.8 mg/g of sugar and maximum hydrogen formation of 19.25 mL at 0.5% NaOH (Cui and Shen 2012). Wang et al. have reported 85% lignin removal from coastal bermudagrass samples with an optimal TRS production of 71% of the maximum theoretical value after sodium pretreatment at 0.75% NaOH for 15 min at 121 °C (Wang et al. 2010). The concentration of sodium hydroxide plays an important role in removing lignin and forming waste after pretreatment. Thus, based on the type of substrate, the concentration of NaOH should be chosen for effective alkaline pretreatment (Ren et al. 2016). In comparison to NaOH, lime (calcium hydroxide) can also be used to treat some of the lignocellulose materials (Ren et al. 2016; Yadav et al. 2019). Cao et al. have reported the efficient utilization of lime pretreatment for the corn stalk, which helped to expose more cellulose to surface by disrupting rigid structures and increasing the biodegradability of the substrate that ultimately enhanced H_2 production (2012). Apart from this, lime kiln technology can also be employed for the recovery of lime, making the use of lime as a cheap and effective method (Yadav et al.2019).

Ionic Liquid Treatment

Ionic liquids (ILs) have ions (cation and anion) as their main composition. The properties of ionic liquids include high polarity, thermally stability, low melting point (less than 100 °C), and negligible vapor pressure (Kumar and Sharma 2017; Literature review of physical and chemical pretreatment processes for lignocellulosic biomass n.d.). Moreover, ILs are inflammable and odorless while having high solubility and less toxicity. They have the capacity to dissolve lignin or cellulose (Salakkam et al. 2019). Fu et al. reported the use of 1-ethyl-3-methylimidazolium acetate and water for pretreatment of triticale straw, obtaining a yield of 81% fermentable sugar (Fu and Mazza 2011). Talbot et al. reported the triethylammonium hydrogen sulfate as an ionic liquid for pretreatment of miscanthus giganteus grass. The results unveiled that around 85% lignin and up to 100% hemicellulose was solubilized into the ionic liquid while 99% ionic liquid was recovered each time (Brandt-Talbot et al. 2017). However, the high cost of ILs is a major factor that restricts its use for wider adoption in chemical pretreatment methods.

Organosolv Treatment

In the organosolv treatment, organic solvents, such as acetone, ethanol, organic acid, methanol, and ethylene glycol have been used to selectively extract lignin from the lignocellulosic biomass in the presence of a catalyst (acid, base, or salt) at the appropriate temperature and pressure (Kumar and Sharma 2017). The method can obtain high-quality lignin while making the cellulosic fibers easily accessible for chemical interactions (Literature review of physical and chemical pretreatment processes for lignocellulosic biomass n.d.). An increase in the accessible surface area and pore volume of cellulose is mainly due to the solvent assisted breaking of hemicellulose and lignin linkages. However, the process demands expensive solvents, which are flammable. Also, solvent presence adversely affects the microorganism growth, enzymatic hydrolysis, and fermentation process (Kumar and Sharma 2017). The various factors, such as catalyst type, reaction time, temperature, and concentration of the solvent, define the physical characteristics of pretreated biomass that ultimately determines the extent of hydrogen production (Kumar and Sharma 2017). The process requires the additional solvent recovery steps while handling a large volume of organic solvents, which ultimately limits organosolv process utilization on a large scale.

2.3 Physiochemical Pretreatments

The combination of physical and chemical pretreatment is referred to as physiochemical pretreatment, and it aims to increase the efficacy of hydrolysis by enhancing the lignin removal. Various physicochemical pretreatments, such as ammonia fiber explosion, steam explosion, sulfite pretreatment, and liquid hot water, have been used for pretreatment of lignocellulose.

Steam Explosion Treatment

The steam explosion pretreatment method is a commonly used process, which is a combination of chemical, thermal, and mechanical treatments. In this method, the residues are exposed to high-pressure steam for a few seconds, followed by sudden depressurization (explosion). The parameters that affect the method are moisture content, residence time, particle size, and temperature (Salakkam et al. 2019; Literature review of physical and chemical pretreatment processes for lignocellulosic biomass n.d.). The method is an energy-efficient and environment-friendly method that requires fewer chemicals. However, the formation of fermentation inhibitors at elevated temperatures and improper digestion of the lignin-carbohydrate matrix limit the process. Further, hydrolysate washing can lead to a drop in overall sugar yield. Also, the method is not competent enough to treat the woody substrate. All of these factors make the process less desirable (Kumar and Sharma 2017; Ren et al. 2016). Datar et al. reported the hydrogen molar yield of 2.84 and 3 for neutral (water) pretreated steam explosion (at 220 °C for 3 min) and acid (1.2% sulfuric acid (H_2SO_4) for 120 min) pretreated steam explosion (at 190 °C for 2 min), respectively (2007). Ratti et al. reported the use of a steam explosion (15.3 kg cm^{-2} at 200 °C for 7 min) followed by alkaline treatment (1% at 121 °C for 30 min) of sugarcane bagasse, obtaining a yield of 1.2 mol H_2/g substrate (2015).

Liquid Hot Water Treatment (LHW)

LHW pretreatment is analogous to the steam explosion pretreatment except that pressurized water is used here to increase its boiling point (170–230 °C). After the pretreatment (hydrolysis of hemicellulose and removal of lignin), the cellulose can be made available for further processing (Kumar and Sharma 2017; Jiang et al. 2015). The advantage of the method is that there is no fermentation inhibitors formation occurs throughout the process (Ren et al. 2016). However, the process may be energy-intensive in order to compress the water to such high pressure. Ko et al. reported the use of liquid hot water at 180–210 °C for pretreating hardwood for 5–15 min obtaining an 80–90% lignin recovery (Ko et al. 2015). The efficiency of this process is generally increased by using a small quantity of chemical reagents. Li et al. have reported 96.4% degradation of hemicellulose from the corn stover when pretreated by a hot water method accompanied by a small quantity of NaOH (2014).

Ammonia Fiber Explosion Treatment (AFEX)

In this method, the biomass is exposed to liquid ammonia at high pressure (250–300 psi) and a moderate temperature range (60–100 °C) for a few minutes, followed by sudden de-pressurization (Kumar and Sharma 2017). The sudden release in the pressure leads to the ammonia vaporization that can be further collected and reused for the next cycle (Kumar and Sharma 2017). The effect of the pretreatment is the bulging of lignocellulose and breakdown of cellulosic crystals (Salakkam et al. 2019). The method requires no additional steps and can be carried out at mild temperatures and forms a lower quantity of inhibitors. Also, ammonia recovered in the process can be easily recycled (Ren et al. 2016; Salakkam et al. 2019; Kumar and Sharma 2017). However, the method involves a toxic compound, i.e., ammonia. Nevertheless, Cao et al. have reported a 67.8% enhanced yield of hydrogen from wheat straw after AFEX pretreatment (2013).

Sulfite Pretreatment to Overcome Recalcitrance of Lignocellulose (SPORL) Treatment

SPORL is an effective two-step procedure for the pretreatment of various lignocellulosic biomass (Xu et al. 2016). The first step involves removing lignin and hemicellulose fraction by treating the lignocellulosic biomass with calcium or magnesium sulfite. In contrast, the second step involves the use of a mechanical disk miller to get the desired fine particle from pretreated biomass (Salakkam et al. 2019; Kumar and Sharma 2017). The method is energy efficient that offers ease of operations. Further, it maximizes the cellulose to glucose conversion rate while having the potential to process a range of biomass. However, the method requires a high amount of water for post-treatment (washing). Also, the chemical recovery cost is significantly high, which ultimately makes the process expensive (Kumar and Sharma 2017). Idrees et al. have studied the effect of sodium sulfite and sodium sulfide, together with sodium hydroxide, on the pretreatment of bagasse, rice husk, corncob, and water hyacinth (Idrees et al. 2013). The pretreatment was found to be very effective in the removal of hemicellulose and lignin from lignocellulosic biomass.

2.4 Biological Pretreatments

Conventional methods, such as physical and chemical pretreatments, require a piece of specific equipment, costly reagents, and high energy input. The biological method could overcome these limitations since it is an environment-friendly method that requires less energy (Kumar and Sharma 2017). The biological pretreatment comprises the use of microorganisms (soft rot, white, and brown fungi), and enzymes (manganese peroxidase, cellulase, xylanase, lignin peroxidase, and laccase) to degrade the lignocellulosic biomass (Yadav et al. 2019; Patil and Thombre 1978). The type of biomass that has to be degraded is highly influenced by the microorganisms employed in the process. Soft and white-rot fungi mostly degrade hemicellulose and lignin, whereas the brown rot fungi degrade cellulose (Salakkam et al. 2019; Patil and Yadav 2019). Biological treatments have several advantages over conventional methods since it is an environment-friendly method that requires less energy and can be carried out at mild reaction conditions. However, the microbial pretreatments, especially with fungi, take a longer time to process due to slower metabolism (Ren et al. 2016). For degradation of various lignocellulosic biomass, several basidiomycetes species, such as *Fomes fomentarius*, *Irpex lacteus, Trametes versicolor,* and *Bjerkandera adusta* have been explored in the recent past (Kumar and Sharma 2017; Kumar et al. 2009). Commonly used white-rot fungi species for lignocellulose pretreatment includes *Cyathus stercolerus, Ceriporia lacerata, Pleurotusostreaus* sp., *Ceriporiopsis subvermispora, Phanerochaete chrysosporium, and Pycnoporus cinnarbarinus* (Salakkam et al. 2019; Kumar and Sharma 2017). Taha et al. have reported a 20-fold increase in the hydrolysis rate during the biological pretreatment of straw waste using fungal consortium (2015). Cui et al. studied the effect of Viscozyme L (20 mL), with a concentration (0.25–4% v/v), pH (3.0–7.0), enzymolysis time (1–5 h), and temperatures (35–55 °C) for pretreating 1 g of dry poplar leaves and reported highest hydrogen production of 44.92 mL at 2% VL concentration with pH 4, time 3 h, and temperature 50 °C (Cui et al. 2010). Even though the biological pretreatment of lignocellulose is fascinating, it is not suitable for large-scale applications since the rate of hydrolysis is very slow (Sun and Cheng 2002).

2.5 Combined Pretreatments

The biological pretreatment in a combination of different convention pretreatments offers a promising approach that can outperform the individual approach (Ren et al. 2016; Kumar and Sharma 2017; Sindhu et al. 2016; Ummalyma et al. 2019). Wang et al. have reported a 2.6-fold increase in the glucose yield after combining the biological and liquid hot water approach, in comparison to the liquid hot water method alone (Wang et al. 2012). Similarly, Yu et al. have reported the combination of biological pretreatment with the physical or chemical method for the efficient removal of lignin from rice husk (2009). On an industrial scale, the combined approach of sulfur catalyzed steam-explosion method is widely used for the pretreatment of lignocellulose (Ren et al. 2009, 2016). This pretreatment resulted in a high yield of fermentable sugar from hemicellulose while enhancing the cellulose accessibility to enzymes for further conversion (Ren et al. 2009). However, the method has few disadvantages, such as the requirement of acid removal or neutralization before fermentation, destruction of a fraction of xylan portion, and it generates few compounds that can inhibit the activity of enzyme and microorganism while affecting the overall productivity of the process (Ren et al. 2009; Palmqvist and Hahn-Hägerdal 2000).

3 Hydrolysis of Lignocellulose Material

In hydrogen production, pretreatment given to lignocellulosic material is generally followed by hydrolysis, a method to transform cellulose and hemicellulose into sugars (Cheng et al. 2011). Hydrolysis of lignocellulosic biomass is also termed as saccharification. In a typical hydrolysis reaction, a molecule of water ruptures one or more chemical bonds. Generally, reducing sugars can be obtained by employing hydrolysis to cellulose, and this sugar can be further subjected to fermentation to obtain ethanol. However, pretreatment has to be given to the biomass prior to hydrolysis. The purpose of pretreatment is to offer an enhancement in the efficiency of saccharification of lignocellulosic residue and, ultimately, the process of H_2 production. This can be achieved by disrupting the lignocellulose crystallinity, removing lignin, reducing the cellulose's degree of polymerization, and increasing the available area of biomass to microorganisms for further fermentation (Chundawat et al. 2010; Ye and Berson 2014). As discussed in Sect. 2, physical, chemical, physicochemical, and biological pretreatments are commonly used before employing the lignocellulose biomass to the hydrolysis (Ravindran and Jaiswal 2016). After pretreatment, hydrolysis must be employed to obtain a high yield of sugars. Chemicals (acidic or alkaline solutions) and enzymes or microorganisms usually perform the hydrolysis reaction. Enzymatic hydrolysis offers various benefits over acid hydrolysis, including higher glucose yields and lower equipment costs (Cara et al. 2007). Hemicellulase and cellulase enzymes can hydrolyze hemicellulose and cellulose associated with lignocellulosic residues, respectively. Several fungal strains secrete cellulases, such as *Penicillium echinulatum, Trichoderma reesei, Aspergillus fumigatus*, *Penicillium purpurogenum,* and *Aspergillus niger* and employed in hydrolysis (Soni and Soni 2010). Exo-glucanases, endo-glucanases, and a few other enzymes secreted by these strains can act synergistically. *Clostridium* sp., *Caldicellulosiruptor* sp., and *Shigella* sp. are anaerobic microorganisms that have also been found to demonstrate hydrolysis of lignocellulosic biomass (Wang et al. 2011). Further, the cellulosome (a large, extracellular enzyme complex) has shown high hydrolysis efficiency. Similarly, several bacterial strains also have been explored in the field. The bacteria isolated from anaerobic cellulose provide bioaugmentation, producing hydrogen, and reducing the processing time while improving the product formation efficiency (Ren et al. 2016). Hydrogen production from lignocellulosic residues can be classified based on the mode of the process employed. When hydrolysis and fermentation are carried out in a separate reactor, it is known as separate hydrolysis and fermentation (SHF). On the contrary, when both processes are offered inside the same bioreactor, the method is known as simultaneous saccharification and fermentation (SSF). When hydrogen production takes place through an only step using combined hydrolysis and hydrogen fermentation, this novel approach is called consolidation bioprocessing (CBP) (Kumar et al. 2015).

3.1 Separate Hydrolysis and Fermentation

SHF, a commonly used, two-stage process, in which cellulosic biomass is solubilized by hydrolysis in the first step, followed by fermentation of H_2 in the next (Nagarajan et al. 2019). Hydrolysis and fermentation are provided in two distinct apparatus, enhances the overall H_2 production performance since the process is carried out at individually optimized experimental conditions. However, a significant barrier of SHF, hydrolysate, which consists of pentose and hexose, needs to be treated further collectively into hydrogen. Though hexose can be easily utilized by microbes, pentose utilization is highly complicated. For complete biomass utilization, microorganisms fermenting lignocellulosic hydrolysate, particularly pentose, is essential (Ren et al. 2016). Moreover, due to the accumulation of monomeric sugars as end-products, hydrolysis may get inhibited in the process (Kumar et al. 2015). This can be overcome in SSF by accomplishing hydrolysis and fermentation in a single apparatus, which is a promising alternative (Nasirian et al. 2011; Zhao et al. 2013).

3.2 Simultaneous Saccharification and Fermentation

In SSF, hydrolysis and fermentation are offered in the same reactor by employing microorganisms or enzymes for H_2 production. SSF improves bacterial-assisted H_2 production while reducing equipment cost and operation time. Further, it also enhances hydrogen yield while eliminating inhibition by end-products during cellulose hydrolysis (Ren et al. 2016). Though the process has several advantages, the commercial feasibility of the process is limited. Cellulose degradation and hydrogen fermentation could have distinct optimized conditions as an individual process, which makes the process less optimized altogether. During the SSF process, the substrate–cellulose concentration, pH, and temperature have a significant impact on H_2 generation (Ren et al. 2016). Moreover, in SSF, efficiency and the production rate are limited by enzymatic saccharification concerning rigidly covered cellulose and hemicellulose with lignin. Several types of wood and agricultural wastes are commonly used in SSF to produce hydrogen directly. Recently, microalgae (third-generation feedstock) have also drawn attention (Cheng et al. 2011).

3.3 Consolidated Bioprocessing (CBP)

A combination of enzymatic saccharification (hydrolysis) of biomass to fermentable sugars, accompanied by biological transformation to hydrogen using a consortium or a single organism, is known as consolidated bioprocessing (Lynd et al. 2005). For hydrogen production, CBP could effectively decrease the expense in installation and lead to more competitive and economically feasible technology. Hydrogen production in CBP is unusually known as the direct microbial conversion. It is a one-stage and integrated design for the utilization of lignocellulosic residues (Parisutham et al. 2014). Fermentation, combined with cellulose solubilization, decreases the expenses in procuring industrial enzymes for separate saccharification makes the CBP a valuable process from the economic viewpoint (Olson et al. 2012). The microorganism used in consolidated bioprocessing can efficiently hydrolyze the lignocellulosic residue while converting it into the aspired products. However, most organisms cannot achieve a satisfying fermentation performance (Nagarajan et al. 2019). Choosing a functional culture with hemicellulose-/cellulose-degrading and hydrogen-producing capacity was regarded as the most critical criteria in the CBP process (Ren et al. 2016). However, hydrogen production experiments are carried out under different pH, and temperature with varying pretreatment methods limits the efficiency of the process. Therefore, in order to assess different production processes for hydrogen, utilizing a single type of substrate with a uniform pretreatment technique may be required (Ren et al. 2016).

4 Bioconversion of Lignocellulose to Hydrogen

The production of H_2 employing a cleaner sustainable route has always been a significant challenge to the scientific community. The biological way has effectively achieved bioconversion of biomass into H_2. Various agricultural wastes have been used as feedstock for the production of H_2. Among them, half of the bioenergy production processes used lignocellulosic biomass. The conversion of simple or complex sugars into hydrogen production can be carried out through biophotolysis, photo fermentation, and dark-fermentation or by the integration of dark- and photo fermentation (two-stage process), or bio catalyzed electrolysis, etc. (Manish and Banerjee 2008).

The hydrogen-producing enzymes fundamentally support hydrogen production using the biological approach. In a typical reaction, the enzyme catalyzes the chemical reaction (Eq. 1). Research evidently supported that all these hydrogen-producing enzymes contain complex metallo-clusters as active sites. Among many of such enzymes, NiFe-hydrogenase, Fe-hydrogenase, and nitrogenase have been found responsible for the bio H_2 generations (Hallenbeck et al. 2002). Fe-hydrogenase mainly carried out the biophotolysis, whereas nitrogenase is involved in photo fermentation. The following section highlights these processes.

$$2H^+ + 2e^- \leftrightarrow H_2 \quad (1)$$

4.1 Biophotolysis

Direct Biophotolysis

In direct biophotolysis, solar energy is directly converted to hydrogen through photosynthetic reactions (Eq. 2). The method has gained significant attention since it processes solar energy to convert available substrate (water) to hydrogen and oxygen. However, hydrogen production can only be possible under specific conditions since Fe-hydrogenase, the enzyme used in the process is highly sensitive to oxygen.

$$2H_2O + \text{'light energy'} \rightarrow 2H_2 + O_2 \quad (2)$$

A direct biophotolysis needs to be operated at a partial pressure of near 1 atmosphere of O_2. The required pressure is almost a thousand times greater than the maximum pressure likely to be tolerated making the reaction challenging to carry out (Hallenbeck et al. 2002). Nevertheless, researchers have reported hydrogen production at the rate of 0.07 mmol/h/L (Kosourov et al. 2002; Melis et al. 2000).

Indirect Biophotolysis

Indirect biophotolysis involves parting of the O_2 and H_2 evolution reactions into two distinct stages, coupled via CO_2 evolution/fixation. Cyanobacteria possess an ability to use CO_2 as a carbon source and solar power as an energy source (Eq. 3). First, CO_2, taken up by cells, produces cellular substances afterward used for H_2 production (Eq. 4). The following reactions can represent the overall mechanism of H_2 production in cyanobacteria:

$$6H_2O + 6CO_2 + \text{'light energy'} \rightarrow C_6H_{12}O_6 + 6O_2 \quad (3)$$

$$C_6H_{12}O_6 + 6H_2O + \text{'light energy'} \rightarrow 12H_2 + 6CO_2 \quad (4)$$

Anabaena species have been explored for their potential to generate higher rates of H_2 production (Levin et al. 2004). Further, a mutant strain of *A. variabilis* was investigated for its ability to produce hydrogen employing indirect biophotolysis. The study unveiled a hydrogen production rate of 0.355 mmol/h/L (Sveshnikov et al. 2006).

4.2 Photo Fermentation

Photo fermentation is a process to convert homogenized simple sugars and organic acids (malic, formic, succinic, acetic, and other acids) into hydrogen and carbon dioxide by employing sunlight and using photosynthetic bacteria under anaerobic conditions (Trchounian et al. 2017). Usually, photo heterotrophic microorganisms, such as purple non-sulfur bacteria (PNSB) and microalgae, are widely used in photo fermentation (Ghosh et al. 2017). Since a renewable energy source is used in photo fermentation, polluting gases and toxic compounds are not formed in the process. Therefore, PNSB assisted biohydrogen production using varied biomasses has massive potential to be instigated as a promising green technology (Trchounian et al. 2017).

Microorganisms

In the last few decades, plenteous microbial strains have been investigated and reported to have a high rate of photo-induced conversion of biomass into valuable hydrogen. Novel microbial strains with enhanced cellulolytic and hemicellulolytic ability boosted the use of these strains for the production of hydrogen from lignocellulosic biomass. An ideal microorganism used in photo fermentation must have high substrate conversion efficiency while able to perform its metabolic activities under anaerobic conditions. Moreover, it should be able to resist the adverse effect of O_2 that significantly affects the activity of Fe–Fe hydrogenase and nitrogenase enzymes.

Pure Culture

The major categories of photosynthetic bacteria employed for photo fermentation are photoautotrophic bacteria, facultative anaerobes, and aerobes (Hu and Wen 2008). The critical factor of photo fermentation is the active participation of the nitrogenase enzyme from the cell membrane of PNS bacteria. PNS bacteria contain light-harvesting complexes, reaction centers, and numerous bacteriochlorophylls

(BChl) and carotenoids. On exposure to light (photon energy), a protein present in light-harvesting complexes liberates electrons that transit to nitrogenase through cytochromes and ferredoxins, leading to the formation of H_2 (Niederman 1857; Gabrielyan et al. 2015). The extensively used microbial strains for photo fermentation include *R. sphaeroides*, *Rhodospirillum*, *Rhodopseudomonas palustris*, and *Rhodobacter capsulatus* under photoheterotrophic environment comprising photon energy, organic electron donors, and anaerobiosis (Trchounian et al. 2017). In H_2 production, H^+ gets reduced to H_2 by [Mo–Fe]-nitrogenase. This conversion is an irreversible process and needs a huge amount of ATP to proceed with the reduction reaction (Eq. 5).

$$2H^+ + 2e^- + 4ATPH_2\uparrow + 4ADP + 4Pi \tag{5}$$

where Pi is inorganic phosphate. The other enzyme, [Ni–Fe]-Hyd enzyme present in *R. phaeroides* species, can uptake H_2 under anaerobic photofermentative conditions (Akroum-Amrouche et al. 2019). The enzyme also involves H_2 production as it possesses small subunits catalytic sites and Fe–S clusters (Trchounian et al. 2017). Gabrielyan et al. highlighted that H_2 production using *R. sphaeroides* strain were found to be increased by 2.5 times when a deficient concentration of N_2 was maintained (Gabrielyan et al. 2014). This helped the nitrogenase enzyme reduce H^+ into H_2 (Eq. 6).

$$8H^+ + 8e^- + 16ATP \rightarrow 4H_2\uparrow + 16ADP + 16Pi \tag{6}$$

where Pi is inorganic phosphate, while in excess of N_2 was provided, nitrogenase transformed N_2 to NH_3 (Eq. 7).

$$\begin{aligned} N_2 + 8H^+ + 8e^- + 16ATP &\rightarrow 2NH_3 + H_2\uparrow \\ &+ 16ADP + 16Pi \end{aligned} \tag{7}$$

Owing to these properties, nitrogenase was extensively used and considered as a potential enzyme for H_2 production. In another study, the pH was balanced during H_2 production by *Rhodopseudomonas palustris* by converting acids into $H_{2,}$ which ultimately boosted the cellulose degradation by *Clostridium cellulovorans* (Lu and Lee 2015). Further, a study unveiled that 712 mL of H_2/L of the substrate was produced when ammonia pretreated wheat straw was explored to photo fermentation enzymatic hydrolysate by *Rhodobacter capsulatus* PK (Mirza et al. 2013). The photo fermentation of hydrolysate produced by the action of cellulase enzyme on corn stalk by a photosynthetic consortium (*Rhodospirillum rubrum, Rhodopseudomonas capsulate, R. sphaeroides*, *Rhodopseudomonas palustris*, and *R. capsulatus*) produced 2.6 mol of H_2 per mol sugar consumed (Jiang et al. 2016).

Mixed Culture

The H_2 production increases by including a mixed culture that comprises several anaerobic bacteria and PNSBs instead of a single culture, during photo fermentation. Asada et al. successfully employed mixed culture comprising *Lactobacillus delbrueckii* NBRC13953 and a photosynthetic bacterium *Rhodobacter sphaeroides* for photo-induced H_2 production (Asada et al. 2006). Similarly, Laurinavichene et al. used integrated purple non-sulfur bacteria *Rhodobacter sphaeroides* N7 into the heterotrophic starch-hydrolyzing consortium containing *Clostridium butyricum*. Three times increase in H_2 production was reported by incorporating mixed culture (2014).

Process Parameters

To make hydrogen production economical, specific bioreactors are required to bring flow in production capabilities at low investment and maintenance costs (Skjånes et al. 2016). The output of photo fermentation directly depends upon temperature, stirring rate, the intensity of light, pH, dissolved oxygen, the culture used, carbon source, and nitrogen source. The high amount of O_2 in bioreactor generally reduces nitrogenase activity. This problem can be rectified by filling the reactor with argon gas, along with fewer concentrations of CO_2. Similarly, high N_2 concentration can also reduce productivity, and thus maintaining the concentration of N_2 is essential in photo fermentation.

4.3 Dark Fermentation

The dark fermentation process is a complex process for the conversion of lignocellulosic biomass into biohydrogen by employing numerous anaerobic microorganisms. The conversion of biomass into H_2 is facilitated through ordered biochemical reactions, which occur under anaerobic condition in the absence of light (Fan et al. 2006; Sharma and Arya 2019). In dark fermentation, the carbohydrate substrates, such as simple or complex sugars or cellulose hydrolysates obtained from hydrolysis of cellulose, mainly comprise of reduced saccharides (hexose and pentose), are degraded into organic acids (volatile fatty acids) in the absence of light using microorganisms (A method for rapid determination of sugars in lignocellulose prehydrolyzate :: BioResources n.d.). In dark fermentation, incomplete degradation of organic substrates produces a stoichiometric ratio of 2 mol H_2 along with 1 mol of aceta and/or 1 mol H_2 along with 1 mol of butyrate. The below-mentioned equation exemplifies the conversion of sugars into hydrogen (Sharma and Arya 2019).

$$C_6H_{12}O_6 + 2H_2O \rightarrow \underset{\text{Acetate}}{2CH_3COOH} + 2CO_2\uparrow + 4H_2\uparrow \qquad (8)$$

$$C_6H_{12}O_6 \rightarrow \underset{\text{Butyrate}}{CH_3CH_2CH_2COOH} + 2CO_2\uparrow + 2H_2\uparrow \qquad (9)$$

Microorganisms

The quest for unique microbial strains that could largely produce H_2 from biomass has been carried out for the last few decades. The selection of suitable fermentative microorganisms depends on the composition of cellulose hydrolysates. In order to ease the degradation of hexose and/or pentose for efficient hydrogen production from lignocellulose, a type of strain used plays a crucial role. In dark fermentation, varied hydrolytic and hydrogenase enzymes are employed for the conversion of the organic matter into volatile fatty acids (VFAs) and hydrogen (Yadav et al. 2019). There are three types of hydrogenase enzymes primarily expressed by microorganisms (e–Fe, Fe–Fe, and Ni–Fe hydrogenase). The Fe–Fe hydrogenase can expedite both the reduction of H^+ and the oxidation of H_2. Whereas, Ni–Fe hydrogenase only expedites the oxidation of hydrogen. Hence, Fe–Fe hydrogenase plays a primary role in fermentative H_2 production (Eq. 10).

$$2Fd^{+} + 2H^{+} \longrightarrow 2Fd^{2+} + H_2 \qquad (10)$$

Pure Culture

Various scientists studied fermentative hydrogen production employing pure microorganisms (pure culture). The extensively utilized microorganisms are *Clostridium* and *E. coli*. The mesophilic microorganisms, *Clostiridium welchii*, *C. acetobutylicum*, *C. cellobioparum*, *C. pasteurianum*, *Clostridium paraputrificum* M-21 and many others have been utilized in dark fermentation (Das and Veziroğlu 2001; Lay et al. 2012). *Clostridium acetobutylicum* X9 engendered a high amount of H_2 from the acid-treated corn with a 68.3% conversion rate (Gomez-Flores et al. 2017). Mesophilic *Clostridium* sp. No. 2 has been found to be a promising microorganism for the degradation of pentose (Ren et al. 2008). The most commonly employed microorganisms to degrade hexose of cellulose hydrolysates are anaerobic *E. harbinense*, *E. harbinense* YUAN-3T, *Clostridia,* and a few facultative anaerobes (Lay et al. 2012; Fan et al. 2006). The sporulation of *Clostridium* species took place under particular conditions and generated acetate and butyrate as by-products, which can be avoided by altering operation conditions (Hawkes et al. 2002; Redwood et al. 2009). Furthermore, the H_2 formation can be enhanced by speeding up the degradation rate of the substrate carrying dark fermentation under thermophilic conditions (50–65 °C). A few isolated thermophilic species such as *C. thermolacticum*, *C. thermoalcaliphilum*, *C. thermobutyricum*, *C. thermosuccinogenes*, and *C. thermosaccharolyticum* were also utilized for hydrogen production (Ren et al. 2016; Bhange et al. 2019; Bharathiraja et al. 2016). *Caldicellulosiruptor saccharolyticus* thermophiles and *Thermosaccharolyticum* W16 were specifically used for the fermentation of pentose (Ren et al. 2008). The pure *C. thermocellum* JN4 culture could effectively degrade cellulose while producing 0.8 mol H_2 per mol of glucose along with lactic acid, ethyl alcohol, and acetic acid (Liu et al. 2008). It was reported that the microbial consortium (NS) strain could efficiently hydrolyze carboxymethyl cellulose and raw cellulosic materials (rice husk and bagasse) under mild reaction conditions (Lo et al. 2008). However, the pure inoculum employed in the process required extreme sterile conditions during operations, led to a high production cost. This issue can be rectified by using a mixed culture.

Mixed Culture

Using mixed cultures can significantly reduce the production cost of hydrogen. Besides, the non-requirement of sterile conditions and degradation of varied carbon sources put mixed culture as a potential choice. Various sources, such as anaerobically digested sludge, cattle dung compost, sewage sludge, etc. can provide mixed anaerobic bacteria for H_2 production (Hallenbeck et al. 2002; Ren et al. 2016; da Silva Veras et al. 2017). Park et al. used soil inoculum and obtained 43% of hydrogen from 1.4 to 2.0 mol of H_2/mol of glucose (Park et al. 2005). Abreu et al. investigated the synergistic effect of mixed culture (*Caldicellulosiruptor saccharolyticus* and *Thermotoga maritimag*) on biohydrogen production and reported higher yield from xylose and cellobiose using mixed culture instead of individual strain (Abreu et al. 2016).

Process Parameters

The practical applicability of dark fermentation depends on various operating parameters. The production efficiency of hydrogen through dark fermentation is based on pH, the concentration of substrate, temperature, etc., along with the anaerobic conditions (De Gioannis et al. 2013). The operating process parameters, such as pH, temperature, nutrient feed rate, and type of substrate, are optimized as per the requirement of culture used (Manish and Banerjee 2008). The high H_2 formation at optimum pH 5–6 was reported in various studies (Das and Veziroğlu 2001; Bharathiraja et al. 2016; Hallenbeck et al. 2002). However, a few studies reported between pH 6.8 and 8.0 (Hallenbeck et al. 2002; Ren et al. 2016). Also, the formation of organic acid along with H_2 restricts the buffering capacity of the medium resulting in low pH. For maintaining anaerobic conditions, N_2 plays an essential role during dark fermentation. Lin and Lay highlighted that the optimized C/N ratio significantly enhanced hydrogen production (Lin 2004). Moreover, the processing parameters and selection of microorganisms used for bioconversion of lignocellulose feedstock into H_2 majorly depend on biomass composition since the lignocellulose materials from different origins comprise different percentages of lignin, hemicellulose, and cellulose (Kucharska et al. 2019). If the percentage of hemicellulose is high in lignocellulosic materials, it indicates that the cellulose is mainly produced along with glucose, xylose, arabinose, and galactose during the enzymatic hydrolysis. Higher the percentage of hemicellulose in lignocellulosic materials, the lower the H_2 production due to the formation of inhibitory compounds, i.e., hydroxymethylfurfural (HMF), and furfural (Jung et al. 2015). On a laboratory scale, dark fermentation is carried in a batch mode considering the ease of operation. However, for larger production of H_2 on the industrial scale, a continuous stirred tank reactor (CSTR) is required. Though several studies suggested that the efficiency of dark fermentation is significantly high (Nagarajan et al. 2019; Ren et al. 2016; da Silva Veras et al. 2017; Patil and Yadav 2018), the overall fermentation is an expensive operative process (Abreu et al. 2016).

4.4 Integrated Dark and Photo-Fermentative Sequential Fermentation

In recent studies, researchers successfully demonstrated that by sequential coupling of dark and photo fermentation, the productivity of the biomass conversion into hydrogen increases many folds (Cui and Shen 2012; Wang et al. 2010). The lignocellulosic biomass can be transformed into volatile fatty acids (VFAs: propionic acid, butyric acid, and acetic acid) and hydrogen by the action of hydrogenase enzymes during the dark fermentation process. These VFAs are then expended in photo fermentation as a substrate and further converted to hydrogen. Thus, a two-step, sequential fermentation process facilitates the optimization of parameters while controlling microbial growth conditions to ease the operation. Typically, the theoretical yield of the first step receives 2 mol H_2 along with 1 mol of acetate and/or 1 mol H_2 along with 1 mol of butyrate forming due to incomplete degradation of organic substrates during dark fermentation. In the second step (photo fermentation), the dark-fermentative (acetic and butyric acid) intermediates can be wholly degraded into CO_2 and H_2 by photosynthetic organisms with a theoretical yield of 4 mol H_2 along with 1 mol of acetate and 10 mol H_2 along with 1 mol of butyrate. In this way, the overall process's efficiency increases by utilizing integrating dark and photo fermentation (Eqs. 11 and 12).

$$\underset{\text{Acetate}}{CH_3COOH} + 2H_2O \rightarrow 4H_2\uparrow + 2CO_2\uparrow \tag{11}$$

$$\underset{\text{Butyrate}}{CH_3CH_2CH_2COOH} + 6H_2O \rightarrow 10H_2\uparrow + 4CO_2\uparrow \tag{12}$$

In most of the integrated studies, the dark phase's optimal temperature falls in the range of 31–37, and 30 °C was maintained during the light phase (Lee et al. 2002). Some studies highlighted the productivity of a two-stage integrated system employing pure cultures, such as *Caldicellulusiruptor saccharolyticus* and *Rhodobacter capsulatus*; and *Rhodobacter capsulatus* hup-mutant and *Rhodopseudomonas palustris* in both stages (Yadav et al. 2019). Su et al. carried out integrated fermentation on Cassava using activated sludge for dark fermentation followed by photo fermentation using *Rhodobacter sphaeroides* and *Rhodopseudomonas palustris*. The incubation period for dark and photo fermentation usually ranged from 1 to 6 days, followed by 5–14 days of photo-fermentative phase. The yield obtained was 2.86–6.07 mol of H_2 per mol of hexose (2009). Zagrodnik and Łaniecki used hybrid culture comprised *Clostridium acetobutylicum* and *Rhodobacter sphaeroides* for integrated fermentation process under repeated fed-batch conditions at optimum pH 7. The results obtained elaborated on the enhanced H_2 production by 2.5-fold as compared to dark fermentation at pH > 6.5 (Zagrodnik and Łaniecki 2017). In another integrated fermentative process, it was found that the dark fermentation of the acid-pretreated corncob using anaerobic mixed culture could produce 120 mL of H_2 per g of biomass. In the second phase of photo fermentation, the effluents of the first step were completely degraded using photosynthetic bacteria that produced 713 mL of H_2 per g of biomass (Yang et al. 2010). Fang et al. utilized co-culture of *C. butyricum* and *R. sphaeroides* with optimal biomass ratio of 1:5.9 for the integrated fermentation process at optimum pH 7 (Fang et al. 2006). Zang et al. developed a coupled solar and light-emitting diode illumination system and a thermal controlling system for integrated two-step fermentation of hydrolyzed corn stover. The temperature (35 °C) and pH (4.5) were maintained in the dark fermentation unit, whereas, in the photo fermentation unit, pH 7.0 and temperature 30 °C were maintained. The production yield of 7.5 m^3 of H_2 was reported by a dark unit, while 4.7 m^3 was reported by a photo unit (Zhang et al. 2018).

4.5 Direct Microbial Conversion

The direct microbial approach or CBP is an attractive method of producing useful products from lignocellulose via the integration of hydrolysis and fermentation. In CBP, the particular microorganism or microbial consortia generates a cocktail of the cellulolytic and hemicellulolytic enzymes for the hydrolysis of pretreated lignocellulose to hexose and pentose, followed by in situ conversion of these products to H_2 (Ren et al. 2016; Olson et al. 2012). The integrating hydrolysis with fermentation reduces the acquiring price of an enzyme for separate hydrolysis. It requires less pretreatment and reduces the total cost of installation, which leads to a reduction in the overall costs of the process and makes CBP an attractive method for H_2 production (Nagarajan et al. 2019). CBP of lignocellulose to H_2 can be performed by either using a pure culture, mixed culture, or co-culture of microorganism.

Pure Culture

A few pure microbes have been used for the direct conversion of lignocellulosic biomass to hydrogen. Ivanova et al. have used thermophilic *Caldicellulosiruptor saccharolyticus* bacterium for the hydrogen production using a variety of untreated lignocellulose biomass, such as maize leaves, sugarcane bagasse, laserwort (silphium), sweet sorghum, and wheat straw. The composition of biomass has a significant influence on the efficiency of substrates utilization and the rate of hydrogen production. The highest optimal H_2 production of 44.7 L.H_2/kg dry biomass and 3.8 mol H_2/mol of glucose yield was obtained for the wheat straw (Ivanova et al. 2009). The thermophilic cellulolytic bacterium *Clostridium thermocellum* was found to be active for the production of H_2 using pretreated and untreated biomass, such as bagasse (Cheng and Zhu 2016; Tian et al. 2015), hemp residues (Agbor et al. 2014), corn stalks (Cheng and Liu 2011), and spent mushroom (Lin et al. 2017). *C. thermocellum* has effectively produced 23.5 mmol/L H_2 and 61.4 mL H_2/g of corn stalk from alkali-treated sugarcane bagasse and untreated milled corn stalks, respectively (Cheng and Zhu 2016; Cheng and Liu 2011). Several other microorganisms, such as *Clostridial* strains, including *C. acetobutylicum X9*, *Clostridium* sp. BOH3, *C. sartagoforme* FZ11, and *C. butyricum* FS3; Thermoanaerobacterium including *T. thermosaccharolyticum* M18 and *T. thermosaccharolyticum* DD32 have found to be useful for CBP of a variety of lignocellulosic biomass to hydrogen (Nagarajan et al. 2019). Recently, *Thermoanaerobacterium* sp. strain F6 was used for producing hydrogen from several hemicellulosic and cellulosic material (Jiang et al. 2019). The pure culture was also used to produce H_2 from the untreated lignocellulosic biomass, i.e., corn cob and bagasse producing 66.7 and 30.2 mmol/L from bagasse and corn cob, respectively (Jiang et al. 2019). Studies unveiled that the pure culture system is attractive and preferred for mechanistic research. Further, a genetic reconstruction approach can be employed to improve the rate of hydrolysis of cellulose and H_2 yield. However, the strain isolation technique is complex and long and cultivates a microbe in a very small fraction that can be employed for CBP.

Mixed Culture

The mixed culture can also be used for fermentative hydrogen production. A detailed investigation of mixed culture activity towards hydrogen production showed a positive relationship between the number of species with the yield of hydrogen (Nagarajan et al. 2019). The natural resources, such as anaerobic sludge, biomass compost sites, and rumen guts, are used to get the microbial consortia that can be employed to H_2 production (Ren et al. 2009; Wang et al. 2010; Chu et al. 2011; Pérez-Rangel et al. 2015; Chen et al. 2012). Mixed microbial consortia resulting from cow ruminal fluids, forest soil, anaerobic sludge, and native microflora of wheat straw was used for CBP of untreated wheat straw (Pérez-Rangel et al. 2015). The native flora of the wheat straw was found to have the highest hydrogen production due to the presence of several fungal strains that played a central role (Pérez-Rangel et al. 2015). Chang et al. have studied the hydrogen production from Napier grass using rumen microbial consortia containing *Ruminococcus* sp., *C. papyrosolvens*, *Desulfovibrio desulfuricans*, *Ethanoligenes harbinese, C. xylanolyticum*, and *C. beijerinckii* (Chang et al. 2010). For each 8-day incubation period, with 1.5% wt. Napier grass and stem, 2% cellulose, and 27% hemicellulose conversion, along with concomitant H_2 production were achieved (Chang et al. 2010). Recently, the mixed culture of *Clostridium acetobutylicum* with microorganism from bovine ruminal fluid has shown a synergistic effect on hydrogen production from acid-treated agave biomass compared to the control experiment (Morales-Martínez et al. 2020).

Co-culture

The co-culture of microbes containing two to three microorganisms interacts synergistically to increase the conversion of substrate and production of H_2 (Nagarajan et al. 2019). The interaction is beneficial as it results in the sequential utilization of substrates, which increases the conversion and provides a potential metabolic intermediate to increase growth while removing inhibitory compounds (Zuroff and Curtis 2012). Studies evidently suggested that the co-culture increases the yield of H_2, reduces the time of fermentation, and results in better performance than mix-culture and pure culture (Nagarajan et al. 2019; Pachapur et al. 2015). In the co-culture system, cellulolytic clostridia, i.e., *C. cellulolyticum* with *C. acetobutylicum*, has shown enhanced hydrogen production from biomass compared to pure culture (Salimi and Mahadevan 2013). In another co-culture system, *Citrobacter amalonaticus*, a hydrogen-producing anaerobic bacterium along with *C. cellulolyticum* have produced a high yield of hydrogen from corn stover, i.e., 51.9 L H_2/kg total solids (Zhang et al. 2016). The co-culture of the thermophilic bacterium has also been used for the production of hydrogen from biomass. *C. thermocellum* is a well-known thermophilic cellulolytic clostridia, which has the capability of hydrolyzing both hemicellulose and cellulose (Akinosho et al. 2014). However, it also generates ethanol as a by-product and lowers the overall yield of H_2. Islam et al. have used the co-culture of *C. thermocellum* and *C. thermosaccharolyticum* for bioconversion of sweet sorghum stalks to H_2. At 55 °C and 5 g/L stalks, the H_2 yield of 5.1 mmol H_2/g substrates along with 1.05 g/L butyric acid and 1.27 g/L lactic acid was achieved (Islam et al. 2017). Several other co-culture systems that have been used for the H_2 production from the lignocellulose are depicted in Table 1.

5 Key Factors Affecting the Hydrogen Generation

Despite high craving for newer, potential green bio-fuel from biomass waste, the research is constrained to the laboratory level. The H_2 production from lignocellulosic biomass on the industrial scale should be accelerated for sustainable development. For the effective large-scale production of H_2, the understanding of key factors affecting the process is essential. The vital key factors influencing the H_2 generation are as follows:

Inoculum Type

Generally, the pure culture of *Clostridium* and *Enterobacter* species has been used in the bioconversion of lignocellulose to hydrogen. The major disadvantage of the use of pure inoculum is the maintenance of energy-intensive sterile conditions during the isolation of strain and fermentation phase, and thus, it increases the operation cost of the process. Apart from that, the isolation of strain is time-consuming and complicated. Hence, the employment of mixed inoculums, such as anaerobically digested sludge, municipal solid waste, soil, cattle dung compost, sewage sludge, etc., are preferable (Baskar et al. 2012). Further, it was illustrated that the co-culture of *E. coli* (dark fermentative) with *R. sphaeroides* (photo-fermentative) effectively enhanced the production of H_2 (Trchounian et al. 2017).

Temperature

The temperature is a crucial factor since it affects the rate of substrate utilization, substrate hydrolysis, the maximum growth rate, H_2 partial pressure, the formation of byproducts, and the activity of hydrogenase. Mostly the ideal temperature for dark fermentative hydrogen production was found to be around 37 °C. Most experimental studies were conducted at mesophilic temperatures (25–40 °C) to produce H_2. The mesophilic temperature condition accelerates the cellulose degradation rate, which leads to an increase in hydrogen production. Recently, few studies illustrated that conducting dark fermentation at thermophilic conditions (mesophilic thermophilic 40–65 °C or hyperthermophilic >80 °C) enhanced hydrogen production. However, the use of thermophilic conditions may increase the cost of operation (Baskar et al. 2012). The degradation of cellulose becomes sluggish at temperatures below 25 °C or above 50 °C. In photo fermentation, an increase in temperature in the range of 10–35 °C using solar energy enhances the activity of nitrogenase and proteins responsible for the cell growth resulting in boosted H_2 production. However, a variation in operating temperature may cause bacteria to spend their energy to adapt to the change in temperature results in a reduction in the hydrogen production efficiency (Tiwari et al. 2020; Aguilar-Reynosa et al. 2017; Kumar et al. 2009).

pH

The acidic or alkaline nature of reaction mass is a crucial factor affecting the rate of hydrogen production and formation of by-product. For the efficient activity of the microorganism, the optimal pH was found to be ranging 5.0–7.5 (Trchounian et al. 2017; Yadav et al. 2019; Li and Fang 2009). At a higher initial pH, hydrogen production decreased due to the formation of propionate and ethanol (Gabrielyan et al. 2015). The low pH reduces the activity of iron-bearing hydrogenase enzymes, resulting in a decline in hydrogen yield (Ren et al. 2009).

Nitrogen and Phosphate

N_2 is an essential nutrient for the growth of hydrogen-producing microorganisms. The various nitrogen sources are classified as inorganic and organic. Ammonia nitrogen, ammonium chloride, and ammonium bicarbonates are examples of inorganic nitrogen sources, while yeast extract, steep corn liquor, and peptone are the organic sources. The ammonia nitrogen in the concentration range of

Table 1 Biohydrogen production by consolidated bioprocessing of lignocellulosic biomass using pure, mixed, and co-cultures

Sr no.	Microorganism	Substrate and pretreatment	Experimental conditions	H_2 yield	References
A. Pure culture microbes					
1.	*Clostridium sartagoforme* FZ11	Untreated corn stalk powder	15 g/L, batch mode, 35 °C	87.2 mL/g corn stalk	Zhang et al. (2015)
2.	*Clostridium thermocellum* 1313	Alkali pretreated spent mushroom compost (SMC)	4% w/v SMC, batch mode, 55 °C	0.74 mol/mol glucose	Lin et al. (2017)
3.	*Clostridium butyricum* FS3	Untreated corn stalk powder	10 g/L, batch mode, 35 °C	92.9 mL/g substrate	Song et al. (2014)
4.	*Caldicellulosiruptor saccharolyticus* DSM8903	Untreated switch grass (SWG) powder	3% (w/v) SWG, batch mode, 65 °C	11.2 mmol/g SWG	Talluri et al. (2013)
5.	*Thermoanaerobacterium* sp. strain F6	Untreated sugar bagasse	30 g/L, batch mode, 60 °C	1.81 mmol/g substrate	Jiang et al. (2019)
6.	*Thermoanaerobacterium* sp. strain F6	Untreated corn Cob	30 g/L, batch mode, 60 °C	2.07 mmol/g substrate	Jiang et al. (2019)
7.	*Thermoanaerobacterium thermosaccharolyticum* DD32	Untreated chipped corn stalk	5 g/L, batch mode, 55 °C	6.38 mmol/g substrate	Sheng et al. (2015)
8.	*E. coli* ZH-4	Untreated corn straw	15 g/L, batch mode, 37 °C	4.71 mL/g substrate	Pang et al. (2017)
B. Mixed culture microbes					
9.	Cow dung compost	Acid pretreated wheat straw wastes	25 g/L, batch mode, 36 °C	68.1 mL H_2/g total volatile solid	Fan (2006)
10	Cellobiose acclimated sludge	Untreated microalga, Chlorella sp. ESP-6	20 g/L, batch mode, 30 °C	0.56 mmol/g biomass	Ho et al. (2012)
11	Untreated sewage sludge	Untreated rice straw	27 g rice straw, batch mode, 55 °C,	0.74 mmol/g substrate	Kim et al. (2012)
12	*Geobacillus* sp. WSUCF1 (aerobic) with Thermophilic consortia isolated from hot spring (anaerobic)	Untreated water insoluble prairie cordgrass	2% prepared cordgrass, batch mode, 60 °C	3.74 mmol/g substrate	Bibra et al. (2018)
13.	*Clostridium acetobutylicum* (ATCC 824) and bovine ruminal fluid (BRF)	Acid treated agave biomass	10% solid loading, batch mode, 35 °C	150 L/kg biomass	Morales-Martínez et al. (2020)
14.	Anaerobic thermophilic bacteria consortium BK16	Untreated cassava pulp,	10% (w/v) cassava pulp, batch mode, 60 °C	23 mL/g substrate	Pason et al. (2020)
C. Coculture microbes					
15.	Enterococcus consortia of wheat straw with Epiphytic xylanolytic	Untreated raw wheat straw powder	2.5% total solid, batch mode, 37 °C	79.54 mL/g wheat straw xylose	Valdez-Vazquez et al. (2015)
16.	Citrobacter amalonaticus NRBC13547 and *C. cellulolyticum* DSM 5812	Steam-exploded corn stover	25 g/L, batch mode, 121 °C	51.9 L/Kg TS	Zhang et al. (2016)
17	*C. thermosaccharolyticum* DSM572 and *C. thermocellum* DSM7072	Untreated sweet sorghum stalk powder	5 g/L, batch mode, 55 °C	5.1 mmol/g-substrate	Islam et al. (2017)

0.1–7.0 g/L is typically used as the source of nitrogen (Tapia-Venegas et al. 2015). In photo fermentation, nitrogenase activity is greatly influenced by the nitrogen, and it is reported that among different amino acids, glutamate is the most suitable nitrogen supplement for the photo fermentation. Ammonia, as a nitrogen source, affects hydrogen production as the high ammonia concentration inhibits the nitrogenase activity. *Rhodobacter capsulatus* produced high H_2 when glutamate as nitrogen source and acetate as carbon source was supplied in the carbon: nitrogen ratio of >35 (Baskar et al. 2012; Kim et al. 2012). Similarly, phosphate is essential for various cellular metabolic processes due to its nutritious value and buffering capacity that enhances H_2 production. However, high phosphate concentration can cause substrate inhibition (Brandt-Talbot et al. 2017; Datar et al. 2007).

Metal Ion

The metallic cofactors, such as Mg, Fe, and Ni are vital for the enzymes in H_2 production. These metallic cofactors are essential for nitrogenase-catalyzed fermentation by easing the transport processes in the microorganisms. The presence of Fe^{2+} is necessary for the hydrogenase and other enzymes. The Fe embedded in enzyme act as an electron carrier and facilitate pyruvate oxidation to acetyl-CoA, CO_2, and H_2 (Sinha and Pandey 2011; Cheng and He 2014; Wang and Wan 2008). Similarly, nickel is a major constituent of [NiFe]-hydrogenase. The activity of [NiFe]-hydrogenase and H_2 yield reduces when Ni present in high proportion. Mg^{2+} can stabilize nucleic acids, cell membranes, and ribosomes and activate many kinases and synthetases in the cell. Copper ions (Cu^{2+}) act as an inhibitor for FoF1-ATPase and hydrogenase enzymes associated with the membrane of *E. coli* (Kirakosyan et al. 2008). The other trace metals, such as Cr and Zn, also affect the hydrogen production rate (Ratti et al. 2015; Jiang et al. 2015).

Partial Pressure of Hydrogen

The development of partial pressure due to produced hydrogen plays a substantial role in lowering the H_2 yields. The hydrogenase enzyme is responsible for the oxidization and reduction of ferredoxin. The activity of the hydrogenase enzyme gets affected by a substantial build-up of H_2 produced as it alters the oxidizing capacity of hydrogenase. The stirring rate, reduction of headspace pressure using a vacuum pump, and biogas sparging methods are employed to reduce partial H_2 pressure (Guo et al. 2010).

Light Intensity

Light intensity is a vital factor for photo fermentation, whereas, it is insignificant for dark fermentation. The light energy is essential to carry out the photon-induced reaction, for transportation of electron, ATP synthesis, and hydrogen production. The photo-bioreactor usually uses solar light with a provision for artificial light (Lu et al. 2016). The high concentration of ATP and high reductive power at the optimal light intensity is essential for nitrogenase to produce hydrogen (Li et al. 2011; Assawamongkholsiri et al. 2019). The high light intensity than the optimum value produces excess ATP and Fd_{red} (ferredoxin reductase), which causes the nitrogenase enzyme to have a photo-inhibition. The combination of different types of light sources enhances the H_2 production rate. For example, an internal illumination of photo-bioreactor with solar energy excited optical fiber coupled with external irradiation of tungsten filament lamp (Li and Fang 2009; Kawagoshi et al. 2010).

Reactor Design

The proper fermentation reactor is the basic need to proceed with any fermentation process, and the reactor's configuration controls the operation and output of the fermentation process (Kadier et al. 2016). Many studies used a batch reactor on a laboratory scale for dark fermentation as it was easy to operate. The batch reactors are very useful in optimizing operational parameters on the pilot-scale level; however, for large production of H_2 on the industrial scale, a continuous stirred tank reactor (CSTR) is utilized. The photo-fermentative reactor requires additional configurations, such as incandescent lamps, a combination of light receiving unit and reflection sheet, and, concentric glass cylinders, etc. (Baskar et al. 2012).

6 Summary

Bioconversion of lignocellulose residue is an attractive method for the production of hydrogen. However, most of the research has been explored at the lab-scale and still requires a comprehensive assessment before moving to pilot or large-scale production. Future research could be in the direction of using the lab data for large scale demonstrations. The current processes for hydrogen production suffer several shortcomings, including a lower yield of hydrogen due to the use of energy-intensive and inefficient pretreatment methods, low activity of microbes, and inhibition of the products. The development of an energy-efficient, economically viable pretreatment method with low or no inhibitor formation can increase the overall hydrogen production. Moreover, an integrated approach could be established as an attractive method. However, extensive research is required concerning the development of novel microbial strains or efficient mix consortia that could advance the bioconversion of lignocellulosic biomass while enhancing hydrogen production. Nevertheless, the production of hydrogen, along with other industrially-valued products from waste via integrated process, can make the process further economical and environmentally viable.

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Bioconversion of Food Waste into Biogas

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Abstract

Quest for sustainable, economic, and environmentally viable alternative for commercial fuels has gained momentum across the world due to the polluting and fast-depleting characteristics of the conventional fuel caused by its extensive use. A global shift from conventional fuel to biomass-based biofuels (especially lignocellulosic waste materials) among the researchers has been observed over the last few years. Hereof, food waste has emerged as a good source for energy recovery as it is an established fact by now that a humongous sum of wastes is generated each year along the different phases of food supply chain system (agriculture, harvesting, storage, distribution, consumption, etc.). However, very subtle attempts have been made to utilize these food wastes as animal feed, although this strategy is not sufficient enough to curb the menace of food waste considering its availability. Scientist in the recent past is considering it as an alternative feedstock for energy generation. In order to achieve this goal, scientists have to overcome the hurdle of economically viable bioconversion technology associated with the conversion of these materials to value-added products. Some of the technological berries associated with the utilization of lignocellulosic biomass are: formulation of technically sound pretreatment and bioconversion process. The current chapter intends to provide a compressive study based on the available pretreatment methods and the various conversion technologies with special emphasis to anaerobic digestion for energy recovery from food waste into biogas.

1 Introduction

Growing concern to tactfully manage global warming due to increasing release of greenhouse gases into the environment caused by burning of fossil fuel has led the researchers to explore economic and environment friendly alternatives. According to the reports, approximately 2 billion tons of municipal solid waste (MSW) was produced in 2011 (Amoo and Fagbenle 2013). Increasing population coupled with industrialization and urbanization is expected to increase the amount of MSW production by many folds. According to the Food and Agriculture Organization (FAO) (2009) of the United Nations report by the year 2050, it is expected to reach 9.5 billion tons. The major constituent of the MSW generated comes from food waste, which is nearly about 25–70% as per the Intergovernmental Panel on Climate Change, (IPCC) report (Eggleston et al. 2006). This food waste amounting 1.3 billion tons is globally generated or wasted along the various phases of food supply chain viz. production, distribution, marketing, processing, handling, and consumption annually (Gustavsson et al. 2011). Food waste can be defined as any material that is appropriate for human consumption that is lost, degraded or wasted along the food supply chain. The estimated monetary value of food waste is roughly about USD$ 1.6 trillion (Food and Agriculture Organisation of the United Nations 2015). According to FAO report (Food and Agriculture Organisation of the United Nations 2015), approximately 4.4 Gt of CO_2 eq./year is released from food waste, which accounts to 8% of the total global anthropogenic greenhouse gas emission. Food waste can be divided into two broad categories depending on the stage at which it is generated in the food supply chain i.e. pre-consumer (production, harvesting, storage, and distribution) and post-consumer wastes (meal preparation and consumption) (Pfaltzgraff et al. 2013). World's 10 largest food waste producing countries are listed in Table 1. It can be observed from the table that according to the food waste per capita per year, Australia ranks the first. However, from

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Table 1 World's 10 largest food waste producing countries (per capita)

World ranking	Country	Food waste per capita (kg) per year	National food waste (kg) per year
1.	Australia	361	8,948,576,300
2.	USA	278	90,767,556,000
3.	Turkey	168	13,408,898,328
4.	Spain	165	7,680,592,425
5.	Japan	157	19,874,630,000
6.	Germany	154	12,708,334,562
7.	Mexico	149	18,427,627,299
8.	Italy	145	8,772,749,110
9.	Morocco	135	4,665,532,500
10.	Portugal	135	1,391,792,355

Source https://www.statista.com/statistics/933059/per-capita-food-waste-of-selected-countries/. Retrieved on 18 June 2020, https://www.magnet.co.uk/advice-inspiration/blog/. Retrieved on 18 June 2020

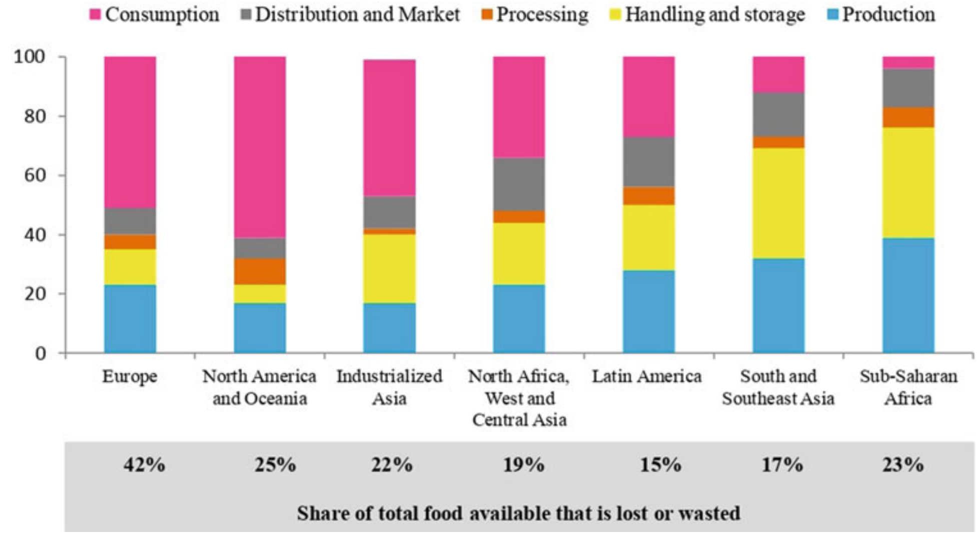

Fig. 1 Zone and stage wise food waste (%) in the food supply chain. *Source* Gustavsson et al. (2011)

the national food waste per year value, the USA is in the top position. Figure 1 shows the zone and stage-wise food waste production in percentage of food supply chain.

To utilize lignocellulosic material including food waste as a feedstock for energy extraction various pretreatment methods namely physical, chemical, or biological are being employed. These methods are well investigated and documented in various literatures. It enhances the assimilation capabilities of enzymes, which further improve bio-degradation of the wastes to ethanol and biogas, thereby increasing its yield (Taherzadeh and Karimi 2008). The emerging possibility of bioconversion of once considered waste into source for energy has led to the emergence of the concept of waste to energy and hence gained popularity among the research community in the world (Irshad et al. 2012). Owing to its biochemical composition and structural properties, it is considered as a suitable candidate for the fabrication of fuels, materials, and chemicals. This chapter is an attempt toward developing an understanding toward various available technologies with special reference to biological pretreatment method. This chapter also tries to shed some light on the potential of lignocellulose material for the generation of value-added bioproducts; solid-state fermentation processing, and lignocellulolytic organisms and their enzymes. The overview of the chapter is represented in Fig. 2. The figure depicts the journey of food waste through various pretreatment methods toward the generation of biogas production.

2 Chemical Compositions

Lignocellulosic materials are essentially composed of three polymers, viz. lignin (10–25%), hemicellulose (20–35%), and cellulose (35–50%). In cellulose, each glucose unit is connected via β (1 → 4)-glycosidic bonds to form the

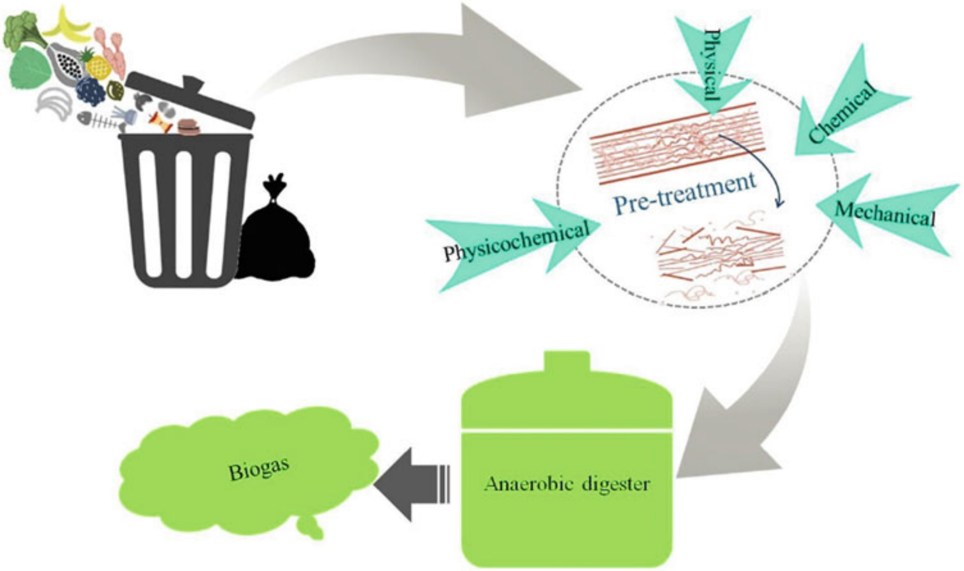

Fig. 2 Schematic representation of the chapter

cellobiose, which is then repeated numerous times along its chain to form a linear polymer. This structural configuration contributes to its highly crystalline, tightly packed and resistance toward depolymerization. Conversion of cellulose into glucose and further into ethanol can be achieved either through chemical (via H_2SO_4) or enzymatic hydrolysis (via cellulases) (Singh and Mishra 1995; Canilha et al. 2011). Hemicellulose with molecular weight lesser than cellulose is the second major fraction of lignocellulosic material. It is a heteropolysaccharide consisting acetic acid, 4-O-methyl-D-glucuronic acid, D-glucuronic acid, pentoses (Dxylose, L-arabinose), and hexoses (D-glucose, D-galactose, and D-mannose). Based on type of sugar in the main chain within the polymeric, hemicellulose is classified as xylan, glucomannan, and galactan (Kuhad et al. 1997). It can be easily hydrolyzed in comparison to cellulose owing to its amorphous nature (Taherzadeh and Karimi 2007). Pretreatment methods such as hydrothermal and acid hydrolysis are employed to remove hemicelluloses from lignocellulosic materials, which release sugars (xylose) that is consequently converted into ethanol (Canilha et al. 2012; Sun and Cheng 2002).

Lignin is amorphous heteropolymer comprised of three phenylpropane units (coniferyl, p-coumaryl, and sinapyl alcohol), and phenylpropanoid monomeric units (p-hydroxyphenyl, guaiacyl, and syringyl). The presence of cellulose elementary fibrils along with hemicelluloses and lignin protects cell wall against chemical and/or biological degradation (da Silva et al. 2010). The resistance towards enzymatic hydrolysis of lignocellulosic materials by restricting enzyme accessibility is caused by lignin content and its distribution. Hence, to improve the rate of enzymatic hydrolysis, delignification plays a crucial role (Hideno et al. 2009).

These three components are unevenly distributed in the cell walls, which depend on the type of tissue, plant species, and its maturity (Canilha et al. 2012). Apart from this, some of the major characteristics investigated for mixed food waste by various authors have been tabulated below (Table 2). From Table 2, it is evident that food waste is primarily acidic in nature and has moderate percentage of carbon.

3 Pretreatment of Biomass

According to the literatures, there are a number of available pretreatment technologies that can efficiently breakdown the biomass components into smaller fractions (e.g., oligosaccharides and monosaccharides) to obtain an array of products. The primary objective of a pretreatment process is to promote cellulose hydrolysis for its conversion into fuels or value-added products. The accelerated hydrolysis rates is achieved due to physical and chemical changes within the structure of lignocellulosic biomass caused by the various pretreatment employed. These changes include the reduction of cellulose crystallinity and lignin removal which in turn increases porosity. The pretreatment and deconstruction method employed in conjugation with physicochemical properties of biomass directly influence the success of the fabrication of biofuels and other bioproducts. Apart from the efficient pretreatment technology, usage of toxic and hazardous material free aqueous media for solubilization is also important factor for the production of carbohydrates with reduced molecular weight. The broad classification and hierarchy of pretreatment methods are shown (Fig. 3) and discussed below.

Table 2 Properties of mixed food waste used in biogas production investigation

Parameters										References
pH	*MC %	*TS %	*VS %	C	H	N	S	C/N	*TC	
–	–	30.9	26.35	46.78	–	3.16	2.51	14.8	–	Zhang et al. (2007)
4.60	–	16.8	16.1	–	–	4.0	–	–	99.0	Kim and Shin (2008)
5.51	83.8	16.2	86.1	–	–	2.3	–	21.0	–	Jayalakshmi et al. (2009)
6.3	85.6	14.4	89.5	45.9	5.8	2.21	0.10	23.2	NR	Ramzan et al. (2010)
6.5	–	18.1	17.1	46.67	–	3.54	0.33	13.2	61.9	Zhang et al. (2011)
4.2	–	23.1	21.0	56.3	–	2.3	–	24.5	–	Zhang et al. (2013)
5.17	–	8.8	8.26	–	–	1.25	–	–	–	Cárdenas-Cleves et al. (2018)
4.74	–	–	–	51.0	–	–	–	12.4	50.6	Ho and Chu (2019)
4.86	–	–	–	48.3	–	–	–	12.6	52.2	
5.53	–	–	–	52.5	–	–	–	17.4	65.0	
4.2	–	23.8	22.9	52.4	7.4	3.3	1.52	9.39	–	Hegde and Trabold (2019)
–	–	–	–	74.51	19.91	5.58	0.00	13.36	137.01	Hamzah et al. (2019)
5.3	78.10	21.90	96.76	53.76	–	2.92	5.33	18.31	–	Jansson et al. (2019)

*MC = Moisture Content, TS = Total Solid, VS = Volatile Solids, TC = Total Carbohydrates

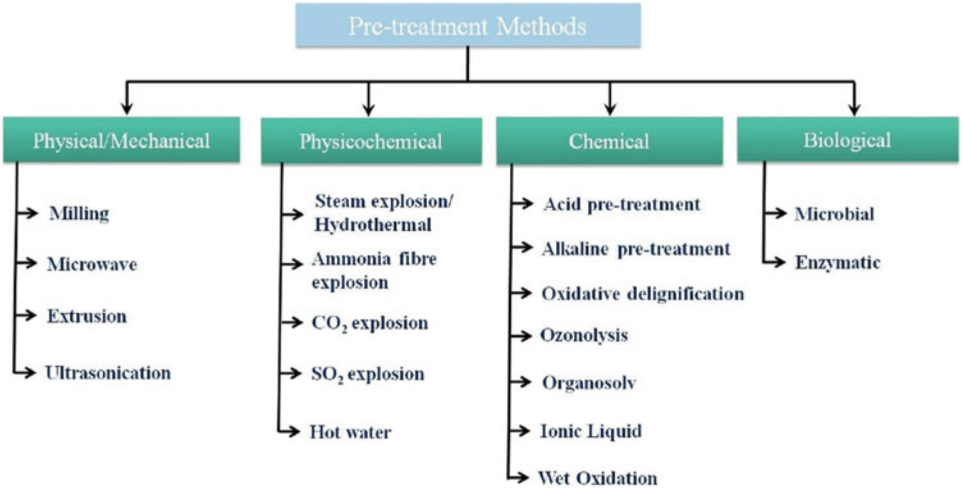

Fig. 3 Graphical representation of the available pretreatment methods

3.1 Physical/Mechanical Pretreatments

(a) Milling

It is a physical/mechanical pretreatment technology where the structural configurations are disrupted thereby reducing cellulose crystallinity of lignocellulosic materials (Vidal and Molinier 1988). The most commonly used technology in this group is the ball milling method, here the balls present within the cycle on interaction with the biomass reduce its particle size (Sarkar et al. 2012). The biggest profit of this method is zero usage of chemical supplements which in turn do not lead to the production of inhibitors; hence it is environment friendly (Sarkar et al. 2012). However, high energy requirements and high energy costs are some of its limitations. For instance, several cycles and passes of longer duration are required for sugarcane bagasse pretreatment (Koo et al. 2011).

(b) Microwave

Microwave pretreatment has emerged as a substitute to heating pretreatment process. In these processes, electromagnetic waves directly interact with the object, which is efficient and easy to operate unlike conventional heating where superficial heat transfer occurs (Binod et al. 2012). Short reaction time and homogenous heating are some of the advantages of this process (Segneanu et al. 2011). Biomass pretreated with microwave showed higher hydrolysis percentages and release of total organic carbons into solution. Solubilization increases significantly with the increase in temperature. During microwave pretreatment lignocellulosic, biomass is solubilized using acid and alkali treatments in conjugation with enzymatic hydrolysis. Hence, it is the most effective method to alter cellulose structure (Xiong et al. 2000), coupled with lignin and hemicelluloses degradation and thereby increases enzymatic vulnerability (Lu et al. 2011). Sugar yield after microwave pretreatment can be enhanced along with some chemicals (Segneanu et al. 2011).

(c) **Extrusion**

It is one of the most extensively utilized physical pretreatment processes where the materials are passed through a die of the desired cross-section having huge potential for lignocellulosic materials for biogas production. In a study conducted by Perez-Rodriguez et al. (Pérez-Rodríguez et al. 2018), a twin-screw extruder was applied for pretreatment of vine-trimming shoots for the production of methane via anaerobic digestion. An increment of 15–21% biogas, 50% reduction in hemicellulose content and increase in soluble chemicals portion (lipids, carbohydrates, minerals, proteins, and vitamins) was observed for pretreated samples in comparison to untreated feedstocks. It was also reported that extrusion induced 50% reduction in hemicellulose content while increased soluble such as. The rapid conversion ability of these soluble components by methanogenic microorganisms causes higher methane yield and also establishes that the process efficiency of ball milling is minute (Jędrzejczyk et al. 2019).

(d) **Ultrasonication**

Cellulose's chemical reactivity and accessibility are increased by many folds due to ultrasound pretreatment as it can penetrate the crystalline regions of cellulose and decompose lignin molecules but gets limited for fine structure of cellulose. The negative impact of fiber-to-surface area ratio on enzymatic hydrolysis is reduced by ultrasonic decomposition of hemicellulose. According to some studies cellulose, saccharification can be improved via ultrasonic pretreatment of biomass (Bosma et al. 2003; Yachmenev et al. 2009; Sun and Tomkinson 2002). Variability in the structure of raw material and its influence on the rate of saccharification both pre- and post-ultrasonic pretreatment has been well documented by Zhang et al. (2008). In their investigation, they suggested that the vibration energy of ultrasound is very low to induce any conformational change at surface. Nevertheless, the hydrogen bond among the molecules of lignocellulosic materials can be broken and reduces its crystallinity by employing ultrasound-assisted alkali pretreatment. Thus, it subsequently increases the rate of lignin degradation and enzymatic saccharification. Furthermore, the sagging of cavitational bubbles generates a mechanical impact, which creates an environment for enzymatic action on substrates (Jędrzejczyk et al. 2019).

3.2 Physicochemical Pretreatments

(a) **Steam Explosion/Hydrothermal**

It is basically a thermochemical pretreatment method where steam is employed to disintegrate lignocellulosic material with zero to minimum utilization of chemical (Chornet and Overend 1988; Kaar et al. 1998). To promote hemicelluloses hydrolysis high temperature (between 160 and 240 °C) and pressure (0.7 and 4.8 MPa) is maintained within the reactor containing mixture of biomass and steam, which is followed by decompression (Agbor et al. 2011). This pretreatment method is responsible for causing elevated solubility of the hemicellulose (chiefly oligosaccharides). Fermentable sugar quantity can be enhanced by using steam explosion process coupled with enzymatic saccharification. The major drawbacks of this pretreatment process are incomplete degradation of hemicellulose and creation of toxic compounds, which can diminish the efficiency of fermentation process. Phenolic and aromatics compounds along with aldehydes, aliphatic acids, bioaclohols, ions and other fermentation products may act as inhibitors.

(b) **Ammonia Fiber Explosion (AFEX)**

Biomass is mixed with liquid ammonia under modest temperature (70–200 °C) and pressure (0.7–2.8 MPa) followed by a rapid release in pressure during ammonia fiber explosion method. Biomass fibers are ruptured due to sudden release of pressure and cause disintegration of lignin, hemicellulose, and cellulose polymers into finer constituents which in turn enlarge the pore number and size within the cell wall. The increased water holding capacity and accessibility toward enzymatic degradation due to structural change in the material leads to higher sugar recovery during AFEX pretreatment (Kumar et al. 2009). Some of the major advantages are: efficient lignin elimination, creation of fewer inhibitors, and high carbohydrates recovery.

(c) **Carbon dioxide (CO_2) Explosion**

The basic principle employed in CO_2 explosion method is that the hydrolysis rate of the material will be accelerated due to the formation of carbonic acid induced by CO_2 (Sun and Cheng 2002). The cellulose and hemicellulose hydrolysis are improved as both water and CO_2 molecules are analogous in size. The penetration of CO_2 molecules within the matrix of lignocelluloses is facilitated due to pressure elevation caused by the explosion. High conversion yield, zero inhibitor formation, nontoxic, cost-effective, noninflammable, and reduced decomposition of monosaccharides are some the advantages of using CO_2 explosion method (Kumar et al. 2009).

(d) **Sulphur dioxide (SO_2) Explosion**

The basic hypothesis behind the operation of SO_2 explosion is comparable to CO_2 explosion. In this method, material is subjected to SO_2 explosion coupled with acids, which leads to solubilization of hemicelluloses even under low temperature and causes partial hydrolysis of cellulose. Generation of high amount of degradation compounds and huge requirement of equipment plagues the efficiency of this process (Chen et al. 2017).

(e) **Hot Water**

Physicochemical pretreatment of biomass by using hot water in the presence of high pressure eliminates an important part of hemicellulose and hydrates the cellulose. No other chemicals are used in this process which thereby eliminates the use of an anti-corrosion product for the hydrolysis reactor. Further, size reduction of raw material is not required (Taherzadeh and Karimi 2008). Mostly, biomass is kept in hot water at a temperature range of 200–230 °C for about 15 min. During the process, hemicellulose fraction has been removed completely by dissolving about 40–60% of the total biomass. This pretreatment process is usually used in the case of herbaceous crops as well as corn fibers (Mosier et al. 2003).

3.3 Chemical Pretreatments

(a) **Acid Pretreatment**

Acid pretreatment of biomass using dilute acid hydrolysis is solitary oldest and frequently used method. This process solubilizes hemicelluloses at higher temperature or high acid concentration, which helps to release pentose sugars (Alvira et al. 2010) and make possible the release of substrate by using enzymatic hydrolysis (cellulignin) (Taherzadeh and Karimi 2008). Use of sulphuric acid (H_2SO_4) helps the breakdown of hemicelluloses into xylose and other sugars. Though, few more acids viz. hydrochloric acid (HCl) (Laopaiboon et al. 2010), phosphoric acid (Carvalho et al. 2004), nitric acid (Rodrıguez-Chong et al. 2004), and oxalic acid (Chandel et al. 2011) are also used for pretreatment process. Usually, the standard condition of performing the process is in temperatures range of 120–180 °C and residence time range of 15–60 min (Alvira et al. 2010). Use of lower and intermediate temperatures and accordingly decrease of energy costs is one of the significant advantages of this process (Gírio et al. 2010). However, acid with high concentration can create problems such as expensive maintenance cost to prevent equipment from corrosion (Alvira et al. 2010). Apart from this, the possibility for generation of other byproducts which are considered as an inhibitory compounds towards microbial fermentation, such as phenolic compounds, carboxylic acids, furfural, furans, acetic, levulinic, and formic acids. In this regard, a step of detoxification is essential for eliminate these unwanted compounds to raise the hydrolysate fermentation (Yamashita et al. 2010).

(b) **Alkaline Pretreatment**

Alkali pretreatment of biomass is carried out by using bases like potassium, sodium, ammonium hydroxides, calcium, etc. In this regard, sodium hydroxide is known as one of the commonly used base. Alkali pretreatment is usually done in ambient conditions though it requires an excess time limit for completion of the reaction. On alkali pretreatment, lignin structure of biomass disturbed and results in acetyl elimination, cellulose decrystallization, and the different substitutions of uronic acid on hemicelluloses. As a result, there is an increase in the accessibility of enzymes to hemicelluloses and cellulose. Thus, a step to neutralize is required to remove inhibitors (furfural, phenolic acids, aldehydes, and salts,) and lignin before enzymatic hydrolysis. Alkaline pretreatments help to recover more caustic salts and make less sugar degradation as compared to acidic pretreatment (Banerjee et al. 2011).

(c) **Oxidative Delignification**

In oxidative delignification process, in the presence of peroxidase enzyme, lignin degradation is catalyzed along with hydrogen peroxide (H_2O_2) (García-Cubero et al. 2009). The process involves delignification as well as chemical breaking of cellulose along with saccharification of enzymatic (Sun and Cheng 2002). This pretreatment process can operate even at low H_2O_2 with high (approximately 40% solids) loading of biomass yet it is very less explored. However, for an enormous diversity of biomass, it becomes an appropriate method such as bamboo, sugarcane bagasse wheat straw, corn stover, barley straw, and rice straw (Ruzene et al. 2007).

(d) **Ozonolysis**

Ozonolysis is one of the most useful pretreatment methods, which uses ozone to corrupt the hemicellulose and lignin part from lignocellulosic materials, for example bagasse, wheat straw, pine, peanut, poplar sawdust, and cotton straw (Kumar et al. 2009). Ozone, soluble in water acts as a powerful oxidant, and is easily accessible. Ozone is extremely reactive in case of compounds that posses functional groups and conjugated double bonds with high electron densities. As a result, ozone can be used to oxidize lignin part of biomass since it has higher number of C = C bonds (García-Cubero et al. 2009). The advantages of ozonolysis lie in the effective removal of lignin without producing any toxic residues. Moreover, the reactions are takeing place at standard pressure and temperature (Vidal and Molinier 1988). However, the demand for more amount of ozone makes it more expensive (Sun and Cheng 2002). Furthermore, it can be assumed that to reduce environmental pollution, different processes can be proposed based on the fact that ozone can easily be decaying by the use of high temperature and catalytic bed (Kumar et al. 2009).

(e) **Organosolv**

In organosolv pretreatment method, strong inorganic acids are used as catalyst against lignocellulosics biomass (El Hage et al. 2009). Use of acids breaks the carbohydrates–lignin and lignin–lignin bonds of biomass. Volume of the material and superficial area are improved on removal of the lignin. Significantly, the process helps the ease of access of enzyme and improves the effectiveness of the procedure to get fermented sugars (Koo et al. 2011). In this process, smaller amount of chemicals (viz. sodium sulfite (Na_2SO_3) or sodium hydroxide (NaOH)) are used as catalyst and generates less quantity of wastes as that of other pretreatments (Ruzene et al. 2007). During this process, high pressure of carbon dioxide along with high effectiveness for lignin removal has been observed (Pasquini et al. 2005).

(f) **Ionic Liquid (IL)**

IL is known as “green solvents” made up of cellulose without the formation of explosive or toxic gases. ILs is made up of small inorganic anions and large organic cations and remains in liquid state with minimum temperature (<100 °C) (Elgharbawy et al. 2016). The various advantages of ILs are as follows: (1) with non-volatile and no vapor pressure; (2) on the basis of the design of alkyl constituents of cation and anion, (3) has large stable range of temperature (25–300 °C) and good chemical stability; there will be some adjustments in case of acidity and polymer solubility, organic and inorganic substance and water. Further, ILs can make a dual phase system with the majority of solvents (Ouellet et al. 2011).

ILs can dissolve both lignin and carbohydrates with anion activity and forms H bonds among the sugar hydroxyl proton and non-hydrated chloride with 1:1 ratio. Thus, the complex network structure of lignocellulose is broken as well as decreases the production of degradation products. Though IL pretreatment is a costly process but due to its environment friendly nature, it can be developed gradually (Chen et al. 2017).

(g) **Wet Oxidation**

This method is carried out in oxygen environment or air mostly using sodium carbonate as catalyst. Wet oxidation allows the conversion of biomass into monosaccharides with small amount of phenolic aldehydes and furan. This method is associated with the growing amounts of aliphatic acids along with degradation of lignin. It is a costly pretreatment method (Carvalheiro et al. 2008). The main advantage of this method is to achieve free sugars together with alkalis with no formation of 5-hydroxymethylfurfural and furfural (Bjerre et al. 1996).

3.4 Biological Pretreatment

Another important category of pretreatment includes the biological treatment that helps to alter the structure of lignocellulosic materials. In this method, lignin and hemicellulose are degraded, which makes the feedstock easily available for enzyme digestion (Sarkar et al. 2012). Advantages include mild environment friendly, operating conditions, and low requirement of energy (Hamelinck et al. 2005). Low amount of toxic substance (hydroxymethyl furfural, furfural, etc.) is formed. Fungi (viz. white, brown, and soft rot fungi), bacteria, and actinomycetes are the main driving forces of microbial treatment (Sarkar et al. 2012). Brown rots are used to degrade lignin in polysaccharides while soft and white affect lignin and carbohydrates. Mostly, brown rot fungi degrade hemicellulose and cellulose more quickly as compared to lignin. White rot fungi are found to be very proficient in case of biological pretreatment of lignocelluloses due to degradation of carbohydrates and lignin efficiently and generate enzymes like laccase, peroxidases, etc. which are used to degrade lignin. Bacteria and actinomycetes have less efficiency compared to brown and white rot fungi (Sun and Cheng 2002).

4 Bioprocessing of Lignocellulosic Materials

Various methods are presently accessible for the conversion of lignocellulosic biomass to ethanol and various chemical value-added products. Usually, bioprocessing of raw biomass into their products involves three steps: system optimization, process design, and model development (Pothiraj et al. 2006).

4.1 Solid-State Fermentation (SSF)

Solid-state fermentation (SSF) is one of the key options that help to recover microbial enzymes with low operating cost and capital investment from lignocellulosic wastes materials (Chahal et al. 1996). Thus, it could an ideal process for developing countries. The process occurs without the presence of free liquid. The most necessary medium for microbial activity (for growth) is the presence of water in an absorbed or complex type (Cannel 1980). Microorganisms in SSF can also cultivate beneath environment comparable to their usual habitats (Jecu 2000). In SSF, the forestry, agricultural and food waste, and other wastes are considered as resources of carbon to produce enzymes (Haltrich et al. 1996). Sun and Cheng (2002) reported few advantages of SSF process: (1) lower enzyme requirement; (2) less reactor volume; (3) increase the rate of hydrolysis by sugar conversion to slow down the action of enzyme; (4) less sterile conditions as glucose has been removed instantly and ethanol is formed; (5) higher product yield; and (6) shorter process time. Malherbe and Cloete (2002) reported that combining SSF technology with a suitable fungus results in a selective degradation of lignin that will be achievable in an industrial scale. Mudgett (1986) reported the disadvantages usually related to SSF are scale-up, buildup of heat, biomass growth assessment, bacterial contamination, and control of substrate content. Based on reactor operation and design part, the SSF can manufacture various microbial products (Lonsane et al. 1992).

4.2 Microorganisms and Their Lignocellulytic Enzymes

Fungi (Baldrian and Gabriel 2003) and bacteria (McCarthy 1987) have been isolated as a varied spectrum of lignocellulolytic microorganisms over the years. Among all the lignocellulolytic microorganisms, *Trichoderma reesei* and its mutants are broadly engaged in profitable manufacture of cellulases and hemicellulases (Jørgensen et al. 2003). *T. reesei* was discovered in 1950s and is the first cellulolytic organisms, which able to degrade hemi- and cellulolytic enzymes but not lignin. White-rot fungi belong to basidiomycetes, which is mainly capable as well as widespread lignin degraders (Akin et al. 1995) with *P. chrysosporium*. *P. chrysosporium* is one of the characteristic set of lignocellulytic enzymes. It has drained significant consideration as a suitable host for the producing enzymes that degrades lignin (Ruggeri and Sassi 2003). White-rot fungi viz. *Phlebia fascicularia, Daedalea flavida, P. floridensis* and *P. radiate* are used to considerably degrade wheat straw lignin (Arora et al. 2002). Pal et al. (1995) reported the hemicellulose and lignin degradation for the period of cultivation of white-rot fungus *Trametes versicolor* on sugarcane bagasse and mushroom *Flammulina velutipes* for about 40 days. Manganese-peroxidase *and* laccase are produced by *Trametes versicolor*. A bacterial strain recovered from plant decompose, *Pseudomonas putida* was also able to degrade lignin-associated compounds (Pothiraj et al. 2006).

(a) **Lignases**

Lignases falls in a family of extracellular enzyme that has been used by fungi in efficient breakdown of lignin aerobically. They are usually low in molecular weight and used to break the lignin structure. In this regard, two families of lignolytic enzymes viz. oxidase (laccase) and phenol peroxidases (manganese peroxidase and lignin peroxidase) play an important role during enzymatic degradation (Krause et al. 2003). Some enzymes role, that are not yet discovered consist of glyoxal oxidase (Kersten and Kirk 1987), glucose oxidase (Kelley and Reddy 1986), veratryl alcohol oxidases (Bourbonnais and Paice 1988), methanol oxidase (Nishida and Eriksson 1987), oxido-reductase (Bao and Renganathan 1991; Call and Mücke 1997) and H_2O_2.

(b) **Cellulases**

Cellulases, an intricate combination of proteins with diverse specificities to hydrolyze glycosidic bonds, are accountable for hydrolysis of cellulose. It is separated into three main classes of enzyme activity (Goyal et al. 1991) viz. endoglucanases or endo-*1, 4-β-glucanase,* cellobiohydrolase, and *β-glucosidase*. Endoglucanases, frequently known as carboxy methylcellulose (CM)-cellulases, are expected to degrade the cellulose fiber which is amorphous in nature. Thus, helps for successive attack by cellobiohydrolases (Wood 1992). Among the fungal cellulase, cellobiohydrolase is a most important constituent which accounts for 40–70% of the total cellulase proteins and use to hydrolyse the cellulose with high crystallinty. Saul et al. (1990) recognized a cellulase with exo- and endo-activities from *Caldocellum saccharolyticum*.

(c) **Xylanase**

Xylanase is an enzyme that helps to degrade hemicellulase. Rabinovich et al. (2002) and Shallom and Shoham (2003) reported the structure, types, classification, function of microbial hemicellulases. Hemicellulases used to hydrolyze plant cell polysaccharides due to its multi-domain nature. Xylan is one of the plentiful hemicellulose and xylanases are important hemicellulases. Xylanases hydrolyses in xylan backbone the *β-1,4* bond that gives the short xylooligomers. Further, xylooligomers are hydrolyzed by *β-xylosidase* into single xylose units (Howard et al. 2003).

5 Technologies for Conversion of Food Waste

A variety of technologies have been investigated for the extraction of energy from food waste such as biological (e.g. fermentation and anaerobic digestion) and thermochemical (e.g. pyrolysis, gasification, incineration, and hydrothermal) technologies as depicted in Fig. 4. Table 3 shows the different processes associated with parameters, products, byproducts, and their various effects. The present study focuses on the advantages and challenges associated with the biogas producing technology.

6 Biogas Production

One of the most important biological conversion processes includes anaerobic digestion (AD) technique where, landfills of organic wastes generate biogas, mostly composed of carbon dioxide (CO_2), methane (CH_4), and very small quantity of supplementary gases viz. oxygen (O_2), hydrogen sulfide (H_2S), and nitrogen (N_2). All gases are responsible for making the environment polluted since they can be easily able to flee into the surroundings (Zhu et al. 2009). In the presence of limited or without oxygen, AD converts organic wastes into biogas and digestates. Further, due to the presence of valuable nutrients, these digestates are used as soil conditioners/fertilizers (Guermoud et al. 2009). As reported in the literature (Murphy et al. 2004), usually biogas of 1 m^3 produced from AD is equal to 21 MJ of energy, which might be able to produce 2.04 kW/h of electricity with 35% of production effectiveness. However, the problem occurs on longer duration, usually within the array of 20–40 days (Table 4). Further, due to breakdown of high nitrogen containing protein fractions, free ammonia (NH_3) is produced in high amount. This free ammonia (NH_3) can cause serious issue to AD process due to its toxic nature by hampering the precise activity of methanogenic bacteria. In this regard, AD could be an alternative way to extract energy from food waste mainly composed o organic components. But, the presence of salt (such as calcium, potassium, magnesium, and sodium) in high concentration may become a hindrance in case AD of food waste (Chen et al. 2008). In such cases, co-digestion could be a solution. To decrease the nitrogen concentration, food waste can be codigested with lipid-containing waste. Thus, this step helps in dropping the troubles related by means of gathering of intermediary volatile compounds and higher concentration of NH_3 (Cristancho and Arellano 2006). Moreover, it was noticed that sewage sludge digested along with food wastes increased the production of CH_4 in biogas (Kabouris et al. 2009). Many researchers have reported the fact that yields of

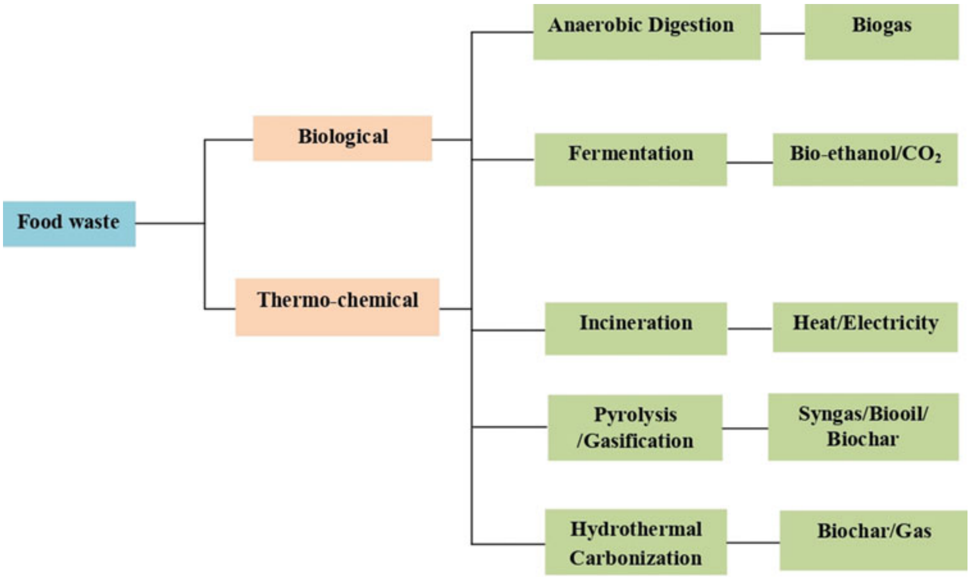

Fig. 4 Technological intervention for food waste utilization

Table 3 Conversion Technologies available for energy generation from food waste

Conversion process	Parameters	Energy products	By-products	Greenhouse effect	Odor problem	Air/water pollution	Time	Energy generation	Capital cost
Incineration	400–540 °C	Heat, electricity	Ash	1*	5*	1*	4*	3*	2*
Pyrolysis	250–750 °C, limited or absence of oxygen, inert gas, heating rate, residence time	biochar, biooil, and producer gas	Biochar (adsorbent, activated carbon, etc.)	3*	5*	3*	4*	3*	3*
Gasification	350–1800 °C, air, 1–30 bar	Syngas	Ash	3*	5*	3*	4*	3*	3*
Anaerobic digestion	35–55 °C, anaerobic, reactor size 10–10,000 m^3	Methane gas	Sludge (potential fertilizer)	4*	1*	4*	1*	1*	2*
Ethanol fermentation	30–35 °C, pH 4.5–6.0 anaerobic	Ethanol and CO_2	Animal feed	4*	2*	5*	3*	3*	2*
Hydrothermal carbonization	180–350 °C, 4–45 bar, wet	Hydrochar and gas	Biocrude oil (value-added chemicals)	5*	5*	5*	5*	5*	3*

*rating 1 = Very poor, 2 = Poor, 3 = Moderate, 4 = Good, 5 = Very good
Source Pham et al. (2015)

Table 4 Operational and performance data of anaerobic digestion of food waste

Substrate	Bioreactor type	HRT (days)	Biogas yield (m^3 kg^{-1} VS)	% CH_4	Energy content (MJ/m^3)	References
Potato waste (Beet leaves as co-substrate)	Batch (0.5 L)	14	–	62/84	23.1/31.3	Parawira et al. (2004)
Potato processing waste	CSTR	–	0.65–0.85	58	21.6	Linke (2006)
FVW	Tubular reactor (18 L)	20	0.707	57	21.3	Bouallagui et al. (2003)
FVW(SW manure as co-substrate)	2-phase system (18 L)	20	0.705/0.997	64/61	23.9/22.6	Bouallagui et al. (2005)
Food waste	Batch system	10/28	–	73	27.2	Zhang et al. (2007)
Food waste	Batch system	20–60	0.49	–	–	Forster-Carneiro et al. (2008)
FVW (Abattoir waste as co-substrate)	ASBR (2 L)	20	0.48/0.73	60/62	22.4/23.1	Bouallagui et al. (2009)
FVW (manure as co-substrate)	Semi-cont. (2 L)	30	1.36	56	20.9	Alvarez and Liden (2008)
Food waste	3-stage semi-cont.	12.4	–	67.4	25.1	Kim et al. (2006)
Food waste	Batch (1.1 L)	90		–	–	Forster-Carneiro et al. (2008)

Slaughter house waste (SW), fruit and vegetable wastes (FVW), anaerobic sequencing batch reactor (ASBR), continuous stirred tank reactor (CSTR), semi-continuous (semi-cont), hydraulic retention time (HRT), volatile solids (VS), Pham et al. (2015)

biogas up to 40–50% has increased once food waste is codigested with municipal waste (Table 4).

In AD, there are a number of factors that disturb the mass transfer. In this case, both the pretreatment and substrate quality played an important role. On the basis of substrates, pretreatments are able to vary among the physical, chemical, thermal, and biological processes. Concerning the physical pretreatments, both high pressure applying and mechanical machines are being widely used. In case of thermal pretreatments, yields can be increased by using microwave devices (Neves et al. 2006). Various studies on pre-treatments also include steam explosion (Nakamura and

Sawada 2003) thermochemical liquidization (Sawayama et al. 1997), and enzymatic hydrolysis (Kim et al. 2006) to improve the hydrolysis rate of volatile solids (VS) for producing CH_4 from. Among the alkaline and acidic pretreatment, acidic one is the most frequently used in the production of biogas (Taherzadeh and Karimi 2008). Acidic hydrolysis is helpful forenzymatic hydrolysis as well as hydrolyzing to fermentable sugars. Further, acidic treatment using HCl increased the biogas formation of bagasse by 31% and coconut fibers by 74% (Kivaisi and Eliapenda 1994).

Moving toward the bioreactors, several verities are presently functional for AD, but the commonly used three main systems contain continuous one-stage, batch, and continuous two-stage reactors. Various bioreactors such as tubular reactor, fixed film reactor, anaerobic sequencing batch reactor (ASBR), continuously stirred tank reactor (CSTR), and upflow anaerobic sludge blanket (UASB) (Bouallagui et al. 2005). Forster-Carneiro et al. (2008) stated the use of food waste as biomass. Biomethanization process is carried out using six reactors and three different total solid (TS) with three different concentrations including 20, 25, and 30% and two dosages 20–30% of inoculums. Out of these, 20% TS and 30% of inoculums containing reactor would become the most suitable for conversion CH_4 from food waste (between 20 and 60 days, 0.49 $m^3\ kg^{-1}$ VS added). Linke (2006) used continuous stirred tank reactor to produce biogas from processing of potatoes via AD.

Table 4 illustrates the content of energy obtained from AD process during the production of biogas from food waste. Fully loaded food waste digester showed probable revival of energy (Morris 1996; Banks et al. 2011). The data given in the Table 4 provide evident that due to ability of high biogas production food waste as better feedstock for AD. Further, AD can be used for dual purpose: one for reduction and another one for recovery of energy from food waste by total conversion into CO_2 and CH_4.

7 Conclusion

Technological intervention to recover energy from food waste is not only environmental friendly but also is economically appealing method, which can resolve problems like price hike associated with energy, waste management, and degradation of environmental quality. Due to its economical and environmental implications, various countries across the globe have prioritized the reutilization of food wastes. Although the utilization of such waste has a technical disadvantage, this needs to be addressed through the introduction of pretreatment technology to extract maximum yield without any impact on cost involved. Both from the perspectives of technically viable solution and capital costs, investment lignocelluloses biotechnology has emerged as one of the tools to extract value-added products from biomass. It can be successfully implemented without any requirement for huge engineering infrastructure due to solid-state fermentation. Some of the significant facts that have to be taken into account while reusing food waste are cost involved, its availability and inherent properties that may lead to variation in the produced compounds. It is a viable option in case of farming filamentous fungi on vegetal materials, which do not function well with hydrolytic enzymes. This study also emphasizes the need to identify and develop a new line of lignocellulolytic enzymes with high efficiency for industrial application.

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Bioconversion of Food Waste to Biogas

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Abstract

Throughout the entire food production chain, vast volumes of food are wasted and end up causing economic losses and risks to health and the environment. Rationally disposing of this waste means not only reducing social, economic and environmental problems but making better use of natural resources and stimulating a sustainable and circular economy. Anaerobic biodigestion appears as an alternative and rational destination of food wastes for the production of clean renewable energy and liquid fertilizer. In this chapter, we present in detail a demonstration unit for the production of biogas from food waste, located at Itaipu Binacional (Foz do Iguaçu, Brazil), which is composed of two biodigesters with 350 m^3. Based on the three years of experience in operating this demonstration unit continuously, we present relevant information regarding the process variables, control strategies and results of analyses of biochemical potential of methane. Finally, we discuss the importance of the composition of the substrate for the establishment of stable and high biogas productivity processes from food wastes.

1 Introduction

Data from the Food and Agriculture Organization of the United Nations (FAO) reveal that around 1.3 billion tons of food is globally wasted each year, which is equivalent to one-third of all food produced for human consumption (FAO 2019). The numbers are even more impressive when added to the losses from food transportation, storage and harvesting. These would be enough to feed more than 800 million people worldwide.

In an attempt to mitigate this problem, the United Nations (UN) established goal 12 of the Sustainable Development Goals (SDGs), which proposes bold actions to reduce food waste per capita and its losses along the production chain, thus resulting in the reduction in global demand for more food and reduced production costs. In addition to the food safety aspect, food waste was responsible for 47% of the worldwide gas emissions in 2016, from a total of 1.6 million metric tons of CO_2 resulting from the inadequate dumping of waste (Kaza et al. 2018). Although it exposes a monumental problem to be faced by the whole society, there is also an opportunity for the energetic use of gases released by the decomposition of this material. This is important once the growing world demand for energy is considered another critical aspect for the near future. The energy consumption (especially gas and electricity) has increased by 2.8% in 2018, for example (Enerdata 2019).

In Brazil, there is much to be done in terms of optimization of harvesting, storing and distributing food in order to reduce waste. In addition to the logistical problems, the country still needs to expand, above all, actions to improve its management of organic solid waste. According to data from the Brazilian Association of Public Cleaning and Special Waste Companies

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(ABRELPE), published in the Panorama of Solid Waste in Brazil 2018/2019 (ABRELPE 2019), among the 72.7 million tons of solid wastes collected in 2018, 59.5% had correct final disposal and were sent to landfills. However, controlled dumps and landfills still persist in the country, with a significant share of 23% and 17.5%, respectively, in the same period. About 3,000 dumps are in operation in the country and received, together, 30 million tons of waste in 2018 (BRAZIL 2010). When it comes to food disposal, the survey by the World Resources Institute (WRI) indicates that 41,000 tons of food per year is wasted in Brazil, with restaurants being responsible for 6,000 tons (15%).

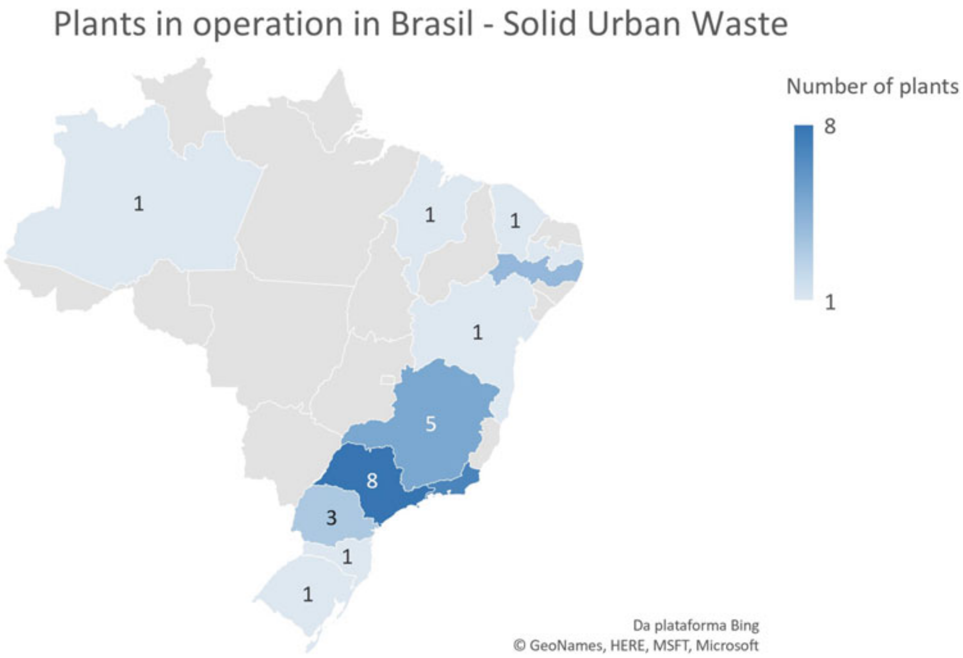
Although challenging, to achieve an adequate management of urban solid waste, it is strategic to recognize the energy value that biomass has and to expand its use for energy production. Technologies for the use of urban waste have been explored in order to combine environmental treatment and energy supply. Biogas is a growing fuel in Brazil (ratified by the 31% growth in the number of plants in operation in 2019) that, given its productive characteristics, can be considered as a solution for the treatment of urban solid waste. According to the International Center for Renewable Energy Biogas—CIBiogás, by the year 2019, 521 biogas production plants were in operation in the country; among them 34 uses solid urban waste as substrates (Fig. 1), divided into landfills and plants that receive and treat food waste in biodigesters. São Paulo is where the largest number of plants are in operation in the country (8), generating an average of 433 million cubic meters of biogas per year.

Although incipient, the recent initiatives by the public authorities and the private sector have been expanding the role that anaerobic biodigestion systems play as a responsible environmental alternative for the disposal of solid urban waste, contributing to the reduction of the organic load destined to landfills and eliminating dumps. An example of a positive initiative carried out in the country was the Brazil-Germany Project to promote the use of biogas energy, known as PROBIOGÁS (Probiogas 2015), which was carried out between 2013 and 2017 as a result of a partnership between the Brazilian and German governments in order to expand the efficient energy use of biogas and reduce greenhouse gas emissions.

Considering this favorable moment for biogas in Brazil, this chapter discusses the use of food waste in anaerobic biodigestion systems, highlighting the advantages of using this technological route. The analyses and discussions carried out in this work are based on data and information collected at a demonstrative biogas plant, which operates in Foz do Iguaçu, state of Paraná (southern region of Brazil). The unit processes organic waste from restaurants in the vicinity of the plant's own facilities to produce biogas and biomethane. It stands out for having an innovative technological arrangement closely related to R&D on new technologies applied to the sector.

Throughout this chapter, practical questions are presented regarding the operation of biogas production plants for the treatment of food wastes, with a broad view of the entire process, from the reception of biomass, pre-treatment of the material and fermentation. The chapter also brings a compilation of the three years' experience of continuous operation of the aforementioned biogas and biomethane production unit, which addresses essential aspects for controlling the biomass fermentation process, and the main variables that impact the efficiency of biogas production and

Fig. 1 Distribution of biogas plants utilizing RSU in Brazil


Plants in operation in Brasil - Solid Urban Waste

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inhibiting compounds. Features and advantages of different types of biodigesters are also presented, as well as laboratory analyses of the organic waste used in the biogas production unit and the importance of the composition of the substrate in the establishment of stable and productive systems.

2 Biogas Production Steps from Organic Waste

Within the biodigester, there are a series of reactions that occur for the production of biogas. These reactions are caused by thousands of bacteria that need ideal conditions for their performance. The biodigestion process is influenced by several factors, such as temperature, substrate composition, presence of oxygen, a model of the biodigester, operational conditions and the presence of materials of a toxic nature, among others.

In comparison to other types of treatment, the anaerobic process is satisfactory in relation to fluctuations in load. It is thus necessary to select the residues that feed in the biodigester and pre-process them to ensure that the ideal conditions for the microbial activity is reached (Ferguson et al. 2016). Techniques for the treatment of these organic residues are necessary before the biodigestion process itself takes place, avoiding problems in the operation of the plant and optimizing biogas production.

2.1 Raw Materials

The main advantage of using organic waste in biogas plants is to combine proper disposal with the concomitant generation of biofertilizer and biogas, which is a renewable and low-cost energy source. However, the biggest obstacle is the variable composition of the waste that goes through the biodigestion process. The range of organic residues is vast and in addition to the possibility of containing substances toxic to bacteria, their poor segregation can cause operational problems for the biodigester.

In the case of organic waste from various sources, the control of the separation of organic waste is more complicated and the presence of contaminants such as plastic, glass, metals, stones, sand, among others, is more common (Wojnowska-Baryla et al. 2020). The segregation of organic waste in a shopping mall and a food industry, for example, would be different. In the shopping mall, the consumers are responsible for the segregation, who often discard the metal cutlery, plastics and other waste together with the organic. In the food industry, however, the employees are constantly trained to segregate correctly, reducing the possibility of contaminating organic waste with other materials.

Due to this problem, greater attention is needed for the reception and segregation process of these residues before inserting them in the process called pre-treatment.

2.2 Pre-treatment of Organic Wastes

Different pre-treatment techniques are used to process organic waste before the biodigestion process. Pre-treatment allows the removal of undesirable inorganic elements and guarantees a suitable compound for biodigestion. This stage is divided into receiving organic waste and crushing it. According to Tabatabaei and Ghavanati (2018), organic waste pre-treatment systems must meet the following essential requirements: (i) digestion of a variety of organic wastes; (ii) substrate homogenization; (iii) removal of contaminants; and (iv) high production of biogas in anaerobic digesters. The composition of the waste is the most essential criterion for selecting an appropriate pre-treatment technology, followed by the model of the biodigester and whether wet or dry digestion system is used.

Wet anaerobic systems are operated at lower concentrations of solids, with a solids content between 4 and 8% (Leite and Lopes 2009) and use pre-treatment systems to remove unwanted contaminants prior fermentation. The digestate after biodigestion can be used directly as a high-quality fertilizer and no additional treatment is usually required. Dry systems are operated at higher concentrations of solids, with solids content around 20% (LEITE et al. 2009) and they depend on elementary pre-treatment systems. Consequently, the digestate needs additional treatment to be used as fertilizer.

Notably, organic waste is heterogeneous, varying both in the moisture content and the level of contamination. Therefore, pre-treatment preceding biodigestion is of great importance, resulting in increased biogas production and yield and high quality of biofertilizers.

2.3 Reception of Organic Wastes

A suitable place for receiving waste is essential. As previously mentioned, many inorganic wastes arrive at the plants mixed with organic wastes. The reception of residues must be simple so that the process does not become impracticable, but it should be efficient so that most of the residues undesirable to biodigestion are removed.

In some cases, the waste arrives at the unit in plastic packaging, so the first stage of segregation is necessary; this stage is called the bag tearing. Equipment called bag breaker is ideal for removing the contents of the bags in an automated way and separating bags that are classified as waste, and organic waste follows in the process.

Through a conveyor belt, the residues can be carried to a magnetic separator where the entire metallic fraction is segregated from the organic material.

2.4 Milling

Some factors, including particle size, influence anaerobic digestion. Physical pre-treatments are used to modify the structure of the substrate and facilitate the degradation of organic matter in anaerobic digestion by increasing the solubility of organic material and the total area for attack by microorganisms (Deublein and Steinhauser 2008). The smaller the particle size of the substrate at the beginning of the anaerobic digestion, the higher the efficiency in the degradation of the material and the shorter the retention time in the biodigester. The two most common techniques used for particle size reduction are grinding discs and mechanized sorting.

Separation by grinding discs is mainly used to treat packaged food scraps and restaurant leftovers. Due to its low density, the plastic fraction is separated by suction of air from the grinding discs. Those plastics that are not detected are crushed together with the organic residue but is further separated in a sieve based on its higher particle size. The resulted crushed organic material free of contaminants is fed into the biodigester.

Mechanized sorting technology is based on a shredder to open plastic bags and reduce the particle size of organic waste. The pre-crushed residue is mixed with process water to produce a homogeneous substrate with approximately 10% of solids. In both mechanized sorting and grinding discs pre-treatments freshwater is commonly added to improve the separation (Andrade 2007).

After plastic removal, the organic substrate can contain inert materials such as sand, glass and stones that must be removed to avoid attrition on the machines and sedimentation inside the digester. Hydrocyclone system is generally used for this purpose (Jank et al. 2017).

2.5 Fermentation

As stated earlier, biodigestion is a sequence of microbiological process of decomposing organic matter in an oxygen-free environment, resulting in the production of biogas and digestate.

The first phase is hydrolysis, where complex organic matter is broken down into simpler parts. After hydrolysis, acidogenesis, acetogenesis and methanogenesis (Fig. 2) steps occur simultaneously in time and space inside the biodigester.

2.5.1 Hydrolysis

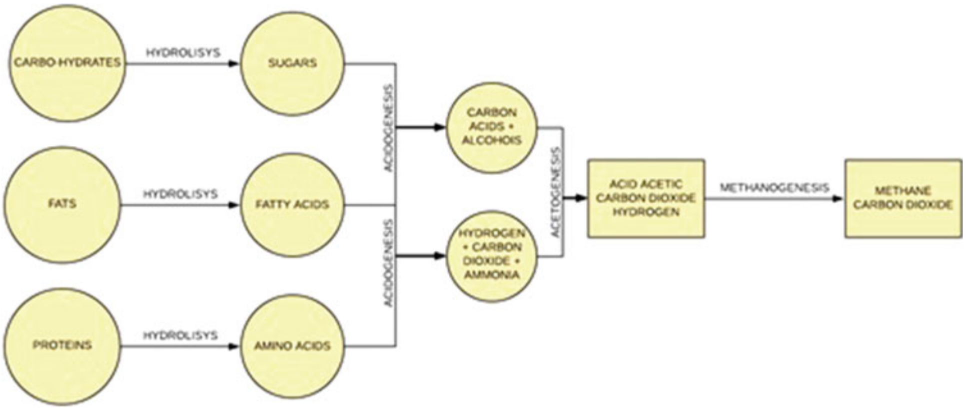
Hydrolytic microorganisms excrete hydrolytic enzymes that convert biopolymers into simpler and more soluble compounds (Bansal 2017) (Fig. 2). The process of breaking complex substrates into simpler substrates is slow and critical, compared to the rest of the process, so it is accepted that hydrolysis is the limiting step of the biodigestion (Pareek and Pareek 2019).

The hydrolysis phase differs from the others due to the action of facultative microorganisms, which use dissolved oxygen from the water and induce a fall in the redox potential, a parameter required by anaerobically strict microorganisms in the next phase of biodigestion (Gioannis et al. 2008). It is common to find a tank specially designed for hydrolysis separated from the biodigester.

2.5.2 Acidogenesis

The simple chemical compounds formed during the hydrolysis are consumed by different strict and facultative anaerobic bacteria and degraded to short-chain organic acids, alcohols, hydrogen sulfide, hydrogen and carbon dioxide (Angenent et al. 2004). The buffer effect of the substrate is

Fig. 2 Main stages of the anaerobic biodigestion process



very important at this stage, as it prevents pH drop inside the biodigester that could kill the methanogenic archaea.

2.5.3 Acetogenesis

In this phase, organic acids and alcohols are converted to acetate, carbon dioxide and hydrogen substrates that are used by methanogenic bacteria. The hydrogen produced in acetogenesis plays a relevant intermediate role, since the reaction occurs when the partial pressure of the hydrogen is low enough. The decrease in partial pressure is performed by bacteria that degrade hydrogen (Yousuf 2019). Acetogenesis is a fundamental step to efficiently produce biogas because approximately 70% of methane originates from the acetate reduction process (Zieminski and Frac 2012).

The symbiotic activity among microorganisms is essential in this phase, as they perform anaerobic oxidation reactions together with methanogenic microorganisms (Yousuf 2019). Acetogenesis produces hydrogen, which can generate excessive partial pressure that is harmful to acetogenic microorganisms. However, due to the presence of methanogens, hydrogen can be consumed quickly, maintaining partial hydrogen pressures to favor acetogenesis (Stams and Plugge 2009).

2.5.4 Methanogenesis

In this last stage of biogas production, organic acids and H_2 are converted into methane. The efficiency of methanogenesis is highly dependent on the last three steps and the methane production microbial community. Methanogenesis is a slow and sensible step severely influenced by operational conditions (Durruty and Gonzalez 2015).

3 Conditions and Parameters

Because some parameters influence the efficiency of the process, appropriate conditions must be provided for anaerobic microorganisms. The growth and activity of anaerobic microorganisms is significantly influenced by O_2, temperature, pH, availability of nutrients, agitation and presence and quantity of inhibitors (Whitman et al. 2006).

3.1 Nutrients

The presence of nutrients such as carbon, nitrogen, potassium, phosphorus and sulfur, and some mineral micronutrients, vitamins and amino acids are necessary for the development of methanogenic bacteria. Microelements are as important as the macroelements for the growth and survival of the microorganisms involved in the process. The insufficient supply of these nutrients can cause inhibition and disturbances in the process (Al Seadi et al. 2008), so knowing the complete composition of the substrate is important. Apart from micronutrients, the C:N ratio of the substrate must be in the range of 1:30–35 (Deublein and Steinhauser 2008). If necessary, the dosage of specific nutrients and chemical activators can be carried out so that a good biomass fermentation occurs.

3.2 pH

Microbial growth in an anaerobic digester is largely dependent on pH (Yang et al. 2015). The ideal growth of the hydrolytic microorganisms involved in the biodigestion process occurs preferentially from 5.0 to 6.0, while the best pH for the methanogenic bacteria is between 6.5 and 8.0 (Kundu et al. 2017).

In one-stage operation, the favorable pH range to meet the requirements of most microbial groups involved in the process must be between 6.8 and 7.4 (Tabatabaei and Ghavanati 2018). At pH below 6.5, the interruption of methane production can be noticed (Ostrem 2004). However, fermentation usually continues but generating other products. Hernandez and Rodrigues (2013) analyzed the impact of low pH values and observed that hydrogen was preferentially produced at pH < 6, with methane representing less than 1%.

There are two systems to ensure the pH balance: bicarbonate and ammonium alkalinity. Alkalinity is important because it represents the capacity of the digester to neutralize the organic acids formed during the acidogenic phase. Bicarbonate buffering systems occur in pH close to 7.0, while ammonium buffering occurs at pH close to 9.25 (Deublein and Steinhauser 2008) and is not recommended for biodigestion (Rabii et al. 2019).

For a stable methane production, average alkalinity should be between 200 and 5,000 mg/L. However, due to the organic acid formation within the biodigester, pH tends to decrease. Trusting in pH control can be tricky because drastic changes in pH values can occur when the buffer capacity of the substrate is outstripped. The time necessary to reestablish the buffering capacity of the system may not be enough to avoid the collapse of the biodigester. In anaerobic digesters with low buffering capacity, pH, partial alkalinity and AGVs are reliable indicators for process imbalance. In these cases where the substrate has recognizable low buffering properties, the codigestion with high alkalinity substrates is recommended (Trabold and Babbitt 2018). On the other hand, in highly buffered systems, pH changes can be small even when the process suffers turbulences, then AGVs can be considered as the unique reliable parameters for monitoring processes (Murto et al. 2004).

Because the solubility of the gases depends on the temperature, the buffering capacity of thermophilic and mesophilic systems differs. The pH value of thermophilic systems is usually higher due to the capacity of carbon dioxide to dissolve in water at high temperatures (Pareek and Pareek 2019). According to Tabatabaei and Ghavanati (2018a), other factors can interfere in the buffering system, such as high organic feeding rates, the presence of toxic compounds, temperature decrease, high organic load, high sulfide content, pH increase as a consequence of H_2S formation and an increase of free ammonia. When acidification is detected, one or more of the following strategies should be considered: stop feeding, increase the retention time, increase the buffering capacity, add pH neutralizing agents and add water.

3.3 FOS/TAC

FOS/TAC is proved to be a critical parameter that serves to quickly assess the stability of a biodigester, as it provides data in an easy and continuous way. FOS stands for volatile fatty acids, while TAC stands for total inorganic carbon (carbon buffering capacity) (Logan et al. 2019). It is considered a more reliable parameter than pH because it gives important information on the increase of FOS even when the biodigester's pH is within the optimal range; thus, allowing interventions that anticipate pH variation.

FOS/TAC values should be ideally between 0.1 and 0.3 (Fachagentur Nachwachsende Rohstoffe 2010). Values above the limit indicate that the proportion of organic acids is very high, which means that acidogenesis is being dominant. The accumulation of acids causes a drop in pH and the consequent inactivation of methanogenic bacteria, leading to inhibition of methane production. Values below 0.1 means system's alkalosis, which is the result of impaired hydrolysis and/or acidogenesis. The most common causes are lack of macro and/or micronutrients, excess feeding with easily degradable material (simple carbohydrates) and constant changes of the substrate composition (Chavarria et al. 2018).

FOS/TAC should be regularly measured to identify any deviations and implement countermeasures if necessary early. However, FOS/TAC is highly influenced by feeding; measurements made right before and after substrate addition provides significantly different results (Voss et al. 2009). Thus, stating clear rules for sampling, preparation and titration of samples is highly suggested.

3.4 Organic Load Rate (OLR) and Solid Content

Another important parameter in the operation of biodigesters is the added mass of organic waste per unit volume of the reactor per time, which is known as organic load rate (OLR). Theoretically, as much substrate is fed to the biodigester so that methane production should be higher. However, higher OLR results in acidification and system collapse. An ideal OLR in CSTR-type mesophilic biodigesters varies between 3 and 5 $kg_{VS}/m^3/d$, according to the substrate (Drosg 2013), while the system failure is observed at rates above 6.4 $kg_{VS}/m^3/d$ (Moriarty 2013).

Most biogas plants are operated, for safety, with OLR lower than the optimum. This strategy minimizes possible errors and process fluctuations, especially when complex substrates such as food wastes are used. On the other hand, the safety margin used is indirectly proportional to the system's efficiency and operational costs (Tabatabaei and Ghavanati 2018). Biogas plants are generally designed to convert 75% of the maximum degradable organic matter (Deublein and Steinhauser 2008).

3.5 Inoculum

Biodigestion depends directly on the action of microorganisms. A microbial community can grow naturally in a biodigestion system or can be artificially added to it. The addition of an inoculum helps to accelerate the process since the development and stabilization of a natural microflora can take months. The presence of a good microbial density in the biodigester favors access to the substrate, facilitating its degradation (Castro and Mateus 2016). Considering that at the beginning of the process naturally occurring acidogenic bacteria (producing acids and hydrogen) first develop the process control, the addition of methanogenic organisms can prevent the imbalance of the system and reduce the time for process stabilization.

Digested sewage sludge, UASB sludge, manure, digested and leached waste are usually used as inoculants (Estoppey 2010). The choice of an inoculum must consider the physical, chemical and nutritional characteristics of the place of origin (Barcelos 2009). As the ideal amount of inoculum (in percentage terms) to be added to the biodigester cannot be easily stated, it depends on the methanogenic activity of the microbial community (Araujo 2017). In continuous feeding systems, the addition of the inoculum occurs only at the start of the biodigester. In many biogas plants, part of the digestate is recirculated to the process in order to take advantage of the stabilized microbial community to increasing the density of microorganisms in the biodigester and, consequently, the efficiency of the process.

3.6 Agitation

The agitation of the substrate in the biodigester is very significant for the process as it favors the transfer of mass, energy and optimizes the access of microorganisms for the substrate (Szamosi and Siménfalvi 2020). Another benefit of agitation is the prevention of sedimentation and dead areas inside the biodigester, making all the organic matter available to the microorganisms (Gueri 2017). The agitation can be operated by automated devices, recirculation of the digestate or the produced biogas (Karim et al. 2005).

3.7 Inhibitors

There is a wide variety of compounds that inhibit the biodigestion that can be introduced through feeding or is formed during the process. Upon entering the process, substances such as oil, grease, phenols, paracetamol, caffeine, ibuprofen, triclosan, volatile aromatic and heavy metals, antibiotics, detergents, chlorine, among others, are able to inhibit the anaerobic process, ceasing microbial activity (Haak et al. 2016). Other agents such as nitrates, cyanides, phenols, sodium, potassium, calcium, magnesium, ammoniacal nitrogen, oxygen and heavy metals can also inhibit partial or complete the production of methane. The level of inhibition depends on (i) the concentration of the inhibitory compounds, (ii) the ability of bacteria to adapt to it (Deublein and Steinhauser 2008), (iii) the process conditions and (iv) the presence of synergistic compounds (when the effect of the inhibitory agents combined is greater than the sum of individual effects).

3.8 Temperature

The anaerobic digestion process is greatly influenced by temperature. The sudden variation of this parameter can lead to the destabilization of the reactor and death of microorganisms (Singh et al. 2017). The microbial population of the biodigester is defined according to the temperature range used in the system. The methanogenic archaea are divided into mesophilic (20–40 °C) and the thermophilic (50–60 °C).

Mesophilic processes are generally operated between 35 and 37 °C (Van and Fujiwara 2019). They are the most used due to installation and lower energy consumption. In addition, mesophilic biodigestion presents greater process stability (Gebreeyessus and Jenicek 2016) because the inhibition by ammonium is substantially reduced due to the preferred formation of free ammonia (Leite 2015).

Thermophilic systems have some advantages, such as faster biogas production and efficient destruction of pathogens (Ruffino and Campo 2015). Thermophilic digesters are usually smaller and feed at higher rates (De La Rubia et al. 2002). In addition, oxygen is less soluble in the thermophilic temperature range so that ideal anaerobic operating conditions are reached more quickly (Leite 2015). On the other hand, maintaining high temperatures requires greater energy expenditure, especially in colder regions, which can overcome the cited advantages of the process. Moreover, the thermophilic process is more sensitive to environmental variations, such as interruptions in food, temperature and load (Kim et al. 2006; Parawira et al. 2004). The thermophilic system is most indicated when the substrate used is generated at high temperatures or when pathogens are present (Ruffino and Campo 2015). Two stages of biodigestion systems in which methanogenesis and hydrolysis are operated at different temperatures exist (Liao et al. 2018) (usually mesophilic hydrolysis and thermophilic methanogenesis).

3.9 Types of Biodigesters

The choice of the most suitable biodigester depends on several factors, including the amount of total solids of the substrate, the need to control parameters such as agitation, heating and economic factors. The biodigesters mostly used for the treatment of organic solid waste are presented.

Continuous Flow Stirred Tank Reactor (CSTR): It is the type of biodigester most used with high organic loads and high content of solids (5–15%) (Furst et al. 2019). Generally, it results in reduced hydraulic retention time (14–28 days, depending on the substrate and the operating temperature) in comparison to other types of biodigesters (Verma 2002).

Batch: Biodigestion carried in batch mode is characterized by the addition of a certain amount of biomass to the biodigester, which is then controlled until no more gas is produced. Then, the reactor is opened, cleaned and a new batch is started. The new batch is usually inoculated with the mixture of solid digestate formed in the previous batch and the liquid digestate is recirculated to increase the contact of the microorganisms with the biomass. The amount of total solids for the use of this type of biodigester is above 30% (Furst et al. 2019).

Piston flow: It is indicated for a wide variety of organic substrates with solids content between 15 and 45%. The biomass is transported (vertically or horizontally) from the beginning to the end of the process by means of pumps, being able to operate in parallel with other digesters and generally operates in the mesophilic or thermophilic phases (Furst et al. 2019).

Covered pond biodigester [BLC]: This model is widely used in rural areas to treat animal waste, industrial and agricultural waste with low solids concentrations (0.5–3%) and hydraulic retention times between 30 and 60 days (Probiogas 2015).

3.10 Biodigester Classification

Regarding the solids content, biodigesters are classified as low and high solids. The presence of water defines the concentration of solids, as it favors the activity of enzymes and the availability of metabolites. Therefore, moisture can be considered as a very important factor in the biodigestion processes of organic solid waste (Leite and Lopes 2009).

In relation to the number of stages, they are classified into one-stage, two-stage and multi-stage systems. In double-stage biodigesters, the biodigestion of organic waste is divided into two phases, hydrolysis and methanogenesis, which occur in different reactors (Prosab: Basic Sanitation Research Program 2003). In the one-stage process, all phases occur in a single reactor (Vandevivere et al. 2002). Multi-stage is the result of also separating the acidogenic and the methanogenic phases, allowing the recovery of H_2 and CH_4, respectively (Nathao et al. 2013).

Moreover, biodigesters can be classified by the feeding strategy as continuous or batch. In the first, the substrate addition occurs continuously in such a way that the volume is constant. In the intermittent feeding system, the total volume to be digested is placed in the biodigester, and after the digestion is complete the digested substrate removed.

3.11 Stabilization Ponds

In organic waste biodigestion systems, it is common to use a stabilization pond after the biodigester to complete the digestion of the substrate and generate high-quality biofertilizer. The resulting digestate has high concentrations of phosphorus, nitrogen and potassium, which give it potential for use as a fertilizer (Logan et al. 2019). The digestate easily penetrates the soil and must be applied in accordance with good agricultural practices in order to minimize the loss of nutrients by leaching and evaporation, especially nitrogen (Wellinger and Murphy 2013).

4 Itaipu Demonstration Unit (DU ITAIPU) Contextualization

The Itaipu demonstration unit (DU ITAIPU) (Fig. 3) is the result of a partnership between Itaipu Binational (IB) and the Renewable Energies International Center [CIBiogás]. It was built with the purpose to be explored as a proof of concept for different organic waste treatment technologies used to treat food waste from restaurants located in the Itaipu area.

One of the main goals is to serve as a reference and model of studies for the implantation, operation and monitoring of other biogas and biomethane production plants. Another important aspect is research and development of solutions and technologies applied to biogas production in Latin America. Furthermore, this unit is also a place to validate technologies and to identify technological gaps aiming the "tropicalization" of equipment and biogas systems contributing to the productive chain in Brazil.

DU ITAIPU utilizes primary food waste from restaurants in the Itaipu area as a source of substrates to biogas production. Eventually, external organic products are received from different customs inspection departments, such as Federal Police, Federal Highway Police, Department of Federal Revenue of Brazil, Ministry of Agriculture, Livestock and Supply of Brazil, from burgling apprehensions. These external organic products are judiciously evaluated by Brazilian government departments and destined for the production of biogas and biomethane. The substrate's diversification strategy used at DU ITAIPU is in accordance to the *Fachagentur Nachwachsende Rohstoffe* [Renewable Resources Agency] (Fachagentur Nachwachsende Rohstoffe 2010). They affirm that the biodigester's feeding with different kinds of substrates (codigestion) is preferable than the simple digestion. However, to reach the ideal relation between organic matter and volumetric organic matter, it is necessary to run tests with different mixtures of substrates. Volatile organic compounds (VOC), according to the FNR, are the amount of dry organic matter (DOM) allowed to be used in the biodigester's feeding per cubic meter of its volume and per unit of time, expressed in $kg_{DOM}/(m^3 \text{ day})$.

Figure 4 presents the processing of food wastes to biogas at DU ITAIPU. The first step in the energy conversion process of the substrates is milling. The substrates are milled and then discharged into a mixing chamber. After the homogenization, the mixture is pumped to the biodigesters. There are two CSTR at DU ITAIPU made of modular fiberglass, an innovative product with national technology. It is 5 m high and 10 m in diameter, with 350 m^3 total volume for each. Regardless, the need of advanced research in the fiberglass biodigesters technology allows geometry and volume flexibility, besides being lighter than concrete and steel structures, which request fewer reinforcements in the structure foundation.

The biodigester's feeding occurs once in a day with the same amount of solids and liquids. Moreover, it is always made at the same time, so there are no sudden changes in the microorganism's routine. There are serpentines at the biodigester's internal walls that allow hot water to circulate and maintain temperature at 37 °C. Besides that, hydraulic and mechanical agitation takes place to ensure biomass homogenization. The hydraulic agitation is performed with the biomass recirculation between the mixing chamber and the biodigesters, while the mechanical agitation is performed with a helicoidal agitator. The agitation is essential to increase the contact area between the microorganisms and the biomass, optimizing biogas production.

Fig. 3 Aerial view of the demonstration unit—DU ITAIPU

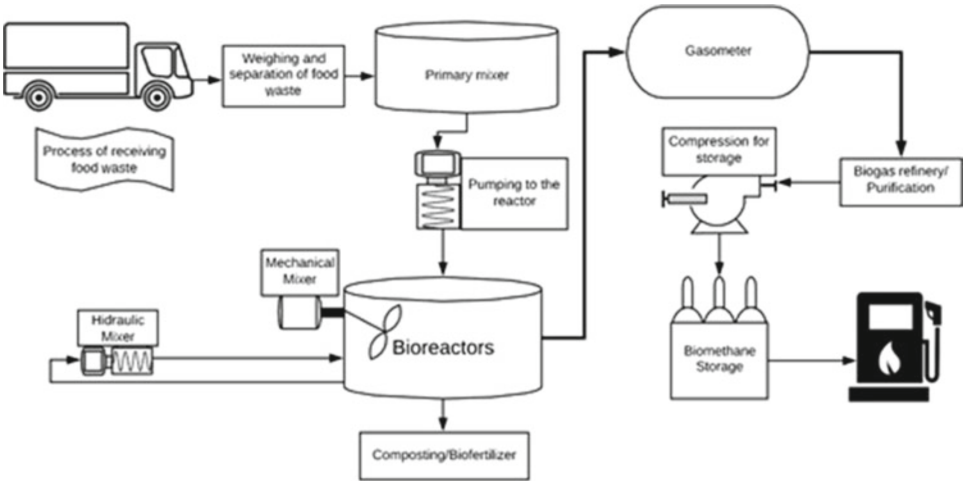


Fig. 4 Flowchart of biogas production from food wastes in the Itaipu demonstration unit

The biogas produced by the microorganisms accumulates at the top of the biodigesters (rigid dome), and then it is conducted by pressure equalization and stored in the gasholders. There are two gasholders with 250 m^3 each at DU ITAIPU, and the average biogas quality is 65% of CH_4 [methane], 34% of CO_2 [carbon dioxide], 600 ppm of H_2S [hydrogen sulfide], 1780 ppm of H_2 [hydrogen] and 0.8% of O_2 [oxygen].

5 Biodigestion of Food Wastes

5.1 Biochemical Methane Potential (BMP)

The anaerobic biodigestion process occurs through the combined and sequential action of several different groups of microorganisms. Therefore, the efficiency of a biodigester depends directly not only on the composition of the microbial community but also on whether they are metabolically active. The existence and activity of a certain type of microorganism in a biodigester is related to the operating temperature, pH, residence time and nutrients present. Therefore, it is essential that the feeding of a biodigester is carefully planned and executed.

The biodigestion process is basically divided into four stages (hydrolysis, acidogenesis, acetogenesis and methanogenesis, as previously described) which are performed by different groups of microorganisms, in syntropy, and that require different nutritional conditions (Nathao et al. 2013). Providing all nutrients in a balanced way is important so that all microorganisms that make up the microbial community are able to operate in optimal conditions.

In most cases, a biodigestion plant is built in order to degrade a specific type or a specific set of substrates. The evaluation of the effect of feeding different types of substrates is therefore restricted to laboratory analysis. The

CIBiogás Biogas Laboratory was the first in Brazil to be accredited by the ISO/ IEC/ 17025: 2017 standard for the determination of the biochemical potential of methane [PBM].

The BPM test is performed based on the German guide "VDI 4630 (2016)—Fermentation of organic materials characterization of the substrate, sampling, collection of material data, fermentation tests and DIN 38414—Part 8 (1985)—Sludge and sediments (group S): Determination of the amenability to anaerobic digestion" and reproduces in a batch reactor the anaerobic digestion of the substrate under normal conditions of temperature and pressure. This methodology has great relevance with regard to the characterization of a sample regarding the production of biogas and methane for sizing anaerobic reactors for biogas plants; inclusion of new substrates to feed biodigesters; decision-making on types and proportions of substrates in codigestion. Since 2011, they have carried out approximately 31,000 tests from more than 150 different samples at the CIBiogás Biogas Laboratory.

The Itaipu demonstrative unit is operated by CIBiogás and was designed to convert food waste from restaurants in the Itaipu Binacional complex. This type of waste is composed of food scraps discarded in meal preparation and not consumed (totally or partially) by users. Generally, it produces more methane than animal waste and domestic sewage (Bozym et al. 2015). In 2019, the unit processed an average of 426 kg/day of restaurant waste and operated with an average volumetric organic load (VOC) of 0.59. The reactor is supplied on a daily basis according to the availability of waste to meet working VOCs. The restaurant waste is quite rich in relation to the macro and micronutrients necessary for the growth of microorganisms and has a high potential for biogas production. Analysis of the biochemical potential of methane (Table 1) shows that, on average, 96.9 ± 53.6 $LN_{CH4}/kg_{substrate}$ can be produced, with a methane content of 66.4 ± 7.8%.

In addition to the restaurant food waste, other food substrates have already been analyzed for BMP at the CIBiogás Biogas Laboratory (Table 2). It is noticed that foods rich in fat, such as olive oil, oil and animal fat, have the greatest potential for volumetric methane production, while fresh vegetables (onions and garlic) have the least potential. Among the residues rich in carbohydrates (e.g. chocolate powder and black beans) and protein residues (e.g. meat and sausages), there is a small advantage for the former (Fig. 5). In relation to lipidic substrates, vegetables, carbohydrate- and protein-rich food wastes produced 38, 3.25 and 3.85 less methane.

5.2 The Role of Substrate Composition

Assessing the ability to produce methane from the main source of carbon available in different foods is a dangerous strategy. This is because a substrate that has a high PBM cannot necessarily be considered to be the ideal substrate. The concept of potential biogas production and the maintenance of an active microbial community must be observed and separated. The ability of a substrate to generate biogas is

Table 1 Characterization of the solids content and the biochemical potential of methane production of solid organic residues from the Itaipu Binacional restaurant

Sample	TS (g/kg)	VS (g/kg)	NL_{biogas}/kg_{sv}	NL_{CH4}/kg_{sv}	NL_{biogas}/kg_{subst}	NL_{CH4}/kg_{subst}	Methane content (%)
1	252.9	951.3	657.0	325.7	158.1	78.4	50
2	253.9	949.5	455.7	332.4	109.9	80.1	73
3	255.0	954.0	619.6	422.3	150.7	102.7	68
4	286.2	950.6	725.7	589.4	197.4	160.4	81
5	290.2	948.2	723.9	539.3	199.2	148.4	75
6	288.9	954.3	704.3	494.7	194.2	136.4	70
7	66.7	66.1	663.0	412.6	38.3	23.8	62
8	269.6	944.2	718.9	501.5	183.0	127.6	70
9	66.7	66.1	585.0	370.1	33.8	21.4	63
10	240.6	940.3	752.8	504.4	170.3	114.1	67
11	101.5	51.5	513.5	316.5	49.6	30.6	62
12	155.6	944.3	611.0	371.5	89.8	54.6	61
13	330.5	947.6	952.0	579.7	298.1	181.5	61
Average	**219.9**	**743.7**	**667.9**	**443.1**	**144.0**	**96.9**	**66.4**
Standard Deviation	**90.3**	**389.1**	**122.4**	**97.1**	**76.9**	**53.6**	**7.8**

TS = total solids, VS = volatile solids in dry base, LN = normal liters, subst = substrate

Table 2 Characterization of the solids content and the biochemical potential of methane production of diverse food wastes carried out at the CIBiogás Biogas Laboratory

Substrate	ST (g/kg)	SV (g/kg)	LN_{biogas}/ kg_{sv}	LN_{CH4}/ kg_{sv}	LN_{biogas}/ kg_{subst}	LN_{CH4}/ kg_{subst}	Methane content (%)
Chocolate powder	950.0	878.4	371.7	234.7	310.2	195.8	63
Black beans	848.0	961.5	564.3	332.3	460.1	271.0	59
Olive oil	999.1	999.9	1237.9	868.0	1236.5	867.1	70
Oil	973.3	996.1	1127.0	778.7	1092.6	754.9	69
Animal fat	999.5	999.9	1103.5	655.7	1103.1	655.4	58,8
Meat	321.4	971.9	781.4	562.8	244.1	175.8	72
Sausages	354.8	925.1	958.3	665.7	314.6	218.5	69
Onions	90.3	936.5	605.8	320.4	51.2	27.1	53
Garlic	345.0	950.7	157.4	36.8	51.6	12.1	23

TS = total solids, VS = volatile solids in dry base, LN = normal liters, subst = substrate

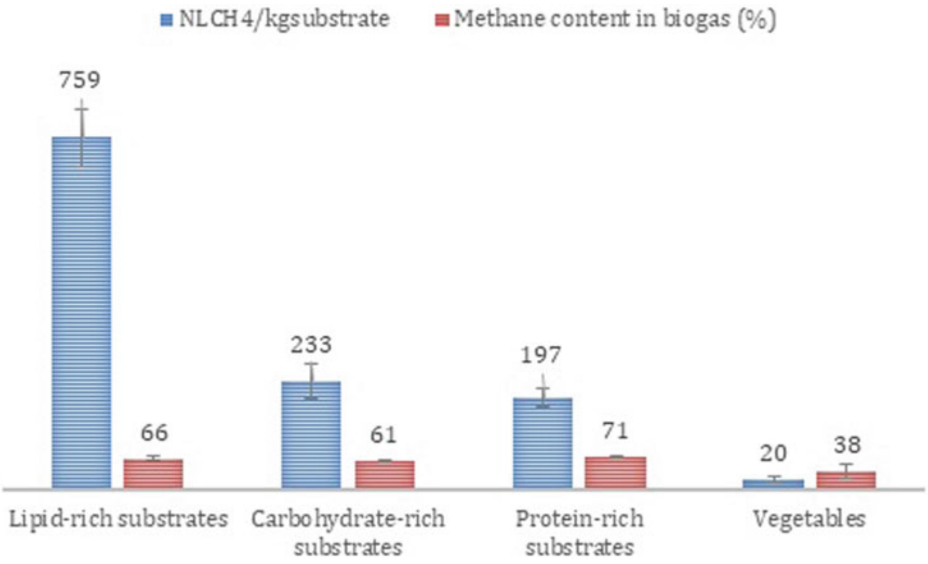


Fig. 5 Methane production potential and concentration in biogas for different types of food. NL_{CH4} = normal liters of methane

related to the conversion of the carbon source into methane, while maintaining the activity of the microbial community requires the supply of balanced amounts of macro and microelements.

A microbial cell is formed mainly by CHONPS, constituting approx. 95% of its weight; the rest are micronutrients such as potassium, calcium, magnesium, zinc, among others. In biodigesters, micronutrient deprivation results in a less stable and efficient process with changes in the microbial community, especially the decrease in the concentration of Methanosarcina (a high-performance methanogen) (Wintsche et al. 2016). A biodigester kept in operation for long periods can begin to suffer acidification even with the decrease in the feeding rate, which may be the result of nutritional imbalance. Lebuhn et al. (2008) demonstrated the recovery of a collapsed system with the addition of micronutrients. Different studies point to several limiting micronutrients, the most common of which are cobalt, nickel, molybdenum, tungsten and selenium (Pobeheim et al. 2011; Plugge et al. 2009; Banks et al. 2012; Munk and Lebuhn 2014). Therefore, the feeding of a biodigester must be well evaluated and planned in order to provide all the nutrients necessary for the survival and multiplication of the microorganisms present there, which makes it essential to know the microbial community present. A well-diversified microbial community is essential in cases where food and environmental conditions are constantly changing (Kallistova et al. 2014).

Olive oil, for example, despite having enormous methane production potential, probably could not be used as an exclusive feed in a biodigester due to the absence of nitrogen and minerals such as phosphorus, zinc magnesium, copper, manganese and selenium, essential for cell multiplication and activity. However, this material can be used in codigestion with another material so that the balance of nutrients is established and the gas productivity has little impact. Other advantages of codigestion are positive synergistic effects on microorganisms, better process stability and increased moisture content required by the biodigester (Alves 2016).

An important factor in the use of food waste for the production of biogas and biomethane is the presence of toxic compounds. In addition to the conditions of temperature, pH, availability of nutrients, agitation, feeding rate and the presence of a high-performance microbial community, it is necessary to ensure that possible toxic compounds are present in concentrations safe for the system. These inhibitors can be produced during the process or added unreasonably during feeding. Each inhibitor is different in terms of its effects, which can occur continuously or intermittently depending on the diet and the consistency of its composition.

Some inhibitory compounds that can be generated during the process are ammonia, volatile organic acids and hydrogen sulfide (Chen et al. 2016; Kwietniewska and Tys 2014). According to Poggi-Varaldo et al. (1997), ammonia is considered an inhibitory compound in mesophilic systems at concentrations of 2.8–8 g/kg and in thermophilic processes from 2.5 to 4 g/kg. Ammonium results in the loss of potassium from methanogenic microorganisms and can have effects similar to Ca^{2+} and Na^+ (Deublein and Steinhauser 2008). The pH has a great influence on the degree of toxicity of ammonia, which is only toxic in its non-ionized state, just as it occurs for hydrogen sulfide (H_2S). The production of H_2S is directly proportional to the concentration of sulfates and proteins in the substrate. According to Mendonça (2009), the organic load and sulfate ratio greater than 10 does not cause the inhibition of bacteria. When this proportion is exceeded, the sulfate-reducing bacteria start to compete with the methanogenic bacteria for H_2 and acetate, reducing the efficiency of the system (Callado et al. 2017).

Feeding with high protein contents can also result in foaming, which is common when adding large loads of lipid materials. Foaming can last up to 3 weeks and reduce biogas formation by 50% (Kougias et al. 2015). To control foaming ideally, the feed rate should be regulated, avoiding overload. Alternatively, especially when foaming is unavoidable, the use of defoamers is used. There are several defoamers available on the market, but the choice must be carefully made in order to guarantee non-toxicity to the microbial community, biodegradability and a minor impact on the plant's operating costs.

Heavy metals, such as cadmium, mercury, arsenic and lead, can act in the enzymatic inhibition, harming the biotransformation of organic matter in terms of yield and speed. Some metals that have a positive effect at low concentrations, such as zinc and copper, can become toxic if the limit is exceeded (Abdel-Shafy and Mansour 2014). In addition to the concentration of metals, toxicity is also influenced by pH in the biodigester and oxidation state. The effect of pesticides on biodigestion is still poorly explored, but agricultural waste is often contaminated; the presence of lindane and DDT, for example, has already been described as an inhibitor of methane production (approx. 34% at a concentration of 5 mg/L and 45% at 10 mg/L) (El-Gohary et al. 1986).

6 Conclusion

Anaerobic digestion of food wastes is a complex process that requires adequate processing of the substrate prior to fermentation. Knowing the chemical composition of this substrate, regarding the content of macro, microelements, contaminants and potential inhibitors is essential to obtain stable and active microbial communities that result in controlled and productive processes. For this reason, the biochemical potential of methane should not be considered as the only parameter for substrate selection. The control of the process also plays an important role to avoid turbulence in the system and the formation of inhibitory compounds that may harm the biogas productivity. The use of food wastes for the production of biogas is an important tool in reducing socioeconomic and environmental losses caused by the considerable losses in the food chain, contributing to the construction of a society that makes more rational use of the available natural resources. The Itaipu demonstration unit is the main reference in Brazil for large-scale biodigestion of food wastes. Visited by researchers and institutions interested in the theme throughout the year, it contributes significantly to scientific and technological advancement in a country in which this technology is undergoing consolidation.

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Bioconversion of Industrial Wastes into Biodiesel Feedstocks

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Abstract

To date, it has not been possible to establish the economic viability of the production of microalgae biodiesel. Relevant issues associated with commercial-scale microalgae cultivation need to be addressed to make this biofuel a reality. The high demand for water and nutrients represents a significant challenge. The use of wastewater for bioenergy production is an economically and environmentally promising alternative. In this context, the main objective of this chapter is to present a landscape of the potential use of microalgae for bioconversion of industrial wastes into biodiesel feedstocks. Initially, the microalgae will be presented as an auspicious feedstock for biodiesel. The use of industrial waste as a nutrients font for microalgae culture and biodiesel production will be discussed. The challenges associated with the bioconversion of industrial waste into biodiesel will be debated in its main aspects. In the end, the biodiesel characteristics and the economic issues of the commercialization of microalgae biodiesel from waste will be addressed.

Keywords

Microalgae • Wastewater • Lipids • Biofuel

1 Introduction

Based on the current biotechnological maturity, unfortunately, it has not yet been possible to establish the economic viability of microalgae biofuels. The technological routes are immature, and the production cost makes it difficult to use microalgae as a producer of bioenergy (Deprá et al. 2018). However, although it has a high production cost, there is a global effort to make microalgae technology commercially attractive. Today, large- and medium-sized companies are investing in research and development to produce microalgae biofuels on a commercial scale. This attempt is supported by the initiative of many companies, such as Euglena, BP plc, and ExxonMobil (Salama et al. 2017).

A viable solution to reduce production costs is cultivation using wastewater. Scientists worldwide have demonstrated the important role of microalgae in bioremediation and nutrient recovery from wastewater (Mondal et al. 2019; Queiroz et al. 2013). The wastewater is a readily available source of water and nutrients for biomass production, which can be utilized to produce biodiesel (Paniagua-Michel 2015; Francisco et al. 2015). The demand for biodiesel is increasing worldwide not only by the urgency to minimize dependence on fossil fuels but also to maintain the sustainability of the ecosystem (Jayakumar et al. 2017).

Until the moment, among renewable bioenergy sources, the microalgae have shown the most promise for biodiesel production. Concomitant, an increasing number of studies have demonstrated the potential for bioconversion of municipal, agricultural, industrial, and agro-industrial waste into bioenergy. The strategy can considerably improve the sustainability of the production chain. It is predicted that, with the advance of research, the production expenses will decrease considerably, leading to the commercial success of the microalgae biodiesel companies.

Today, great emphasis has been given to the massive generation of industrial and agro-industrial waste, such as flue gases and wastewater. The wastewater from these sources has an expressive content of organic matter and is being evaluated for microalgae cultivation and biodiesel production (Udaiyappan et al. 2017). Given the potential use of these wastes for the economic viability of microalgae

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biodiesel production, the main objective of this chapter is to present a landscape of the use of microalgae for bioconversion of industrial wastes into biodiesel feedstocks.

2 Microalgae as a Biodiesel Feedstock

The overexploitation of energetic natural resources has driven the research and development (R&D) sector to seek alternative sources of energy to supply the growing demand and reduce the dependence on fossil fuels. Environmentally friendly fuels that do not harm human health and the ecosystems are the focus of researchers around the world (Ingrao et al. 2018). In particular, the biodiesel with properties similar to diesel, a non-renewable fuel widely used by trucks, buses and tractors, and other machines that require high power, is gaining more and more space. It is worth highlight that among the advantages of biodiesel using is the significant reduction in the emission of polluting gases, providing thus a high environmental gain (Cavalheiro et al. 2020).

The substitution of non-renewable fuels by renewable ones reflects helpful contributions to the economy and preservation of the environment. As sustainable and renewable alternative sources of energy have been full-blown the biofuels of the first, second, third, and fourth generations. The biodiesel generated from the oilseeds is named first generation, generated from the non-edible inputs of second generation, and generated from the organisms with elevated lipid synthesis of third generation. The fourth-generation biodiesel production uses microorganisms genetically modified and is an emerging approach (Kumar et al. 2020).

Currently, biodiesel produced from food sources, through the exploitation of vegetable oils and others that are from an edible source, is already being applied directly to diesel engines, or in parallel with fossil diesel (Ayoola et al. 2019). However, the use of arable lands is one of the disadvantages of using these sources. With the current concerns of international agencies, related to hunger and a significant growth in the price of foods, new sources have been explored, as is the example of oleaginous microorganisms, among them microalgae. These microorganisms have high synthesis and lipid storage in their cells (Severo et al. 2019).

The benefit of biodiesel fabrication from microalgae includes the fast growth of cultures, high oil productivity, and utilization of non-arable land (Maroneze et al. 2019). As potential biological agents, these microorganisms can valorize wasted resources, mitigate carbon dioxide (CO_2), and the biomass generated can be utilized for biodiesel production (Patidar and Mishra 2017).

3 Low-Cost Waste as Feedstock for Biodiesel

The use of alternative fuels to oil products is promising in reducing the negative environmental impacts caused by the consumption of fossil fuels. The excessive use of these causes an increase in greenhouse gas emissions; thus, the focus of the research has become the development of renewable and environmentally friendly technologies that serve as a commercially available energy source (Rajaeifar et al. 2016).

Biodiesel is a promising biofuel to replace diesel (Oh et al. 2012). The use of oleaginous microorganisms is an option for biodiesel production. It offers advantages due to its short cultivation period, higher productivity, and similarity in the fatty acid composition with the vegetable oils generally used (Alptekin 2017; Cho and Park 2018).

Oilseed microorganisms accumulate a high concentration of lipids in their cells, many times greater than 20%, and using organic and inorganic carbon sources; the metabolism is carried out (Xu et al. 2015; Amara et al. 2016). Unfortunately, the cost of cultivating these microorganisms is very high, hampering the economic viability of microbial oils (Cho et al. 2015). However, the commercial and sustainable production of this bioproduct can be carried out when cultivated in low-cost substrates, such as organic and inorganic waste (Cho et al. 2017).

Waste treatment is mediated by primary and secondary, where the removal of solids occurs with the subsequent bioremediation of organic and inorganic materials by microorganisms. Microalgae appear as an alternative approach to biological treatment and act as removers of organic and inorganic fillers with subsequent conversion to biomass, which can be exploited to obtain various bioproducts, such as biofuels (MohdUdaiyappan et al. 2017).

According to Pittman et al. (2011), Lundquist et al. (2010), only cases involving the treatment of industrial effluents with subsequent production of biofuel can generate biodiesel at a competitive cost in the market; without this process, it is economically unfeasible and does not offer a positive return. Therefore, microalgae applied to wastewater with subsequent generation of biodiesel can be considered a sustainable and renewable production of bioproducts.

Based on a study with microalgae, Chisti (2007) observed a regular life cycle and concluded that in 24 h, the lipid capacity in the microalgae biomass varies between 20% and 50%, and with genetic engineering techniques, this time can still be reduced. Mathimani et al. (2017) were successful in testing the biodiesel harvested from microalgae mixed with petroleum diesel, which obtained a reduction in the emission of carbon monoxide and CO_2 from the engine.

The application of residues as a media of cultivation to decrease the high expense of producing microalgae has been an alternative option favorable. This type of process has similar or superior potential in the production of lipids in microorganisms, besides reducing charge mainly nitrogen and phosphorus of residues to treated, these substrates are ideal for the generation and development of algae lipids (Cho et al. 2017). It is worth mentioning that besides residue's composition, the efficiency of each strain must be explored simultaneously, according to the number of nutrients available for the development and production of lipids (Cho and Park 2018).

There are several types of waste, including agricultural, industrial, and municipal wastewater, and each can offer a different lipid production potential (Chiu et al. 2015). According to Table 1, it is possible to evaluate some types of waste and its composition favorable to the current production of lipids in microalgae to obtain biodiesel.

4 Industrial Waste as a Nutrients Font for Biodiesel Production

In the last decades, there has been a massive generation of industrial and agro-industrial waste. These residues, such as wastewater and flue gases, have organic and inorganic compounds that are useful for the commercial cultivation of microalgae. The use of these wasted resources can generate high value and low added-value products such as biodiesel.

Typically, the textile industries produce a high amount of residual water; in them, several fabric dyes are found (Wang et al. 2016). The textile industry's wastewater contains essential nutrients for the growth of microalgae; they are characterized by intense colors, high salinity, unstable pH, and high demand for chemical oxygen. The nutrients are converted chemically and biochemically to lipid content, which reaches up to 85% of dry biomass, and later biodiesel production is used (Chernova and Kiseleva 2017). This

Table 1 Types of residues and characteristics favorable to microalgal lipid production

Wastes	Composition characteristics of waste	References
Secondary effluents from palm oil mill	Nitrogen and inorganic phosphorus	Cheirsilp et al. (2017)
Textile wastewater	Organic and inorganic nutrients, nitrate and phosphate anions, carbon	Salama et al. (2017), Fazal et al. (2018)
Pharmaceutically wastewater	Pharmaceutically active compounds (PhACs) including a wide range of compounds used to prevent/treat human and animal diseases, Pharmaceuticals and personal care products (PPCPs)	Cecconet et al. (2017)
Sewage sludge	Nitrifiers, inorganic contaminants	Torres et al. (2017), Leong et al. 2018)
Swine wastewater	Suspended solids, organic materials, heavy metals, antibiotics, and hormones	Kuo et al. (2015)
Broth mixture of beer and fermentation residues crude glycerol	High level of nitrogen, glycerol, carbon	Feng et al. (2014)
Anaerobically digested milk manure	Organic and inorganic nutrients, high turbidity, competitive microorganisms, phosphorus, and NH_4^+	Levine et al. (2011)
Cane bagasse hydrolyzate	Xylose, arabinose, and glucose	Mu et al. (2015)
Rubber wastewater	Washing water, protein whey, non-coagulated latex, lipids, carbohydrates, salts, chemical and biochemical oxygen demand, ammonia, nitrate, phosphorus, and total solids	Udaiyappan et al. (2017)

Adapted from Ref. Cho and Park (2018)

percentage is a determining factor in the application of microalgae for the production of biodiesel since a large part is composed of neutral lipids, mainly triacylglycerides (TAG). The use of industrial textile waste as a biodiesel production process is a sustainable strategy that reduces large-scale damage to the wastewater receiving environment (Salama et al. 2017; Fazal et al. 2018).

Regarding rubber production, carried out through the transformation of latex, is a large amount of wastewater is generated, such as washing water, protein whey, non-gelled latex, lipids, carbohydrates, salts, ammonia, nitrate, phosphorus, and total solids (Udaiyappan et al. 2017). Few studies have been carried out with microalgae applied to industrial rubber waste since they are not produced in abundance in different regions. However, Bich et al. (1999), Ayyasamy et al. (2008) reported that microalgae consumed the nutrients contained in the waste by up to 93.4%, with high biomass productivity and lipid biosynthesis that improve the production of biofuels (Udaiyappan et al. 2017).

The industrial sewage sludge contains nitrified compounds and inorganic pollutants such as cadmium, copper, lead, and selenium. According to Lim et al. (2013), the use of microalgae combined with the symbiotic application with bacteria improves the denitrification process. Besides this, increases the performance of the microalgae with high lipid production. Torres et al. (2017) concluded that the lipid content is not affected, the contaminants favored the increase of the biomass, demonstrating that the microalgae integrated to activated sludge substrates for the simultaneous production of components for biodiesel, simultaneously support the environmental sector through waste treatment.

About pharmaceutical wastewater, they have a significant and diverse amount of organic compounds that can remain in aquatic environments and are persistent in degradation by microorganisms. However, the use of microalgae has become a sustainable and comprehensive strategy (Tolboom et al. 2019). Combined with the subsequent extraction of microalgae oils to the biodiesel manufacturing from the biomass produced, a symbiotic system, microalgae, and bacteria can remove 60–90% of the contaminating compounds (Bai and Acharya 2017; Xiong et al. 2018).

A large group of wastewater includes agro-industrial waste, such as swine wastewater, milk manure, sugarcane bagasse hydrolyzate, beer fermentation waste, effluents from palm oil mill among others (Cheirsilp et al. 2017; Feng et al. 2014; Levine et al. 2011; Cheng et al. 2018). A common aspect of this type of waste is the presence of a high concentration of ammonium and chemical oxygen demand (COD) (20,180 mg L^{-1}). Thus, the co-culture of microalgae in these residues is a potential solution (Wang et al. 2015). The technology for reducing the nutrient load, and having a high accumulation of lipids, through the facility to tolerate stress, becomes an efficient means for biodiesel manufacturing (Cheng et al. 2018).

Noteworthy, Chinnasamy et al. (2010) reported that the application of algae in the industrial residues of a carpet factory could produce approximately 15,000 tons of microalgae biomass, with the production of up to 4 million liters of biodiesel, and removal of around 1500 tons of nitrogen and 50150 tons of phosphorus from this wastewater a year. Notably, the microalgae are promising for the biodiesel production with the cultivation of low-cost waste, such as industrial waste. The yield of lipid production and composition from microalgae has emerged as an attractive path in large-scale biodiesel production. Additional studies and explorations of the yield of each strain in different kinds of waste for the production of biodiesel can promote the commercialization of this biofuel (Kumar et al. 2020).

5 Challenges of the Bioconversion of Industrial Waste to Biodiesel

The biodiesel production from microalgae involves upstream and downstream processing, which includes the unit operations of strain selection, cultivation, harvesting, drying, extraction, and conversion techniques, as shown in Fig. 1. Until today, the technology to transform microalgal biomass into biodiesel is technically feasible but uneconomical at commercial scale. The economic feasibility of any microalgae-based process depends on the choices of methods for each unit operation in the upstream and downstream phases.

The most significant challenges to improve the economic viability of any microalgae-based process are related to three main aspects: (i) improve cultivations productivity; (ii) reduce the energy demand for the downstream processing, especially for harvesting, drying, and oil extraction; and (iii) explore the full potential of microalgal biomass in a multi-product biorefinery concept (Cuevas-Castillo et al. 2020). The first challenge includes selecting the strain, finding a low-cost cultivation medium, prioritizing industrial wastes, and choosing the most suitable cultivation system. Downstream processing of microalgae biodiesel represents about 60% of the total production cost of the biofuel, so in the second approach, more economical and integrated techniques are required for the main steps of the process. The last issue refers to process design strategies that not only aim a single product but also to a whole valorization of all biomass fractions.

The first, and critical, step in microalgae-based processes for biodiesel production, or any other product is the choice of the microalgae strain to be grown (Borowitzka 2013; Aravantinou et al. 2013). To date, there are more than 158,300 strains cataloged, according to algaebase.org, each with its characteristics and requirements. Due to this large number of species available, a robust selection is challenging

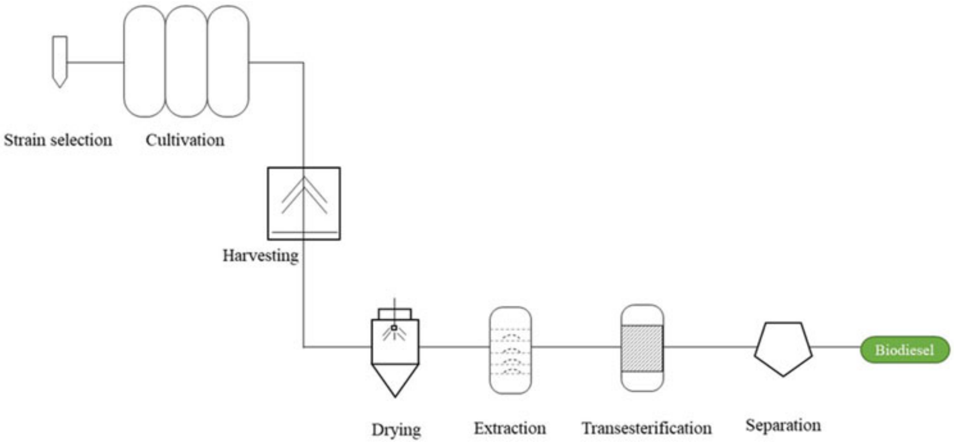

Fig. 1 General process flow diagram of microalgae biodiesel production

due to the limited information on most of these microalgae and their distinct characteristics (Sydney et al. 2019).

In general, the desired characteristics of microalgae strain for biodiesel production include rapid growth rate, high lipid content, growth over a wide range of temperature, salinity and irradiation (for photosynthetic cultures), high shear and oxygen tolerance, growth in a selective environment to reduce the possibility of contamination, ease of harvesting, weak cell wall, and suitable fatty acid profile (Borowitzka 2013, 2018). Considering that the building blocks for biodiesel production are lipids and that they are intracellular, lipid productivity is typically considered as a decisive parameter in the choice of the strain, since it considers both the lipid content and the biomass productivity (Griffiths and Harrison 2009; Queiroz et al. 2011). Additionally, when the culture medium is wastewater, the selected strain must have resistance to the nutrients present, especially ammoniacal nitrogen, which at high concentrations can become toxic and inhibit growth (Osundeko et al. 2019).

As for their origin, microalgae strains can either be obtained from stock culture collections or be isolated from environmental samples (Neofotis et al. 2016). Still, it is difficult to find a strain that includes all the required properties. In this sense, one option to improve the strains is to modify them by mutagenesis or genetic engineering techniques, including genome editing tools and metabolomic re-programming. The use of these techniques becomes increasingly crucial for the industrial viability of microalgal-based products, especially for low-value products such as biodiesel. This becomes even more imperative when using industrial wastes as a culture medium, as it requires greater robustness of the culture (Bharadwaj et al. 2020).

Once defined the strain, the cultivation aspects need to be addressed, especially the unresolved bottlenecks. The first point to consider is the cultivation mode and system. One of the advantages of microalgae is their metabolic versatility. Although the preferred route is photoautotrophic, these microorganisms can also assume other types of metabolisms, including heterotrophic and mixotrophic. Regarding cultivation systems, on industrial scale, microalgae are usually cultured in open or closed systems (Maroneze and Queiroz 2018).

Photoautotrophic cultivation refers to the process in which light energy is captured and an inorganic source of carbon is used to form chemical energy through the photosynthesis process. In this cultivation model, microalgae primarily require an inorganic carbon source, like CO_2, and light energy (Maroneze et al. 2019). Since CO_2 can come from industrial waste and light energy can be supplied by sunlight, this type of process is considered environmentally friendly and has so far been the most widely used. In this type of cultivation, open raceway ponds are still the most adopted system to cultivate microalgae for industrial production of low-cost products, including biofuels, since these facilities are inexpensive and easy to operate than closed systems. On the downside, open systems have some operational problems as the dependence on climate conditions, contamination, evaporation, and extensive land requirements. Due to the high cost, closed photobioreactors are more suitable to be used to produce higher market value products like carotenoids and fatty acids. Besides this, the dependence on light energy restricts the scale-up and hinders the design of the cultivation systems (Severo et al. 2019; Suparmaniam et al. 2019).

A feasible alternative is the heterotrophic growth in the absence of light, supported by an exogenous carbon source, which can overcome the major limitations of autotrophic cultures. Although not all species can use respiratory metabolism, when possible, the heterotrophic cultures can be efficiently conducted in conventional fermenters, e.g., stirred tank and bubble column bioreactors, where, in general, are cheap, simple to construct, and easy to scale and maintain on a large scale (Perez-Garcia et al. 2011; Francisco et al. 2014). On the other hand, the biggest challenge of heterotrophic cultures is the demand for exogenous organic carbon, since, in these types of cultivation, the carbon source represents about 80% of the cost of the culture medium (Francisco et al. 2015). In this sense, the obtainment of organic carbon and other nutrients from industrial wastes may offer an inexpensive alternative for microalgae cultures, with parallel wastewater treatment (Queiroz et al. 2018).

Another option is the mixotrophic cultivation that is a variant of the heterotrophic growth regime. In this case, the microorganisms simultaneously assimilate organic carbon and CO_2 and use both photoautotrophy and heterotrophy (Mohan et al. 2015). Since photosynthesis is not the only route available for obtaining energy, microalgal growth is not strictly dependent on light. This eases the geometry of the photobioreactors, making the scaling-up easier. The differential of this mode of cultivation is that it is possible to use both wastewaters as culture medium and CO_2 from industrial wastes (Wang et al. 2014).

Regardless of the cultivation method, on a commercial scale, the algal cultures require an enormous amount of freshwater and compounds like carbon, nitrogen, phosphorous, and several other trace nutrients (Pandey et al. 2019). Thus, the production of microalgae-based products in an economical way depends on the source of water and nutrients used. As already discussed, industrial wastes are a source of nutrients useful to support the microalgae growth, nonetheless still has some bottlenecks that need to be considered. The main setbacks are the possibility of the presence of biotic or abiotic growth inhibitors and complicated harvesting processes. These issues will depend on the source of wastewater, and for this reason, they must be washed into consideration when choosing the waste for biotechnological use (Osundeko et al. 2019).

The biotic factors can be present in the form of viruses, fungi, bacteria, zooplankton, and predators. Once established, herbivorous consumers can reduce or inhibit the microalgae growth within just a few days. Besides, the contamination with fungi and viruses can negatively affect microalgal growth and induce changes in microalgal cell arrangement, diversity, and succession (Park et al. 2011). To overcome these biological barriers, the integrated pest management that involves the application of chemical herbicides and pesticides has been identified as a viable solution, on the other hand, it will result in an augmentation in the costs of the process, and with the prolonged use, the microbiota may acquire resistance to these substances (McBride et al. 2014). Other options with great potential for success include ecological engineering strategies of aquatic communities to promote beneficial interactions and genetic and metabolic engineering techniques to improve the resistance of the microalgae strains (Bagwell et al. 2016).

The abiotic contaminants that can be present in wastewater include heavy metals, nitrogen oxides, sulfur oxides, and ammonia, in which high concentrations can inhibit microalgae growth. Clijsters and Assche (1985) demonstrated that in the presence of several heavy metals, the chloroplast ultra-structure was disorganized. Besides this, these compounds can inhibit microalgae photosynthesis at physiological levels by blocking the prosthetic metal atoms in the active site of important enzymes (Arita et al. 2015). At the same time, when concentrations of essential nutrients in wastewater are low, they need to be supplemented so that there is no reduction in growth rates and lipid productivity (Osundeko et al. 2019).

6 Biodiesel Characteristics

The biodiesel properties depend on the fatty acid profile of the feedstocks used, which may vary from one another. Table 2 shows the fatty acid profile of distinct biodiesel feedstocks. The biodiesel from the different feedstocks must meet a specifications series. The biodiesel properties established by ASTM International (ASTM D6751), European Union (EN 14214), and Brazil (ANP 45) are shown in Table 3 (ASTM 2002; European Standard (EN) 2003; ANP 2014).

The biodiesel quality is influenced by the fatty acid profile, contaminants presence of the feedstock, production process, and storage. The properties of biodiesel related to fatty acid profile and contaminants inherent to the feedstock include the iodine value, viscosity, cloud point, cetane number, and phosphorus content. On the other hand, the properties of biodiesel directly related to the production process include free and total glycerin, carbon residue, ester content, methanol content, and flashpoint, while those related to storage include oxidative stability, acidity value, and content of water (Cavalheiro et al. 2020; Lobo et al. 2009).

As shown in Table 3, the biodiesel from microalgae biomass grown in agro-industrial wastewater has an ester content of about 99%, a cetane number of 55, an iodine value of $73.5\text{gl}^{2}100\text{g}^{-1}$, and a degree of unsaturation of 75% (Maroneze et al. 2014). Noteworthy, the microalgae appear to be the most realistic biodiesel feedstock, capable of replacing traditional fuels in way more environmentally friendly. These microorganisms can be capable of compensating and balance the growing demands for bioenergy (Maroneze et al. 2019).

Many countries of Europe and America have begun to assess the possible commercialization of biofuels from the microalgae biomass. Many microalgae are favorable to the production of biofuel due to the high content of lipids. The current unfeasibility of microalgae biodiesel is due to the elevated production cost (Khan et al. 2018). However, this cost can be reduced considerably with the use of industrial residues as a source of nutrients and water for cultivation (Jacob-Lopes and Franco 2013).

Table 2 Fatty acid profile in different biodiesel feedstocks

	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2n6	C18:3n6	C20:0	C20:1	C22:1
1st generation										
AlmondKernel	–	–	6.5	1.4	70.7	20	0,9	–	–	–
Soybean	–	–	6–10	2–5	20–30	50–60	5–11	–	–	–
Coconut	45–53	16–21	7–10	2–4	5–10	1–2.5	–	–	–	–
Mustard	–	–	–	1–2	8–23	10–24	8–18	–	5–13	20–50
Olive	–	–	9–10	2–3	72–85	10–12	0–1	–	–	–
2nd generation										
Cottonseed	–	–	22.9–28.3	0.8–0.9	13.27–18.3	–	0.2	–	–	–
Jatropla	–	14.1–15.3	0–13	–	34.3–45.8	14.1–15.3	0–0.3	–	–	–
Karanja	–	–	3.7–7.9	2.4–8.6	44.5–71.3	10.8–18.3	–	–	–	–
Linseed	–	–	4–2	2–4	24–40	35–40	25–60	–	–	–
Neem	–	–	13.6–16.2	–	49–62	–	–	–	–	–
3rd generation										
Chicken fat	–	3.1	19–82	3.1	37.6	–	–	–	–	–
Arthrospira platensis	–	7.50	25.0	7.7	34.7	12.5	8.2	–	–	–
Scenedesmus obliquus	–	–	34.0	2.6	5.7	1.7	0.4	–	–	–
Chlorella vulgaris	0.9	6.1	22.6	21.4	6.9	6.6	14.3	2.3	6.0	–

Adapted from Refs. (Severo et al. 2019; Maroneze et al. 2019; Singh et al. 2019)

Table 3 Properties of the biodiesel reasoned on EU (EN), USA (ASTM), and Brazilian (ANP) standards and biodiesel properties produced by microalgae

	ASTM D6751	EN 14214	ANP 45	Microalgae Sludge
Ester content	–	≤ 96.5%	≤ 96,5%	99%
Density	–	860–900 kg/m^3	850 a 900 kg/m^3	–
Viscosity	1.9–6 (mm^2/s)	3.5–5.0 (mm^2/s)	3.0–6.0 (mm^2/s)	–
Flash point	≥ 130 °C	≥ 101 °C	≥ 100 °C	–
Sulfur content	≤ 50 (mg/kg)	≤ 10 (mg/kg)	≤ 10 (mg/kg)	–
Carbon residue	≤ 0.05 (m/m %)	≤ 0.3 (m/m %)	–	–
Cetane number	≥ 47	≥ 51	–	55
Water content	≤ 0.05 (v/v %)	≤ 500 (mg/kg)	≤ 200 (mg/kg	–
Copper strip corrosion as degree of corrosion	3 h	–	–	–
Oxidation stability	≥ 3 h	≥ 4 h	≥ 6 h	–
Acid value	≤ 0.50 (mg KOH/g)	≤ 0.50 (mg KOH/g)	≤ 0.50 (mg KOH/g)	–
Iodine value	–	130 (gI$_2$100 g^{-1})	–	73.5 (gI$_2$ 100 g^{-1})
Methanol content	–	≤ 0.02 (m/m %)	≤ 0.02 (m/m %)	–
Monocylglycerols	–	− ≤ 0.80 (mole %)	≤ 0.70 (mole %)	–
Diacylglycerols	–	≤ 0.20 (mole %)	≤ 0.20 (mole %)	–
Triacylglycerols	–	≤ 0.20 (mole %)	≤ 0.20 (mole %)	–
Degree of unsaturation	–	–	–	75%
Free glycerin	≤ 0.20 (m/m %)	≤ 0.02 (mole %)	≤ 0.02 (mole %)	–
Total glycerin	≤ 0.25 (m/m %)	≤ 0.25 (m/m %)	≤ 0.25 (m/m %)	–
Pour point	−15–16 °C	–	–	–
Phosphorus	≤ 0.001 (m/m %)	≤ 4 (mg/kg)	≤ 10 (mg/kg)	–
Cloud point	−3–12 °C	–	–	–

Adapted from Refs. (Severo et al. 2019; Maroneze et al. 2014)

Besides, one of the advantages of utilizing microalgae is that they can grow from distinct routes, such as photoautotrophic, heterotrophic, and mixotrophic. Through these routes, different sources of organic and inorganic carbon are assimilated. It is worth mentioning that it is crucial to select the most suitable strain for oil production for biodiesel. Typically, microalgae have an oil content between 20% and 50% of dry weight but can reach 70% (Khan et al. 2018; Dias et al. 2019).

7 Economic Aspects of the Commercialization of Microalgae Biodiesel from Waste

The world is facing an energy crisis due to the progress of industrialization and the high exploitation and depletion of natural resources, such as fossil fuels. These represent about 88% of the total energy consumption (Amaro et al. 2012; Shah et al. 2018). Biofuels are a promising new source of energy; they are renewable and can be obtained through existing biological resources (Cho and Park 2018).

Microalgae-based biodiesel and its economic viability have received extensive academic exploration (Zhou et al. 2015; Beal et al. 2015). To be considered a viable substitute for fossil fuels, the production of microalgae biodiesel needs to have its high cost reduced, which may be possible through technological and management innovations. Microalgae stand out for growing without the need for considerable territorial space and end up not competing with other food crops for land use (Sun et al. 2019).

The economic viability of biodiesel production systems, combined with the use of effluents, unfortunately, is not widely discussed on a pilot and commercial scale. The vast majority of techno-economic studies focus on photobioreactor or open lagoon processes. However, to fully understand the performance of wastewater use, some factors must be considered, such as reducing waste treatment costs, selling other generated by-products, such as bio-oil, biogas, and biofertilizers (Xin et al. 2016).

According to the report by Grand View Research Inc., (2017), by 2025, the world market for biofuels for microalgae is expected to reach US$ 10.73 billion, with an 8.8% growth rate due to research by alternative sources of products to replace fossil fuels. Microalgae biodiesel has a 20 times higher yield than plant derivatives, serving as an environmentally friendly source of biofuels (Milano et al. 2016). Namely, three criteria are essential when evaluating a process for the biofuels industry: energetic, economical, and mainly environmental and sustainability (Delrue et al. 2012). According to Fig. 2, we can see the price of classic products manufactured through traditional refinements and biorefineries.

According to the monthly report of the International Energy Agency (IEA), the value of the oil barrel is around US$ 27–34, varying according to the exporting country (IEA 2020). Oil diesel and gasoline are fuels with higher demand and global production; relatively low prices are quoted by these, between US$ 0.85 and 0.75/L (Severo et al. 2019).

With the discoveries of oil exploration sources, natural gas, pre-salt, shale gas, there is a reduction in the availability of crude oil, an increase in prices, and expansion in search of substitutes (Onukwuli et al. 2017). With this, explorations in biorefineries appear, serving as a circular economy for biodiesel production through edible oils was produced. However, the cultures of edible vegetable oil, besides requiring large tracts of land, could cause an economic crisis in the food market due to rising prices; besides this, the production cost is up to three times higher than traditional diesel (Deprá et al. 2018).

According to Chen et al. (2018), the biodiesel cost based on microalgae production is from US$ 0.42 to 22.60/L. Based on a techno-economic study, Xin et al. (2016), evaluated that obtaining biofuel from microalgae produced with wastewater is considered favorable, making the cost of this bioproduct competitive with that of oil and more imminent to the commercial reality.

According to Ventura et al. (2013), the use of industrial wastewater in the microalgae cultivation reduces about 30% of the total operating cost, reducing the cost of nutrients for biomass production by US$ 550,000/year. To improve economic viability, higher biomass productivity and the lipid composition of microalgae must be explored for more considerable expansion in biodiesel production. Concerning capital investments for microalgae biodiesel, these are still high.

Still, the primary contrast between the commercialization of algae biodiesel and vegetable oil biodiesel is sustainability. For planting lipid-producing seeds are needed many hectares and large amounts of water for irrigation. On the other hand, the microalgae application in industrial waste has emerged as an attractive service scale. It results in low-cost production and lipid yield for the large-scale production of superior biodiesel, can be able to generate other bioproducts with high added value, making it more realistic—the biodiesel industrialization (Jacob-Lopes et al. 2019; El Shimi and Moustafa 2018).

8 Concluding Remarks

Microalgae are widely hailed as one of the most sustainable resources for biodiesel production. Nevertheless, the economic viability of the industrial production of microalgae biomass is still in shadows of doubt. In this sense, the use of industrial wastes is an option to upgrade the economic sustainability of the bioprocess, besides contributing to the

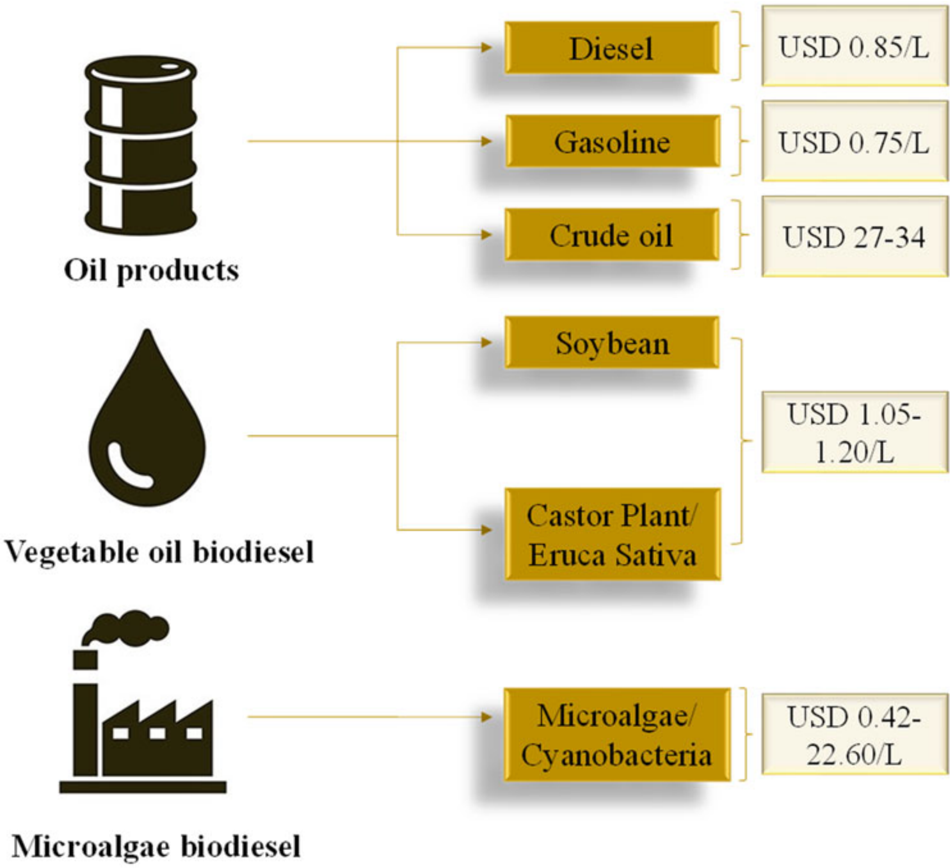

Fig. 2 Price of classic products manufactured through refinements and traditional biorefineries. Adapted from Refs. (Deprá et al. 2018; Severo et al. 2019; Chen et al. 2018; IEA. International Energy Agency. Oil market report 2020; Subhadra and Edwards 2011)

environmental management of wastes. Even so, we still are on the way to improve this futuristic idea and raise it to a commercial level, since there are still technical and economic bottlenecks to be solved. In order to consolidate the third-generation microalgae biofuel industry, in addition to the use of industrial waste, other strategies are also crucial to achieving this goal, including: (i) harness the full potential of biomass, through the use of a biorefinery approach; (ii) use of genetic and metabolic engineering to improve the microalgae strains resistance and the yields of the bioproducts of interest; and (iii) improve downstream processing techniques, aiming at integrated and more economical processes.

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Palm Oil Industry—Processes, By-Product Treatment and Value Addition

Rashid Shamsuddin, Gobind Singh, H. Y. Kok, M. Hakimi Rosli, N. A. Dawi Cahyono, Man Kee Lam, Jun Wei Lim, and Aaron Low

Abstract

The palm oil industry has continued to grow in Malaysia and worldwide. It provides job opportunities to at least 3 million people along its beneficiation chain and contributed RM37.7 billion to Malaysia's Gross Domestic Product (GDP) in 2018. At only 10% oil yield from a palm tree, this growth leads to an excess of palm oil by-products in Malaysia. From mill operations alone, palm oil mill effluent (POME) and empty fruit bunch (EFB) accounted for up to 80% (wet basis) of the total mill residues. Malaysia produces approximately 53 million cubic meters of POME annually and typical treatment processes using open ponds are inadequate to cope with this amount efficiently. Anaerobic digestion (AD) and aerobic composting (AC) are potential alternative treatment processes suitable for POME treatment while simultaneously producing value-added products such as biogas and compost fertilizer. To further promote sustainability, other by-products can be used as additives in AD and AC to improve the overall process by formulating the ideal feedstock material which helps to provide optimum conditions for the process. However, technical knowledge is required to sustain bacterial activity in both processes otherwise the fermentation processes are easily disrupted resulting in low methane yield and unhealthy compost. This chapter describes the palm oil industry overview from global and Malaysian perspectives. It outlines the processing approach in the mill, type of products and by-products generated in each processing stage and the treatment strategies used. Two commonly used treatment processes; AD and AC are described in detail with the potential of using co-digestion additives to improve the processes.

Keywords

Palm oil • By-products • Anaerobic digestion • Composting • Co-digestion • Value addition • Palm oil mill effluent • Empty fruit bunch • Oil palm frond • Oil palm trunk • Palm kernel shells • POME • EFB • OPF • OPT • PKS

1 Introduction to Palm Oil Industry

1.1 Introduction to Oil Palm

Elaeis guineensis Jacq. is in the family of *Palmae* and genus *Elaeis*, commonly known as oil palm. After planting, harvesting can occur after approximately 24–30 months. Each tree could produce about eight to fifteen fresh fruit bunches (FFB) annually, with each bunch containing approximately 2000 palm fruits about the size of a small plum. The yield varies according to the planting variety and its age (Henson 1992). The outermost part of palm fruit is the mesocarp, this surrounds the endocarp layer which consists of a hard kernel and shell (Fig. 1) (Harun et al. 2016). Depending on the species, the mesocarp layer and kernel nut can contain approximately 49% crude palm oil (CPO) and 50% palm kernel oil (PKO) (Basiron and Chan 2000).

The species of *Elaeis guineensis* are categorized by the fruit colour and characteristics. There are three fruit types: Dura, Pisifera and Tenera that can be differentiated based on shell thickness and mesocarp content (Fig. 2) (de Almeida Rios et al. 2018). Dura palms have endocarp thickness of

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Fig. 1 Cross-section of oil palm fruit Harun et al. (2016)

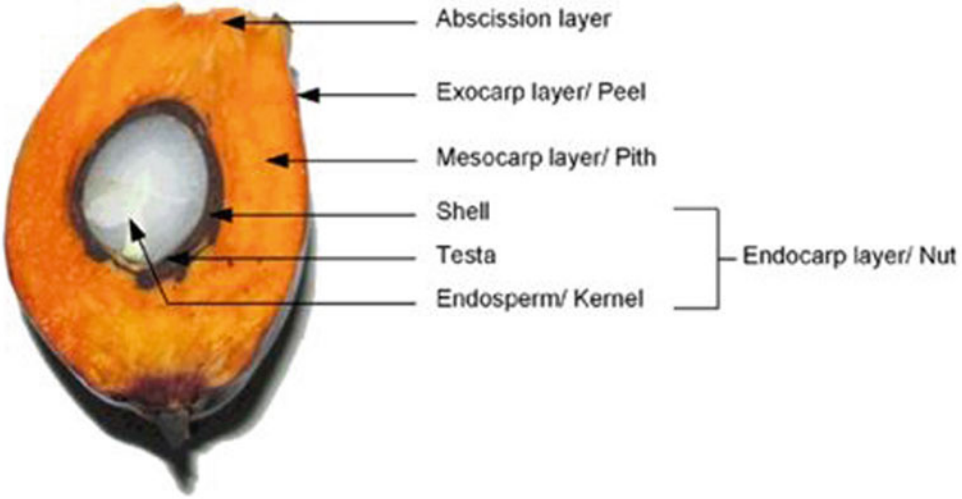
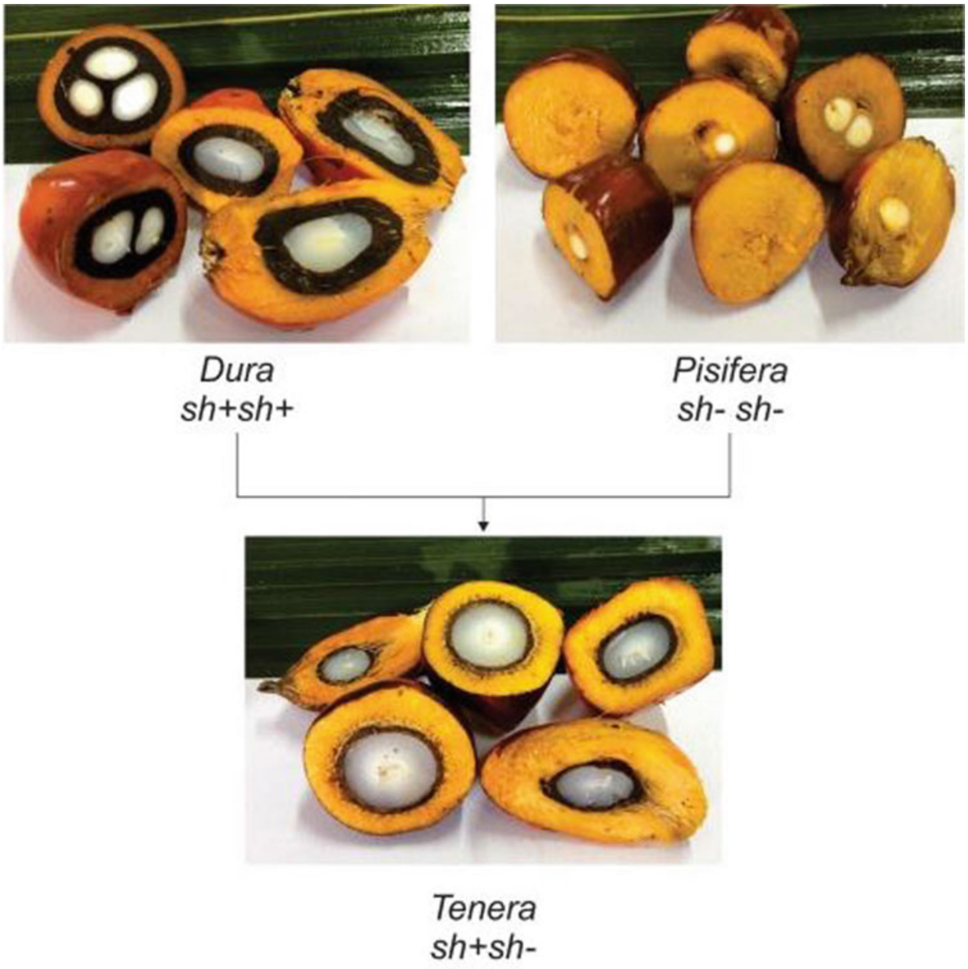


Fig. 2 Three different species of oil palm: Dure, Pisifera, Tenera (de Almeida Rios et al. 2018)



about 2–8 mm with a mesocarp content of 35–55%. The Pisifera palms do not have an endocarp layer but have around 95% mesocarp content. The Tenera palms, a hybrid variety of Dura and Psifera have an endocarp thickness of about 0.5–3 mm with high mesocarp content at around 60–95%. This hybrid species is widely cultivated in palm oil plantations due to its relatively short tree height and higher fruit and oil yield (Wening et al. 2012).

1.2 Oil Palm Industry Worldwide

Global consumption for oils and fats is projected to increase, particularly from China and India, which are the major consumers of oils and fats. Out of the 17 major oils and fats consumed in the world, 13 oils are from vegetable origin and 4 oils are from animal origin. The 13 common vegetable oils are palm oil, PKO, soybean oil, sunflower oil, coconut oil, olive oil, corn oil, groundnut oil, rapeseed oil, cottonseed oil, sesame oil, castor oil and linseed oil; whereas the four most consumed animal fats are butter, tallow, fish oil and lard. Figure 3 shows the major consumers of 17 vegetable oils and animals fats worldwide (Commodities et al. 2019). In 2019, China alone had consumed approximately 39.1 million tonnes (16.5%) of the world oils and fats production whereas the European Union (EU) and India consumed 35.6 and 25.4 million tonnes of oils and fats, respectively (World 2019).

Among all the oils, palm oil is the most produced oil. In the last decade, worldwide palm oil production has surpassed the production of other vegetable oils. Crude palm oil and PKO have accounted for 35.7% (83.4 million tonnes) of the world's oils and fats output, 48% higher compared to the production of soybean oil which is at 56.5 million tonnes of production globally in 2019 (World 2019). The six of the most produced vegetable oils in the global market throughout the years are shown in Fig. 4 (Commodities et al. 2019).

India, European Union (EU), China, Pakistan and Bangladesh imported more than half of the world's palm oil production (>27.4 million tonnes). The commodity imported to India had accounted for 18.6% (10.2 million tonnes) of the global output. The vegetable oil consumption of India is projected to continue to grow at 3.1% p.a., reaching a consumption rate of 15 kg per capita in 2028, hence further driving the demand (OECD 2019). Indonesia, Malaysia, Thailand, Colombia and Nigeria are currently the top 5 producers of palm oil. In the year 2019, approximately 75.6 million tonnes of palm oil were produced internationally. Whereas, 54 million tonnes of palm oil were exported globally. Figure 5 shows the top exporters of palm oil in the world (Commodities et al. 2019). As the two main producers and exporters of palm oil, production amount from Indonesia and Malaysia alone accounted for 83.6% (63.2 million tonnes) of the global output (World 2019). Being the second highest ranked producer and exporter, Malaysia produces 19.9 million tonnes of palm oil in 2019, which accounted for 26.3% of the global output. Of this, 18.5 million tonnes are exported or 34.2% of the international palm oil exports (World 2019; MPOB 2020).

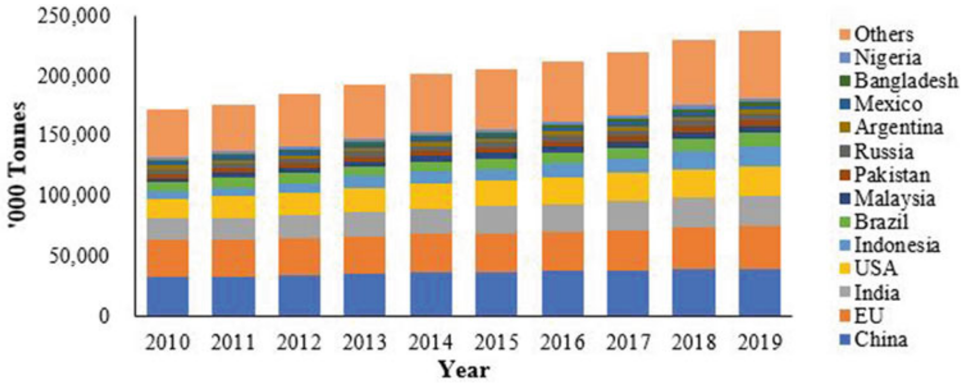


Fig. 3 Major oil consumers in the world (based on published data (Commodities et al. 2019)

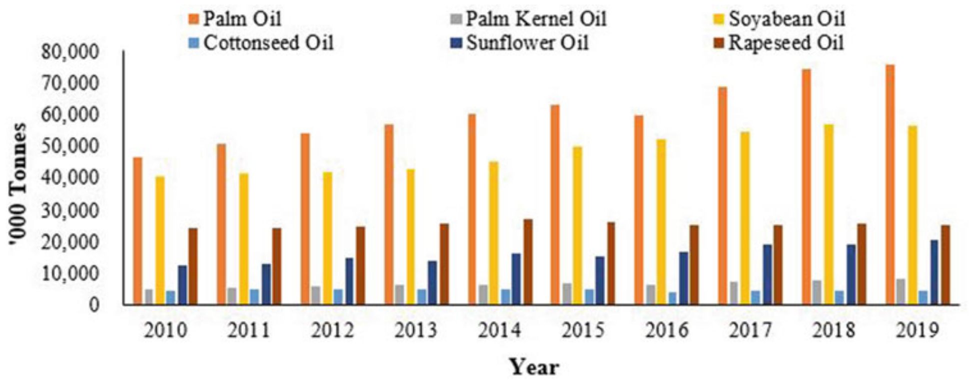


Fig. 4 Global supply of main vegetable oil (based on published data (Commodities et al. 2019))

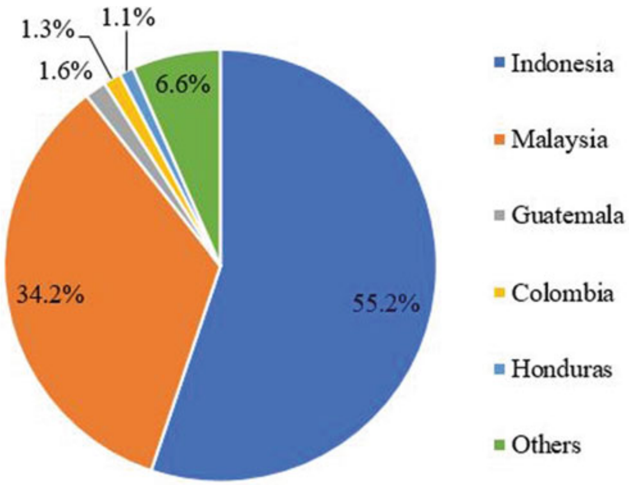


Fig. 5 Major exporters of palm oil (based on published data (Commodities et al. 2019))

1.3 Oil Palm Industry in Malaysia

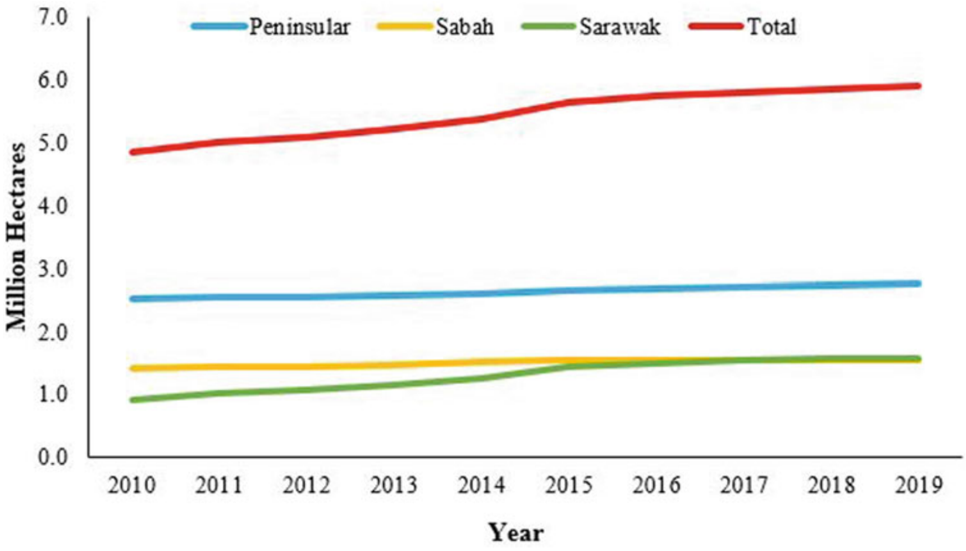
The first commercial palm oil estate was developed in Tennamaram Estate, Selangor in 1917, after a decrease in coffee and rubber commodity prices (Hai 2002). Then in the 1960s, oil palms were commercially developed on a large scale in response to the Government's diversification policy to reduce economic reliance on natural rubber, which in that period had seen reduced demand and price due to the production of synthetic rubber. Smallholders started to cultivate oil palm throughout the country and in 1989, oil palm became the nation's main economic crop (New Straits Times 2017).

The planted area of oil palm tree had increased exponentially throughout the years from only 55,000 ha in 1960 to 5.90 million hectares in 2019. This is expected to reach 6.5 million hectares by 2023 (Yusof 2019). For the past 10 years, the total palm oil plantation area in Malaysia increased by 21.6%, especially in Sarawak state, with an increment of 72.8% from 0.92 to 1.59 million hectares of the planted area (Fig. 6) (Commodities et al. 2019). Sarawak is currently the largest oil palm planting state in Malaysia, with 26.9% of the total oil palm planted area. Sabah and Peninsular Malaysia have a planting area of 1.54 million hectares (26.2%) and 2.77 million hectares (46.9%), respectively (MPOB 2019). Of all the oil palm planted area in Malaysia, 71.7% are under private ownership (mainly by plantation companies), 16.7% belonged to individual smallholders, while the remaining 11.6% were under Government land schemes, such as Federal Land Development Authority (FELDA), Federal Land Consolidation and Rehabilitation Authority (FELCRA) and others (MPOB 2019).

The FFB yield increased in tandem with the expansion of cultivated land. The overall yield of FFB in Malaysia increased by 0.2% from 17.16 tonnes per hectare in 2018 to 17.19 tonnes per hectare in 2019. A higher FFB quantity results in a higher oil extraction rate (OER). The OER performance improved by 1.3% to 20.21 per cent compared to the previous year. Due to a higher FFB yield and OER, the production of CPO increased by 1.8%, from 19.52 million tonnes to 19.86 million tonnes (MPOB 2020).

The agricultural sector contributed RM99.5 billion (7.3%) to the Gross Domestic Product (GDP) in 2018, in which oil palm, Malaysia's fifth major export commodity contributed 37.9% to the national agriculture income. The nation's total export of palm oil and palm oil derivatives of 27.9 million tonnes generated RM64.8 billion in export revenue. Palm oil was responsible for 66.25% of the palm products exported in 2019 (DOSM 2019). Figure 7 shows the breakdown of the export products (Commodities et al. 2019).

Fig. 6 Oil palm-planted area in Malaysia: 2010–2019 (based on published data (Commodities et al. 2019))



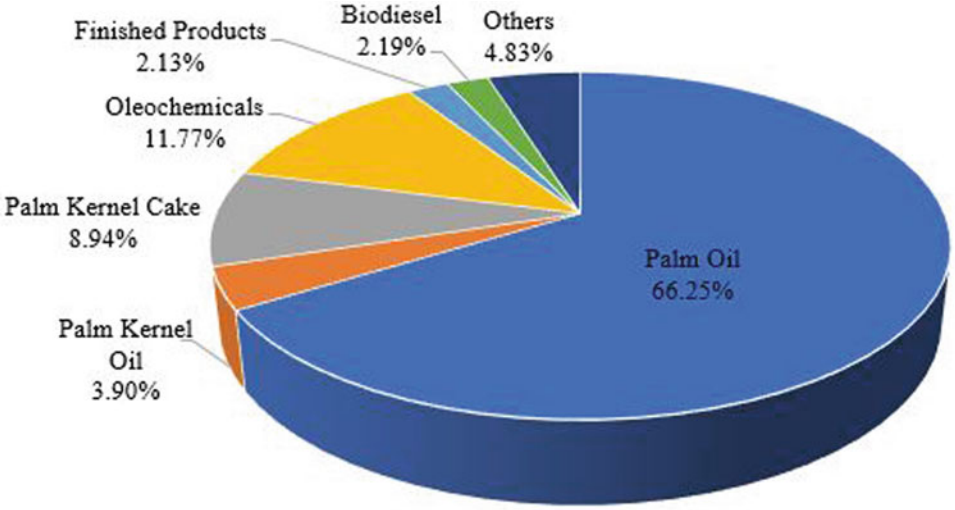


Fig. 7 Breakdowm of oil palm products exported in 2019 (based on published data (Commodities et al. 2019))

Malaysia exported about 18.5 million tonnes of palm oil with an approximate value of RM38 billion in 2019, 12% higher than in 2018 (Commodities et al. 2019). The volume of palm oil exported increased due to higher demands, especially from various import countries such as India, China, EU, Vietnam and Turkey (MPOB 2020). Besides its direct economic contribution, the industry contributes significantly to the social agenda by providing jobs to more than 3 million people along its business chain with more than half a million smallholders (Yamei 2019).

1.4 Malaysia Current Challenges

Malaysia has enjoyed stable demand and production of palm oil and their derivative products for decades until recently where the export value has begun to decrease. This is due to the oversupply of the commodities worldwide since Indonesia has taken the lead as the biggest producer in the industry (Kushairi et al. 2019). To stay competitive in the global market, Malaysia must increase palm oil production as well as diversify its products. However, due to the small geographical area in Malaysia, the availability of arable land for cultivation is the limiting factor for this industry (Nambiappan 2018). In the past, Malaysia increased the oil palm planted area by expanding onto degraded land or secondary forest or land that was used to cultivate other crops. As suitable land banks for oil palm cultivation were limited, the industry cannot depend on expanding plantation acreage to increase production in the long term (May 2012).

Another factor affecting the production of palm oil is the shortage of suitable labour. The oil palm industry is dependent on manual labour for up-keeping the condition of plantations such as fertilizing, weeding and pruning activities. Most workers are particularly needed for the harvest and collection of FFB, lack of labour for these work activities can result in loss of income as FFB is directly tied to the production of CPO (Ismail 2013). In pursuit of reducing labour dependency, the government introduced the Transformasi Nasional 50 (TN50) programme to boost the implementation of mechanization in order to increase productivity (Kushairi et al. 2019). For this purpose, the government has provided incentives to farmers through the Oil Palm Mechanization Incentive Scheme to encourage the adoption of mechanization, in which owners are given a discount for machine purchases (Nambiappan 2018).

Besides the challenge of oversupply, the industry is also facing lower demand from the EU. EU Parliament made a statement on 10 June 2019, announcing the passing of Delegated Act, planning to phase out and eventually ban the import of palm oil biofuel by 2030 (Tee Ching 2019; Yoga 2019). The Delegated Act is regulated to ensure that feedstock for biofuels does not contribute to deforestation and ensuring the sustainability of the transport fuels. The decision was made purportedly to stop deforestation of rainforest and declining of biodiversity, classifying CPO as an unsustainable product. However, the International Union for the Conservation of Nature reported that banning of palm oil will lead to increasing demand for other oils, warning that other land-intensive crops such as soy, sunflower and rapeseed would require up to nine times as much land to produce similar quantities of oil; therefore, resulting in a greater impact on global diversity (Meijaard 2018).

On the other hand, EU had neglected the effort taken by the Malaysian government since 2015 to mandate the implementation of the Malaysian Sustainable Palm Oil (MSPO) certification across all mills, plantation and smallholders by 31 December 2019 (Kushairi et al. 2019; Rosner 2018). In addition, a certified plantation by the Roundtable on Sustainable Palm Oil (RSPO) scheme cannot clear primary forest and land that have rich biodiversity (Rosner 2018). Currently, 1,341,748 ha of palm oil farms are MSPO-certified and

950,588 ha of palm oil farms are RSPO-certified (NEPCon 2018). The much stricter environmental policies implemented by major importers and pressure exerted by NGOs affected the prospect of oil palm industry, hence the growth of palm oil output must increasingly focus on productivity improvements such as FFB and CPO yield improvements, as well as speed up replanting activities.

2 Palm Oil Mill Processes and Waste Treatments

2.1 Palm Oil Production Process

Two common methods to extract CPO by the mills are either using a dry or wet process. The most common method used is the wet process which involves a large amount of water and steam in the process to remove dirt and to sterilize the fruit bunch in different steps, thus generating a high volume of effluent termed as palm oil mill effluent (POME). It poses a substantial threat to water pollution if released directly into the water bodies without treatment. Figure 8 illustrates the typical extraction process of palm oil followed by the description of each stage (Hashim et al. 2012).

2.1.1 Sterilizing Fresh Fruit Bunch (FFB)

The first stage of crude palm oil extraction is the sterilization or steaming process (Hashim et al. 2012). The fresh fruit bunches are exposed to high-temperature pressurized steam at 140 °C for 75–90 min to deactivate the natural hydrolytic enzymes which breakdown oil to free fatty acids. Exposure at high temperature helps for easier detachment of fruits from bunches in the subsequent process of stripping and threshing (Liew et al. 2015; Rupani et al. 2010). The sterilization process stage is crucial to maximize fruit recovery (Junaidah et al. 2015). The high volume of steam condensate from sterilization is one of the main contributors to the mill effluent.

2.1.2 Stripping or Threshing

The sterilized FFB are transported to the thresher platform using a scraper conveyor. Fruits are lifted and dropped constantly in a rotary drum stripper to strip off and separate the oil fruits or pulps from the bunches. A bucket conveyor is used to collect the detached pulps and to transfer into a digester (Iskandar et al. 2018; Ahmed et al. 2015). The remaining empty fruit bunches (EFB) are discarded as a solid waste (Rupani et al. 2010).

2.1.3 Digestion and Pressing for Crude Palm Oil (CPO) Extraction

Digestion is a process of palm oil extraction by breaking down the fruits via steam-heating in a vertical cylindrical digester. Fruits are softened at 80–90 °C using a steam jacket or by direct live steam injection (Ahmed et al. 2015). Under high temperature and pressure, the oil-bearing cell of the fruits will break to release the oil and a screw press machine is used to enhance the extraction process. Hot water is added during this process to enhance the oil mixture product known as crude palm oil. Once CPO is extracted, fine solids and water are removed using a vibrating screen, hydro cyclone and decanters (Rupani et al. 2010).

2.1.4 Clarification and Purification of Crude Palm Oil

Extracted CPO slurries contain a mixture of 35–45% oil, 45–55% water and small portions of fibrous materials (Rupani et al. 2010; Iskandar et al. 2018; Ahmed et al. 2015). The oil–water mixture is further processed in a clarification tank to collect oil by constantly skimming-off oil at the top of the tank using a rotary strainer. The temperature of the tank is maintained at 90 °C to keep the oil viscosity low for easier separation. The bottom phase liquid in the tank is passed through a centrifugal separator to separate CPO and oil sludge. The recovered oil is returned to the clarifier and the sludge is sent to a treatment facility for disposal. The CPO is further refined using a centrifuge and vacuum dryer to remove more solid residues prior to transferring into a storage tank (Ahmed et al. 2015). The oil sludge produced during these clarification processes contributes to the overall wastewater of this industry or also known as palm oil mill effluent (Iskandar et al. 2018).

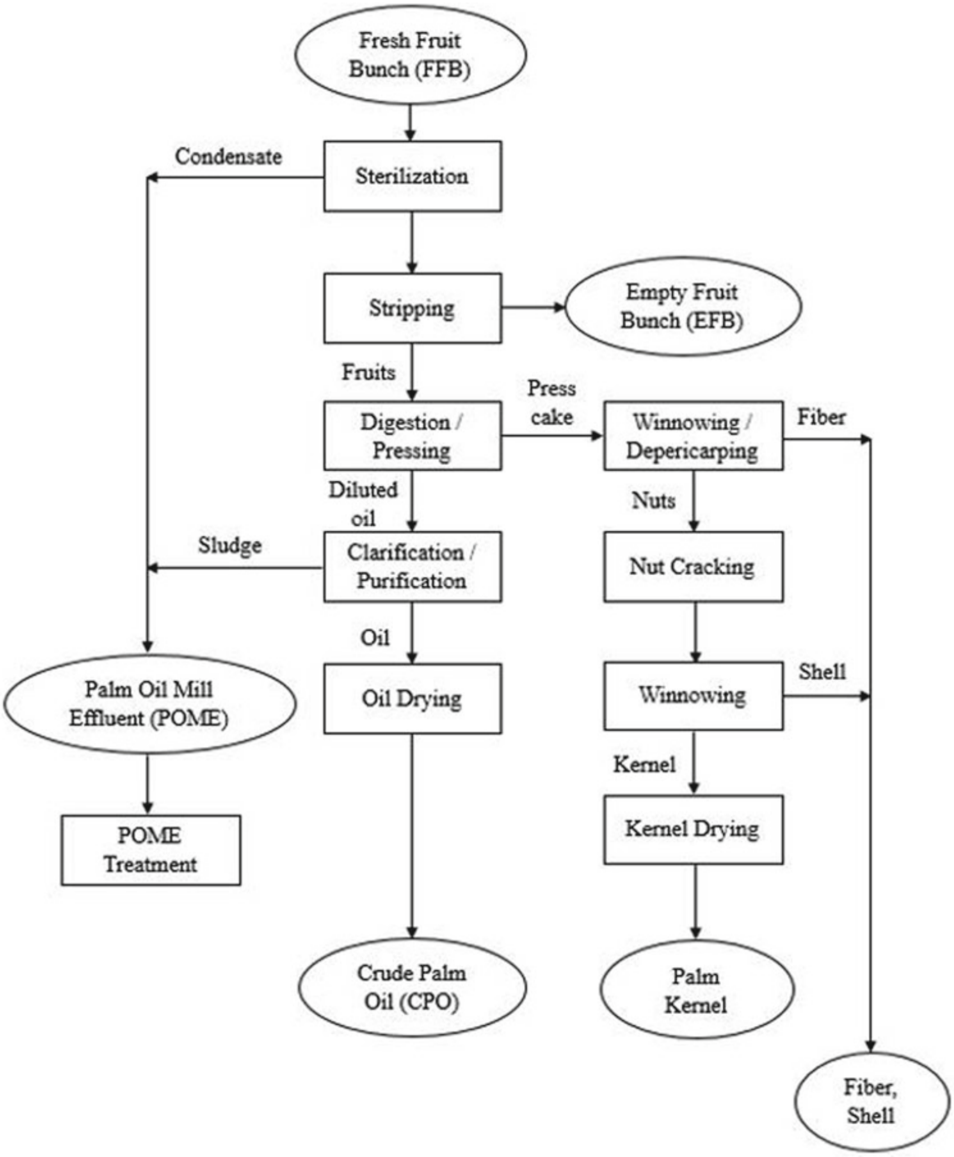
2.1.5 Depericarping and Nut Fibre Separation

During the screw pressing process, the crude oils are extracted from the fruit, forming the leftover press cake which consists of moisture, nut and oily fibre. The pressed cakes are sent to a depericarper to separate the fibre to be used as fuel at the boiler house (Ahmed et al. 2015).

2.1.6 Separation of Kernels and Drying

The remaining nut will undergo winnowing and a hydro cyclone process to separate palm kernel from its shell. The liquid component or wastewater from the hydro cyclone is discharged, while the palm kernel will undergo a drying process in silos (Iskandar et al. 2018; Ahmed et al. 2015).

Fig. 8 Simplified palm oil extraction process (Hashim et al. 2012)



2.2 Palm Oil Mill Effluent (POME)

In the CPO extraction process, approximately 5–7.5 tonnes of water are needed to produce 1 tonne of CPO with more than 50% of the processing water could finally become POME. In addition, 0.5–0.75 tonnes of POME are produced for every tonne of FFB processed (Yacob et al. 2005). Simple mass balance in a processing mill suggests that 36% and 60% of POME is contributed by the sterilization of FFB and clarification of extracted CPO, respectively (Sethupathi 2004). According to Lorestani (Lorestani 2006), Malaysian palm oil industry generates about 53 million cubic meters of POME annually.

POME contains 95–96% water, 0.6–0.7% oil and 4–5% total solids (of which 2–4% are suspended solids). Freshly produced POME has a pH value of 4–5, chemical oxygen demand of 51,000 mg/L, biological oxygen demand of 25,000 mg/L, suspended solids of 18,000 mg/L, oil and grease of 4000 mg/L and nitrogen content of 750 mg/L (Iskandar et al. 2018). POME is a chemical-free effluent and is considered non-toxic. It is often treated in aeration ponds which is a very slow process, contributing to environmental problems such as leaching of contaminants into groundwater or soil and methane gas released into the atmosphere. In addition, the naturally present microorganisms in POME will compete for oxygen uptake with aquatic species, resulting in the depletion of dissolved oxygen and slowly inhibit their growth, eventually causing the death of the aquatic species over time (Iskandar et al. 2018).

The Malaysian government has enforced well-designed regulatory standards and policies specifically for palm oil mill discharges to control the industrial pollution effectively.

Table 1 General characteristics of raw POME and allowable discharge standards of POME into water sources in Malaysia

Parameter	General characteristics of raw POME (Iskandar et al. 2018; Ahmed et al. 2015)	Limit of POME final discharge (Rupani et al. 2010; Iskandar et al. 2018; Wu et al. 2010)
Temperature (°C)	80–90	45
pH	3.4–5.2	5.0–9.0
Oil and grease (mg/L)	130–18000	50
Biological oxygen demand (BOD) (mg/L)	10250–43750	100
Chemical oxygen demand (COD) (mg/L)	15000–100000	–
Total solid (mg/L)	11500–79000	–
Suspended solid (mg/L)	5000–54000	400
Total nitrogen (mg/L)	180–1400	200[a]
Ammoniacal nitrogen (mg/L)	4–80	150[a]

[a]Value of filtered sample

Before the introduction of the regulation in 1977, the CPO processing industry was the biggest contributor to water pollution in the country without any control (Ahmed et al. 2015). The regulations that help to control the effluent discharged from the palm oil industry are stated in the Environmental Quality Regulations 1977 (Prescribed Premises—Crude Palm Oil) under Section 51 of the Environmental Quality Act (EQA) 1974, the principal governing regulation for discharge standards of industrial effluent (Rupani et al. 2010; Ahmed et al. 2015). The general characteristics of raw POME and its allowable discharge limits into water bodies are summarized in Table 1.

From a waste-to-wealth perspective, POME can be a potential raw material to produce value-added products via biological processes. An efficient treatment system and effective disposal techniques are required to convert POME into useful materials that are environment-friendly such as biogas and compost. This is important to balance between the economic viability of mill operation and environmental protection for sustainable development of palm oil industry.

2.3 Solid Wastes

2.3.1 Empty Fruit Bunch (EFB)

Empty fruit bunches are fibrous materials that are typically considered as solid biological waste. Together with palm kernel shell (PKS) and mesocarp fibre (MF), they account for 25% residual solid wastes from palm oil mills. Empty fruit bunches alone contribute to approximately 12.4 million tonnes (fresh weight) solid wastes yearly (Awalludin et al. 2015). Normally, the EFB will be returned to the plantations for direct land application as mulch to help control weed growth and maintain the soil moisture. However, this practice could contribute to oil spills and soil contamination if the oil was not recovered properly at the mill. Its cellulose content accounts for 45–50% of EFB total weight which is a good substrate for microbial growth (Embrandiri 2015). Due to the steam sterilization process, EFB can contain as high as 67% moisture making it unsuitable as boiler fuel. It may be free from foreign objects such as gravel and wood residues depending on the handling process at the mill (Zafar 2019).

2.3.2 Oil Palm Frond (OPF)

Omar et al. (2018) suggested that OPF is the most abundant waste generated from the oil palm mills that contributes to 50.3% of the total residues (solid and liquid) at over 83 million tonnes (wet weight) annually (Zahari et al. 2012). Oil palm frond is an underutilized biomass and often left to rot in between palm trees for nutrient recycling into the soil. Potential uses of OPF include material for mulch, paper pulp and animal feed (Fadzilah et al. 2017).

Four major components of OPF are petiole, stem, rachis and leaflet. The petiole alone accounts for half of the OPF weight. The physicochemical properties of each component vary, for example, the C/N ratio of the leaflet, rachis, stems and petiole is 25:1, 56:1, 90:1 and 77:1, respectively (Roslan et al. 2014). The leaflet has high nitrogen content from the high amount of hemicellulose and lignin which give the lowest C/N ratio. Its high nitrogen content makes it suitable to be used as a natural fertilizer and soil conditioner via decomposition by microbial activities. On the other hand, the high content of starch and cellulose in petiole is suitable for press juicing. A study done by Zahari et al. (2012) reported that OPF has a low metal content with high carbohydrates in simple sugars form. The OPF sap or juice can be extracted by using a conventional sugarcane press machine and centrifuged at 15,000 g for 15 min at 4 °C

(Zahari et al. 2012). The juice is then used as fermentation feedstock to produce bioethanol, succinic acid, lactic acid and bioplastic.

A study done by Wanrosli et al. (2007) found that OPF shows an excellent strength property that is comparable to hardwoods after the chemical pulping process. It has potential as reinforcement pulp in newsprint production using softwood thermo-mechanical fibres (Wanrosli et al. 2007).

2.3.3 Oil Palm Trunk (OPT)

Oil palm trunk and fronds obtained from oil palm growing on plantations are abundantly available during the replanting period which is approximately in every 25 years. It is a non-wood monocotyledonous species that consist of vascular bundles and parenchyma cells rich in fibres, tracheid, vessels parenchyma and ray parenchyma cells which are different from hardwoods and softwoods (Sulaiman et al. 2012). It contains the highest amount of starch and total sugar (generally cellulose and hemicellulose) with the concentration varied depending on the position along the trunk (Ramle 2015). According to Yamada et al. (2010), OPT contains a large quantity of sap that is almost 70% from the whole trunk weight, where the total sugar content in the sap after storage of 30 days is comparable to sugar cane juice. The glucose, sucrose, fructose and galactose content are able to be fermented by industrial bacterial activities making OPT a potential precursor material for bioethanol production (Yamada et al. 2010).

In addition, OPT has a high mechanical strength that is exploited for the production of binderless particleboard, laminated board, plywood, fibreboard and furniture. Compared to the old trunk, the young trunk has greater mechanical and physical properties which contribute to a higher quality final product (Sekaran 2019).

2.3.4 Palm Kernel Shells (PKS)

Palm kernel shells are the remaining shell portions after the kernel nut is extracted following the crushing process in the oil mill (Hashim et al. 2012). Its fibrous nature makes it easy to handle in large quantity from the production line to the end-user. The moisture content in PKS is between 11 and 13% which is low compared to other palm oil biomass residues. It contains residues of palm oil that contributes to a higher heating value compared to average lignocellulosic biomass. An experimental study by Uche Paul, John (Uche Paul 2015) discovered that the PKS has a calorific value of 23,605 kJ/kg, while the palm fibre and EFB has a value of 14,512 kJ/kg and 17,855 kJ/kg, respectively. Therefore, PKS has potential as a good solid fuel material that will combust more effectively as well as being sustainable (Uche Paul 2015). In addition, PKS produced from mill operation is generally uniform in size that makes handling easy and it has low biological activity due to its low moisture content (Ikumapayi et al. 2019). The PKS has been characterized for its excellent bioenergy generation as biochar, bio-oil and biogas production (Ikumapayi et al. 2019). A study by Oti et al. (2015) stated that PKS is a potential partial substitute for cement and lightweight aggregate as crushed PKS is hard and able to physically bond with the hydrated cement paste. Table 2 summarizes the potential usage of solid wastes from oil palm.

2.4 Current Oil Palm Waste Management

2.4.1 Ponding System

A common method for treating POME is the open ponding system that uses mostly biological treatment methods such as acidification, anaerobic, facultative and aerobic degradation (Loh et al. 2013). Syahin et al. (2020) summarized the advantages and limitations of various ponding systems for POME treatment. The ponding system is considered a simple technology with low operating cost and low maintenance. However, a huge land area and long HRT are required. In addition, the final discharge still has a high residual COD and BOD, implying an inefficient treatment system (Zhang et al. 2008).

2.4.2 Solid Fuels and Mulching

Palm pressed fibre and shell produced by the oil mills are normally used as burning materials or solid fuels for steam boilers. The calorific value of dried fibres is about 5 MJ/kg (Embrandiri 2015). Boiler operation is needed to generate steam to operate turbines for electricity generation. Energy generated from these two solid fuels is more than sufficient to power up the palm oil mill (Zafar 2019). In contrast to shells and fibres, EFB is usually returned to the plantations as mulch to control weed growth, prevent erosion and maintain soil moisture. Application of EFB as a solid fuel is limited due to its high moisture content of up to 70%.

2.5 Alternative Green Technology

2.5.1 Anaerobic Digestion (AD) System

Anaerobic digestion can be defined as an engineered methanogenic decomposition of organic matter by various species of anaerobic microorganisms in the absence of oxygen (Nour et al. 2013). Most palm oil mills in Malaysia employ an AD process as the primary treatment of POME due to its high concentration of organic content (Nour et al. 2013). During the AD process, organic content in POME is converted into methane, carbon dioxide and water through a series of processes. Since no aeration is required, low energy is consumed during the AD process. Furthermore, the methane gas produced is valuable as an alternative energy

Table 2 Summary of potential uses of oil palm wastes

Oil palm waste	Uses	References
POME	• Fermentation media for antibiotics and bioinsecticides production	Wu et al. (2010), Madaki and Seng (2013)
	• Organic fertilizer through composting with EFB or on its own	Hashim et al. (2012), Madaki and Seng (2013)
	• Biogas generation for alternative energy supply by the anaerobic digestion process	Hashim et al. (2012), Madaki and Seng (2013)
	• Live food for animals and aquaculture organisms	Madaki and Seng (2013)
PKS	• Fuel or for conversion into other carbon products	Hashim et al. (2012), Embrandiri (2015), Ikumapayi et al. (2019)
	• Activated carbon for water purification	Ikumapayi et al. (2019)
	• Replacement for cement and aggregate for concrete production	Ikumapayi et al. (2019), Oti et al. (2015)
EFB	• Mulch for soil moisture retention	Embrandiri (2015)
	• Organic fertilizer through composting process	Hashim et al. (2012), Embrandiri (2015)
	• Fuel for additional energy and steam generation	Embrandiri (2015)
	• Biofuels production	Hashim et al. (2012)
	• Dried fibre for various industrial applications	Hashim et al. (2012)
OPF	• Bio-oil production by pyrolysis	Omar et al. (2018)
	• Mulch for nutrient recycling	Zahari et al. (2012), Fadzilah et al. (2017), Roslan et al. (2014)
	• Pressed juice for production of bioethanol, biobutanol, lactic acid and bioplastics	Zahari et al. (2012), Fadzilah et al. (2017), Roslan et al. (2014)
	• Biofertilizer by bacterial composting	Fadzilah et al. (2017)
	• Pulp and paper production by chemical pulping	Wanrosli et al. (2007)
	• Fuel pallet as an alternative energy source	Trangkaprasith and Chavalparit (2011)
OPT	• Bioethanol production	Yamada et al. (2010)
	• Binder less particleboard production, plywood	Sekaran (2019), Abdullah and Sulaiman (2013), Dungani et al. (2013), Rosli et al. (2016)
	• Compressed wood for furniture	Sulaiman et al. (2012), Yamada et al. (2010)

source and can be utilized in the mill, while the by-product sludge generated could be used for land applications.

However, an AD process requires a long start-up period and retention time for the bacteria in each AD process to adjust to the new environment before they are able to use the organic matters for growth. Another disadvantage of AD is that the digesters require large land space to ensure complete digestion of organic influent. These problems can be solved by utilizing granulated seed sludge and high-rate anaerobic bioreactors to shorten the start-up period and retention time and to maintain a conducive pH and temperature conditions in the reactor for bacterial growth (Poh and Chong 2014).

2.5.2 Composting Technology

Composting technology involves a microbial activity in which the organic wastes are being stabilized under controlled pH, temperature and humidity. Aerobic microorganisms decompose the biodegradable organic materials to produce a stabilized end product known as compost which is rich in humic acid-like substances (Rupani et al. 2010). Rapid activation of microbes around the root system consumes high amount of oxygen, resulting in partial organic decomposition and unstable final compost (Rupani et al. 2010). Hence, it is crucial to increase the treatment period to improve the quality of the compost. Co-composting is one of the methods to alter the organic content to achieve an optimum C/N ratio of 30. For example, sawdust was added in a composting pile of palm oil mill sludge (POMS) (Embrandiri 2015) and EFB-POME mixtures (Hau 2020) to adjust the carbon content, to prevent air pollution and to increase composting process efficiency. Composting is an ideal process for palm oil by-products due to its simplicity, treatment effectiveness and ability to produce value-added products (Rupani et al. 2010).

3 Anaerobic Digestion of Palm Oil Mill Waste by-Products

3.1 Biological Process

Anaerobic digestion is a well-studied and simple technology that is widely used as a treatment process for biodegradable organic materials. Anaerobic digestion is a series of biological processes (Fig. 9) that involves different groups of bacteria to break down biodegradable materials in the absence of oxygen to produce biogas (containing methane), carbon dioxide and digestate (solid remain) as the end-products. This process is divided into four steps which are hydrolysis, acidogenesis, acetogenesis and finally methanogenesis where a different group of bacteria is responsible for each step (Kumar and Samadder 2020).

3.1.1 Hydrolysis

In hydrolysis process, insoluble organic matters such as cellulose, proteins, lipids and polysaccharides are decomposed into soluble molecules such as fatty acids and amino acids by a group of hydrolase enzymes such as lipases, proteases and amylases produced by the hydrolysing bacteria *Streptococcus* and *Enterobacterium* (Zemiński and Frąc 2012). Cellulose and cellucottons are polymers that are barely degraded during the hydrolysis process which limits the rate of digestion. This hydrolytic activity is considered as the rate-limiting step in anaerobic digestion of organic solids (Monnet 2003). The lack of diverse enzymes participating during the process causes only 50% degradation of organic compounds, while the rest remains in their initial stage (Ziemiński and Frąc 2012). Size of substrate particles, number of enzymes and slurry pH are among the factors affecting the rate of the hydrolysis process. Hydrolysis is optimum at a pH range of 5–7 and temperature of 30–50 °C (Meegoda 2018).

3.1.2 Acidogenesis

Acidogenesis is the next step of AD where the acidogenic bacteria produces hydrogen, carbon dioxide, acetates and volatile fatty acids (VFAs) from the initial hydrolysis process through the cell membranes. The concentration of hydrogens that are produced from this stage will affect the final products produced during the digestion process. The VFAs composed of organic acids such as propionate, butyrate and acetic acid. However, these products cannot be used directly by methanogenic bacteria in the methanogenesis stage (Khan et al. 2016) and it must be converted first into hydrogen in the process called acetogenesis by obligatory anaerobes (Ziemiński and Frąc 2012). Unlike hydrogens, carbon dioxide and acetates formed can be directly used as substrates and energy source by the methanogens (Ziemiński

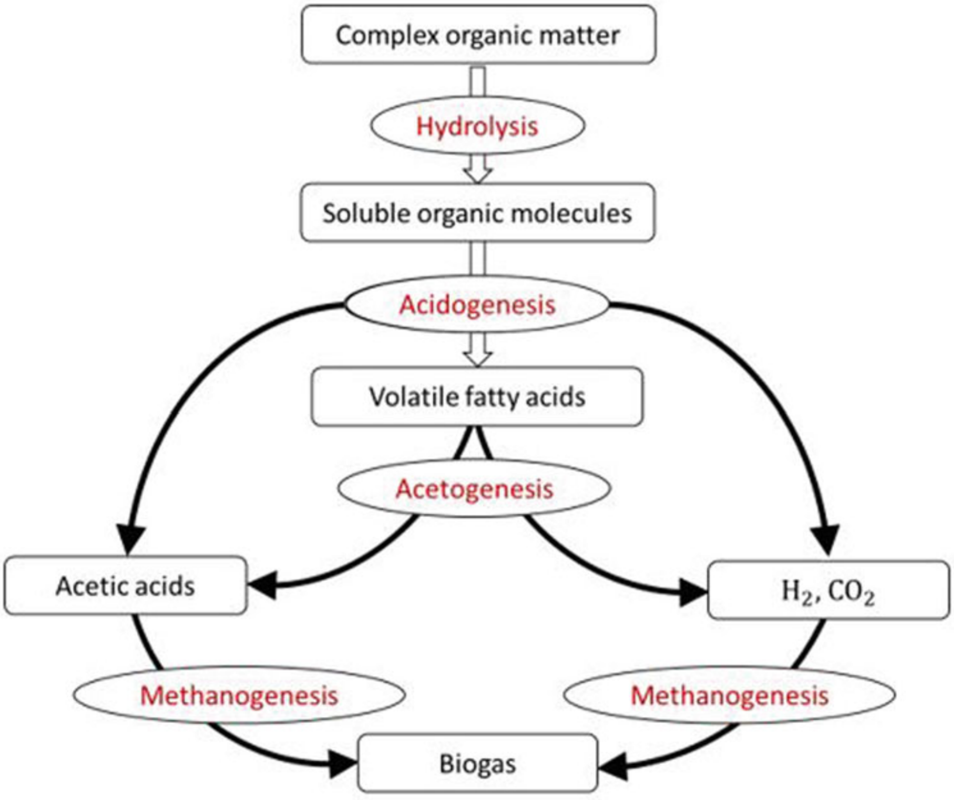


Fig. 9 Anaerobic digestion process (Kumar and Samadder 2020)

and Frąc 2012). The concentration of VFAs may differ according to the conditions and design of the digester. The produced VFAs during this phase will reduce slurry pH. The bacteria involved in this stage are less sensitive, which require a pH of 5 and above compared to methanogens (Kumaran et al. 2016).

3.1.3 Acetogenesis

During the acetogenesis stage, VFAs and alcohols are converted into hydrogen, carbon dioxide and acetate. Long chain VFAs of more than four carbon chains could not be used directly by methanogens. The long chains must be first converted into acetate prior to being converted into methane. In this stage, acetate will be accumulated into a higher concentration and will affect the pH value (Wang et al. 1999).

3.1.4 Methanogenesis

Methanogenesis is the most crucial phase in the entire AD process where methane is produced by the methanogenic bacteria. Up to 70% of methane formed originated from acetate while the remaining 30% is produced from the conversion of hydrogen and carbon dioxide. This stage has the slowest biochemical reaction among the four stages of anaerobic digestion. Limitation of methane production may occur if there is a large entry of oxygen, temperature change, pH change (optimum pH is between 6.5 and 7.2) or overloading of digesters as the methanogens are very sensitive towards the environmental conditions (Kumaran et al. 2016).

3.2 Parameters Affecting Anaerobic Digestion

Factors which affect the anaerobic digestion of palm oil by-products are listed in Table 3, while Table 4 summarizes selected operational conditions on various anaerobic digestion processes of palm oil by-products. The tables summarize key information of the process such as the types of feedstock materials, reactor used, application of inoculum, operating OLR, HRT and their findings. To conclude, the anaerobic digestion process depends on various feedstock parameters such as the pH and C/N ratio, as well as on the processing conditions of temperature, OLR, HRT and mixing. Wide range of research done as shown in Table 4 prove that anaerobic digestion is a suitable process for palm oil by-products to treat the wastes prior to disposal while simultaneously generating value-added products.

3.3 Anaerobic Co-digestion of Palm Oil Mill Waste Derivative

Lately, the co-digestion method is preferred for treating a mixture of solid and liquid waste simultaneously which can increase the efficiency of the overall process by enhancing the stability of the process and stabilizing the macro and micronutrient content to sustain microbial growth. Co-digestion of substrates can give synergistic or antagonistic effects (Labatut et al. 2011). A synergistic effect can be defined as having cumulative advantage from various organic matters in the feedstock formulation, for example, co-digestion of POME with DC can increase the biogas and methane production compared to mono digestion of POME alone (Tepsour et al. 2019). In contrast, an antagonistic effect is a counter-productive effect that can come from pH inhibition, toxicity, highly acidic environment and others when two or more incompatible materials are mixed together (Labatut et al. 2011).

Table 4 highlights various studies of palm oil by-products co-digestion for biogas production. A synergistic effect of co-digestion can be seen in many feedstock combinations, for example; EFB and DC (Tepsour et al. 2019), EFB and POME (Kim et al. 2013) and EFB and POME with chemical and biological sewage sludge (Suksong et al. 2017). However, the author reported an antagonistic effect at sewage sludge contents between 6 and 42% in EFB and POME co-digestion system (Suksong et al. 2017). The positive effect may be due to the balance of chemical composition or an increase in microbial activity, while too much of one component will result in methane reduction. Another successful co-digestion application was POME and cattle manure digestion. It was revealed that the addition of ammonium bicarbonate improved biogas production significantly (Zaied et al. 2020). This could suggest that the addition of alkali compound may enhance the overall stability of the process by balancing the pH from acid accumulation due to microbial action.

Co-digestion is one of the ways to improve the overall production of biogas. Other than co-digestion, POME pretreatment which consist of POME de-oiling, POME sedimentation, POME pre-hydrolysis, inorganic additive supplementation, biological additive supplementation and bioreactor modification may also be used to improve the overall quality of the biogas and methane production (Choong et al. 2018). Besides enhancing methane yield, co-digestion provides an avenue for by-products utilization

Table 3 Factors affecting anaerobic digestion process

Factors	Description
pH	• Critical factor that affects methanogens which directly impacts the production of biogas and methane production • Optimum range of 6.5–7.2 for methanogens, pH higher than 9.5 and lower than 4 are not tolerable by the microbes (Poh and Chong 2014; Kumaran et al. 2016) • VFAs produced will reduce system pH that will disrupt biogas production. Control strategies such as pH adjustment and tailoring feedstock formulations prior to fermentation are important • Adjusting pH for anaerobic digestion of POME is common to ensure the anaerobic digestion process performs well (Choong et al. 2018; Saelor et al. 2017; Khemkhao et al. 2015)
C/N Ratio	• Microorganisms require carbon and nitrogen as the source of protein and energy to live • Too high C/N ratio will reduce microbial metabolism while too low C/N ratio will inhibit methane production and increase the production of ammonia. It is commonly reported that the suitable C/N ratio for anaerobic digestion is in the range of 20–30 (Choong et al. 2018)
Temperature	• Common temperature range for the conventional anaerobic digestion is divided into two which are mesophilic (35–45 °C) and thermophilic (55–70 °C) temperature (Choong et al. 2018) • Mesophilic temperature has higher stability performance for digestion process but produces lower volume of biogas (Choong et al. 2018) • Thermophilic temperature can degrade organic matter faster but is usually not favourable as it contributes to high VFAs accumulation that will reduce system pH and affect methane content (Choong et al. 2018)
Organic Loading Rate (OLR)	• OLR is the amount of organic materials per unit of reactor volume that determines the balancing between acidogenesis and methanogenesis (Choong et al. 2018) • Previous studies suggested that COD removal efficiency is reduced at higher OLR in wastewater treatment system (Torkian et al. 2003; Sánchez et al. 2005; Patel and Madamwar 2002) • To generate more biogas, the organic load must be achieved and maintained at the highest OLR where it enables a continuous and stable biogas production which can be sustained by the reactor • Production of gas will increase with OLR to a point where the methanogens are not able to cope with the increase in available acetic acid for methane conversion (Poh and Chong 2009). Beyond this point, high acid accumulation will reduce the surrounding pH and could upset the overall process
Hydraulic Retention Time (HRT)	• Inversely proportional to OLR • Can be defined as the average amount of time required for a liquid or soluble compound to stay or pass through in a reactor (Arimi et al. 2015) • An ideal HRT of substrate contributes to optimized biogas production with high methane yield while maintaining good bacterial population within an acceptable treatment period
Mixing	• Mixing is essential to provide good contact between the substrates and microbes, to form uniform spatial substrate distribution, lessen the accumulation of repressive intermediates and reduces the resistance of mass transfer (Gómez 2006) • Adequate mixing can be achieved through mechanical mixing using a propeller to re-circulate slurry • Continuous and vigorous mixing is not recommended for reactors operating at high OLR since it can disrupt the process (Raskin 2001) • Horizontal mixing for 30 min intermittently for every hour was found to produce the highest methane yield from anaerobic digestion of POME (Sulaiman et al. 2009)

Table 4 Summary of the operational condition of the anaerobic digestion of palm oil mill by-products

Feedstock	Reactor	Digesting temperature (°C)	Inoculum/seed sludge source	Manipulated factors	Operating conditions		Findings	References
					OLR	HRT		
POME	250 mL batch reactor	55	Anaerobic seed sludge from the oil mill	Solid: liquid ratio	–	–	• Higher solid loadings reduce AD performance • TSS removal (%), COD and BOD decrease as solid content increases • 40S: 60 L is the best solid loading, producing 1431 ±17 mL biogas and 48.89 ±1.12 CH_4/g COD	Khadaroo et al. (2020)
EFB Decanter Cake (DC)	500 mL of serum bottle	35–55	Anaerobic sludge from commercial biogas production of POME	Addition of oil palm ash (OPA), raw materials, substrate: inoculum (S: I) ratio	–	–	• AD of EFB produces higher methane yield compared to DC • Addition of OPA reduces methane production • At 3: 1 ratio, methane yield for AD of EFB is 353.0 mL-CH_4/g-VS without the addition of OPA and AD of DC with the addition of 10% OPA is 101.5 mL-CH_4/g-VS • Liquid anaerobic digestate can be an effective inoculum for AD of EFB and DC	Tepsour et al. (2019)
POME	5.81 L CSTR	55	Anaerobic seed sludge obtained from water quality control plant	Configuration of CSTR, POME: water ratio, OLR	2.0–19.0 g COD L^{-1} d^{-1}	3.3 days	• Modified CSTR with deflector captured higher amount of palm fibres compared to ordinary CSTR • Average methane yield: 0.27 L/g COD • Biogas production of 6.23 L/L d • COD removal efficiency of 82%	Khemkhao et al. (2015)
POME	Anaerobic hybrid reactor (UASB with AF)	37–55	Mesophilic seed slurry from a brewery	Temperature, OLR	2.0–15.0 kg COD m^{-3} d^{-1}	5.8–6.2 days	• OLR of 15 kg [COD] m^{-3} d^{-1} gave 90–95% total COD removal • Thermophilic temperature gave better COD removal and biogas production (20.0 L/d) compared to mesophilic temperature (13.5 L/d)	Jeong et al. (2014)
POME	UASB-HCPB	55	Thermophilic mixed culture	Start-up strategy, OLR	4.28–27.65 g COD L^{-1} d^{-1}	2–5 days	• After 36-day treatment: – COD removal: 88% – BOD removal: 90% – Methane (%) in biogas: 52% at OLR of 28.12 g L^{-1} d^{-1} • More than 90% of BOD and COD removal was achieved and approximately 60% of methane was achieved at – HRT: 2 days – OLR: 27.65 g L^{-1} d^{-1} – MLVSS concentration: 14.7 g L^{-1}	Poh and Chong (2014)

(continued)

Table 4 (continued)

Feedstock	Reactor	Digesting temperature (°C)	Inoculum/seed sludge source	Manipulated factors	Operating conditions		Findings	References
					OLR	HRT		
POME	Combination of high rate anaerobic reactors (AHR +ABF and AHR+ADF)	36	–	Type of reactors, reactor configuration, OLR	0.91–23 kg COD m^{-3} d^{-1}	0.7–2.4 days	• COD removal of 93.5% was achieved • Having secondary reactor enhances COD removal efficiency and performance stability • Production of biogas of up to 110 L/d • Methane content of 59.5–78.2%	Choi et al. (2013)
POME	50 L bioreactor	30–35	POME sludge from methane recovery test plant	Reactor configuration, OLR	0.5–6.0 kg COD m^{-3} d^{-1}	79–92 days	• Mix and settle system were preferred compared to semi-continuous mode as it improves the biomass retention • Biogas production at OLR of 6.0 kg COD m^{-3} d^{-1} is 2.42 m^3/m^3 of reactor/day (0.992 m^3methane/m^3 of reactor/day)	Basri et al. (2010)
EFB PPF DC	500 ml batch reactor	37	–	Feedstock to inoculum (F: I) ratio, raw materials	–	–	• Increasing F: I ratio reduced methane generation • F:I ratio of 2:1 produced the highest methane yield for SS-AD of EFB (144 mL CH_4/g-VS) followed by PPF (140 mL CH_4/g-VS) and DC (130 mL CH_4/g-VS) • Methane production recorded are EFB (55 m^3 CH_4/ton), PPF(47 m^3 CH_4/ton) and DC (41 m^3 CH_4/ton)	Chaikitkaew et al (2015)
EFB + DC	500 ml of serum bottle	35–55	-	EFB: DC ratio	–	–	• Synergic effect at EFB: DC ratio of 1: 1 only, while other ratios showed antagonistic effect • Thermophilic temperature enhanced methane production by 5 times as compared to mesophilic temperature	Tepsour et al. (2019)
POME + EFB	250 ml serum bottle	35	Anaerobic sludge	EFB: POME ratio	1.8 g VS/L	25 days	• Addition of EFB improved the overall production of methane • Production of methane from EFB: POME ratio of 0.25: 0.31 is 1.2 times higher than AD of POME alone	Kim et al. (2013)
POME + SCS, POME +SBS, EFB + SCS, EFB + SBS	500 ml serum bottles	35	Mesophilic methane sludge	Feedstock, co-substrate, co-digestion ratio	–	–	• Co-digestion of POME and EFB with sewage sludge increased methane production – POME: sewage chemical sludge at 99: 1 gave 456 mL CH_4 g^{-1} VS methane yield	Suksong et al. (2017)

(continued)

Table 4 (continued)

Feedstock	Reactor	Digesting temperature (°C)	Inoculum/seed sludge source	Manipulated factors	Operating conditions		Findings	References
					OLR	HRT		
							– EFB: sewage chemical sludge at 95: 5 gave 18 mL CH_4 g^{-1} VS methane yield • Methane yield reduced with increasing sewage sludge content of 6–42%	
Cattle manure + POME	Solar assisted bioreactor	35	–	Dosage of ammonium bicarbonate	–	–	• Addition of ammonium bicarbonate improved overall biogas production • Optimum dosage of ammonium bicarbonate was 10 mg/L	Zaied et al. (2020)

ABF: Anaerobic baffled filter; AD: Anaerobic digestion; ADF: Anaerobic downflow filter; AF: Anaerobic filter; AHR: Anaerobic hybrid reactor; COD: Chemical oxygen demand; CSTR: Continuous stirred tank reactor; HCPB: Hollow centred packed bed; MLVSS: Mixed liquor volatile suspended solids; PPF: Palm press fibre; SBD: Sewage biological sludge; SCS: Sewage chemical sludge; SS-AD: Solid state anaerobic digestion; TSS: Total suspended solids; UASB: Up flow anaerobic sludge blanket; VS: Volatile solids

for treatment and value addition rather than being left underutilized. Moreover, by capturing the biogas for energy use, rampant methane release into the environment can be prevented.

4 Aerobic Composting of Palm Oil Mill Waste by-Products

4.1 Biological Processes

Aerobic composting is the decomposition of organic matter (OM) by microorganisms under certain controlled conditions whereby microorganisms consume oxygen (O_2) while feeding on organic materials (Pace et al. 1995). The composting process is a rapid bioconversion of OM into compost which is also known as humic substances (Ravindra 2015). Composting is a useful method to recycle waste and to produce compost fertilizer that is chemically stable, which can be used as a fertilizer to provide nutrients for plants and to improve soil structure (Nutongkaew 2011). The matured compost is good for land application without harming the environment. According to Zahrim and Asis (2010), composting is a proven technology for processing EFB from palm oil mills and it can reduce the initial weight and volume of the fresh EFB by 50% and 85%, respectively.

Vegetative wastes like palm oil mill derivatives contain high amounts of cellulose, lignin and hemicellulose which could serve as crucial sources of carbon (C) and nitrogen (N) for a balanced composting process (Maheshwari 2014). However, the contents of N in the majority of the palm oil mill or vegetative waste is simply not enough for effective composting (Maheshwari 2014). In most cases, additives like urea, manure, dairy, meat waste, fish and others are added into the composting pile of palm oil mill wastes to promote a healthy composting process (Imbeah 1998).

4.2 Parameters of Aerobic Composting

During the early stages of composting, O_2 and other easily degradable components of raw material are consumed rapidly by the microorganisms (Pace et al. 1995). A good indicator of knowing the composting progress is through the observation of temperature change of the windrow or pile from the release of heat during microbial activity (Rynk et al. 1994).

From a typical temperature and pH profile of composting shown in Fig. 10, the temperature usually follows a pattern of rapid increase to 43–70 °C where it remains for a few weeks depending on the raw materials (Sánchez et al. 2017). The temperatures will steadily decrease until the compost reaches ambient air temperature as the active composting slows down. The composting process is affected by numerous factors such as pH level, temperature, aeration rate, carbon to nitrogen ratio, moisture content and the physical structure of raw materials as listed in Table 5.

The curing period begins when windows or piles no longer reheat after turning and it usually lasts up 3 to 4 weeks. During this time, the materials continue to compost but at a slower pace with a decreasing rate of oxygen consumption (Rynk et al. 1994). Curing happens at mesophilic temperatures and the significance of curing increases if the active composting stage is either poorly managed or

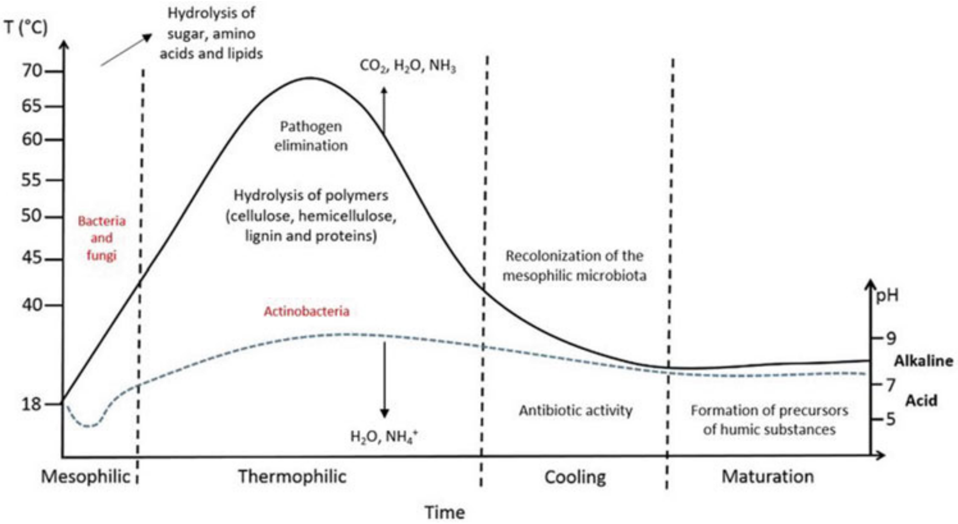


Fig. 10 Compost temperature pH variation with time (Sánchez et al. 2017)

shortened. Immature compost can contain high C/N ratio, elevated levels of organic acid, harmful pathogens and other negative attributes that could make compost land application unsuitable (Sánchez et al. 2017).

The composting process does not just stop at a specific point, the material continues to break down until the nutrients are consumed by the final remaining microorganisms and until most of the carbon is converted to CO_2. Be that as it may, the compost turns out to be relatively stable and useful before this point. Compost is said to be "ready" when the ideal characteristics of compost such as good C/N ratio, less O_2 demand, ambient temperature, neutral pH and earthy odour are attained (Rynk et al. 1994).

To conclude, the composting process relies on numerous factors as discussed, particularly on C/N ratios, moisture content, aeration, temperature and surface area. It is important to balance these factors to accomplish a quality product within a reasonable composting period. Imbalance in feedstock formulations and process parameters can cause upsets to the process such as accumulation of acids, poor growth of composting bacteria, generation of methane due to anaerobic conditions and a highly odorous pile.

4.3 Co-composting of Palm Oil Mill Waste Derivative

Co-composting is characterized as the composting of a blend of two or more types of wastes to achieve superior compost quality (Maheshwari 2014). For example, EFB with POME mixture was co-composted with fishmeal, bonemeal and bunch ash to increase the nitrogen (N), phosphorous (P) and potassium (K) content of EFB compost (Hau 2020; Lew et al. 2020). These additives are essentially by-products of the fishing, meat and palm oil industries. As a result of the addition, the author reported improvement in compost texture, odour reduction and enhanced NPK content with an ideal final C/N ratio. Another example is co-composting of chicken manure with sawdust, where the addition of sawdust increases the pile C/N ratio from 3.83 to a healthy range of 20–30 (Singh et al. 2018).

Various co-composting strategies are employed in the palm oil industry as outlined in Table 6, where EFB makes up the bulk of the composting blends due to its sheer mass of production. For every 1 tonne of FFB processed, 20% will end up as EFB with up to 70% moisture content (Zafar 2019; Vakili 2014). Its use as a solid fuel is unsuitable due to the high moisture content (Singh et al. 2010). Therefore, EFB needs to be recycled or repurposed into compost. Rapid degradation of EFB can be attained within 45 days by co-composting with mill by-products such as with POME (Stichnothe and Schuchardt 2010; Schuchardt et al. 2002; Baharuddin et al. 2009, 2010; Vakili et al. 2012; Yahya et al. 2010), POMS (Al-Madhoun 2005) and banana skin (Ravindra 2015). The additives provide extra nutrients for the growth of composting bacteria.

In terms of carbon to nitrogen ratio, co-composting between palm oil by-products alone generally resulted in a low C/N ratio value of less than 20 and could achieve an ideal C/N ratio value of between 20 and 30 with the addition of chicken manure, sewage sludge, poultry litter and banana skin (Table 6). A study by Thambirajah et al. (1995) revealed that the initial composting pile of only EFB, EFB with cow manure, EFB with goat manure and EFB with chicken manure at starting C/N ratios of 52, 48, 35, 47, respectively, were remarkably reduced to 24, 18, 14 and 12, respectively, after 60 days of composting (Thambirajah et al. 1995). In the aforementioned study, the compost pile

Table 5 Factors affecting composting process and their functions

Factors	Description
Oxygen and aeration	• Three types of aeration for composting are forced aeration, passive aeration and natural aeration without any sort of adaptations (Imbeah 1998; Aviani et al. 2010) • Limited oxygen supply leads to slow composting process (minimum O_2 concentration of 5%) or in worst cases the composting process may turn anaerobic degradation (Pace et al. 1995; Rynk et al. 1994) • Maintaining aerobic condition is important to avoid a competitive advantage over anaerobic and to rescind the offensive odours related to anaerobic degradation (Rynk et al. 1994)
Nutrients (C/N ratio)	• C, N, K and P are the primary supplements needed by the composting microorganisms • C is used for energy and growth while nitrogen is required for reproduction and production of protein by microorganisms (Nutongkaew 2011) • An appropriate C/N ratio (25–35) of compost feedstock is vital to ensure the required nutrients are available sufficiently for the microorganisms (Maheshwari 2014) • Many researchers suggested for C/N of 30:1 as the most optimum for composting (Tuomela et al. 2000; Larsen and McCartney 2000)
Moisture	• Water is needed to support the microbial metabolic processes and acts as a medium for chemical reactions and transferring nutrients to microorganisms • A range of 40–65% moisture content should be maintained, anything less than 40% makes the composting process inhibited, limits the air movement and leads to anaerobic digestion (Rynk et al. 1994) • A humidity of 50% is to be taken as a minimum limit (Maheshwari 2014)
Porosity, structure, texture and particle size	• Additives or bulking agents can improve porosity which will increase the rate of composting process (Doublet et al. 2011) • The rate of degradation increases as the particle size decreases due to larger surface area. However, this trait reduces porosity of the material, so compromise is needed (Rynk et al. 1994) • Yañez, Bueno (Yañez et al. 2010) reported that particle size reduction to around 1 cm resulted in more active chemical changes during composting and a higher relative content of humic substances
The pH of the material	• The composting process is generally insensitive to pH. • The preferred range of pH is around 6.5–8.0 but the natural buffering limit of the process makes it possible to work over a broader range • As decomposition occurs, the material's pH will experience changes until a stable pH at around neutral is obtained at the end of the process (Rynk et al. 1994)
Temperature	• Composting takes place within three ranges of temperature which are mesophilic (40−55 °C), thermophilic (over 70 °C) and a cooling stage or also known as curing process (Maheshwari 2014) • From the work of Tuomela et al. (2000) and Mahimairaja et al. (1995), the most active oxidizing degradation of organic waste is at the mesophilic stage • Thermophilic stage can last between 5 and 25 days or more as this stage involves active destruction of pathogenic bacteria and has the highest losses of flying organic substances (Mahimairaja et al. 1995) • The final stage of curing can take many weeks or even months and will proceed to end when the ambient temperature is achieved (Serramiá et al. 2013; Killi and Kavdır 2013; Paradelo et al. 2011; Boldrin et al. 2010)
Time	• Composting time can be reduced by providing proper C/N ratio and moisture content to the feedstock material as well as providing regular aeration and mixing during composting • Normal composting reaches maturation between 1 and 2 months. However, it is not uncommon for some raw materials to take longer than two months due to the cellulosic nature of the materials and unfavourable composting conditions (Rynk et al. 1994)

sustained a maximum temperature of 70 °C for three days in co-composting setups where mesophilic and thermophilic bacteria revealed a consistent activity, while fungal activity was suppressed entirely during this high-temperature phase (Thambirajah et al. 1995).

Salètes et al. (2004) studied the addition of ripe compost and urea to adjust the initial C/N ratio of EFB. The authors stated that after a period of 70 days of composting, almost 50% of the phosphorus (P), 70% of the potassium (K), 45% of the magnesium (Mg) and 10–20% of the calcium (Ca) initially applied were lost. In order to utilize the leaching nutrients and minimize the loss, the authors proposed for a better dispersal of effluent applications and to integrate a leachate collection system while maintaining suitable humidity for microbial decomposition during composting (Salètes et al. 2004).

Baharuddin et al. (2010) investigated the co-composting of POME anaerobic sludge with mesocarp fibre (MF). It was postulated that MF addition improved the maturation period to 40 days with the final C/N ratio of 12.4. The process

Table 6 Summary of co-composting of palm oil biomass residues

Material	Co-composting period (day)	Maximum temperature (°C)	Moisture content (%)	Final pH	Final C/N ratio	References
EFB + POME + DC Slurry	51	79	50−60	8.5	18.6	Yahya et al. (2010)
EFB + POME	40−98	60.2−75	50−75	7.5−8.6	12.4−28	Stichnothe and Schuchardt (2010), Schuchardt et al. (2002), Baharuddin et al. (2010), Baharuddin et al. (2009), Vakili et al. (2012), Yahya et al. (2010)
EFB + Frond + Poultry Litter	80	49−57	40−65	7.2−7.4	17.6−26.1	Vakili et al. (2012)
MF + POME	60	60	55−60	7.5	12.6	Hock et al. (2009)
POMS + Sawdust	300	40	–	5.7	19	Yaser et al. (2007)
EFB + POMS + Sandy Soil + Biosolids	49	25−26	20	–	–	Al-Madhoun (2005)
EFB + Fermented Liquid Waste + Chicken Manure	50−85	70	65	4.5−6	16	Suhaimi and Ong (2001)
MF + Poultry Litter + Urea	56	70−72	65	7−8	16−17	Thambirajah and Kuthubutheen (1989)
EFB + Trunk + Frond + Sewage Sludge	84	28−43	60	5.8−6.9	19−42	Kala et al. (2009)
OPF + Rice Bran + Chicken Manure	21	56	40−60	–	15.8−21.3	Kausar (2012)
POMS + EFB	60	44.7	50−70	7.5−7.8	12.6−15.8	Nutongkaew (2011), Ahmad et al. (2011a, b)
POMS + DC	60	–	50-65	7.75	7.6	Nutongkaew (2011)
POMS + DC + EFB	60	49	50−65	7.8	13.5	
Palm Kernel Cake + Poultry Litter	42	58	–	7.4	23.2	Kolade et al. (2006)
Palm Kernel Cake + Goat Litter	42	64	–	7.5	17.4	
MF + POMS	60	–	50−70	7.5	12.6	Ahmad et al. (2011a, b)
OPF + POMS	60	56	50−70	8.2	18	
EFB + Goat/Cow/Chicken Litter	60	75	65	9.5	12−24	Thambirajah et al. (1995)
EFB + POME + Banana Skin	45	40.5−47.5	75−79	6.8−8.5	27−29	Zahrim (2015)

experienced a higher thermophilic temperature (60–67 °C) followed by maturing or curing phase after four weeks of treatment. The pH of the co-composting piles was relatively constant (pH 8.1–8.6) during the process while the humidity was reduced from 64.5 to 52.0%.

Decanter cake (DC) generated during CPO purification is about 4–5% of the FFB processed, contributing to the overall solid waste produced that requires land space for storage and disposal. Another problem occurs when DC is dried, it becomes a fire hazard around the mill area (Dewayanto et al. 2014). Co-composting of EFB and DC slurry with POME addition showed promising potential for a treatment strategy (Yahya et al. 2010). Decanter cake slurry addition increased the rate of the co-composting process of the EFB. After day-51, the C/N ratio for the matured co-compost with the DC slurry was found to be 18.65 while compost without DC slurry gave a higher ratio of 28.02 from an initial C/N ratio of EFB at 63.67. The final product with the addition of DC slurry to EFB and POME contained 46.4% N, 17.9% P, 17.7% K and 23.1% Ca more than that without DC slurry (Yahya et al. 2010).

In another study done by Zahrim (2015) on the addition of banana peels into composting pile of EFB and POME showed that maturation was reached within 45 days with the maximum temperature of 47.5 °C. Banana peels addition improved the final C/N ratio to be in the range of 27–29 and potassium content from 2.7 to 3.0%. Addition of more than 5% of banana skin did not increase the K-content any higher and this might be due to the solubilisation of K in the leachate. In Malaysia, banana peels are generally considered as waste. At 30–40% of banana weight, the peels account for several tonnes of waste generated daily from small-to-medium scaled food production factories, households, restaurants and marketplaces (Zahrim 2015).

Co-composting of palm oil by-products such as the two major waste products EFB and POME is a cleaner and safer process. It can result in up to 76% reduction in greenhouse gas (GHG) emissions by avoiding the uncontained release of methane from the open storage of EFB and POME treatment ponds (Krishnan et al. 2017). From the literature summary, underutilized biomass such as abundant palm oil mill by-products are proven as suitable additives for co-composting processes for a faster maturation and better final quality of compost with balanced C/N ratio and suitable pH while simultaneously possessing a healthy dose of soil-friendly bacteria. This technique serves as a treatment strategy as well as producing useful products to support circular economy activities in the palm oil and other industries.

5 Conclusion

The palm oil industry plays a major role in the global supply of oils and fats. It has the highest oil yield per hectare and yields about 10 times more oil per hectare than soy oil. The demand for palm oil is expected to increase steadily, however, environmental concerns such as deforestation has slowed its growth. Furthermore, this industry is suffering from an overabundance of mill residues which require treatment prior to disposal and the increasing oil demand will contribute to increased generation of waste from the mills and plantations.

Current waste treatment processes employed globally, as well as in Malaysia specifically, are inefficient and unable to accommodate the large production of various palm oil by-products. Anaerobic digestion is gaining popularity due to its potential to generate biogas as a clean energy alternative for the mill operation and a slurry digestate for nourishment to the plantation. Composting is another widely applied treatment method to turn palm oil by-products into a soil-friendly fertilizer or compost. These two processes can be further enhanced by the addition of additive materials from the industry itself. Various studies revealed the potential of co-digestion to improve the process and the products of anaerobic digestion and composting.

Integration of palm waste materials will promote sustainability for the mill operation and oil palm plantation. This approach combined with palm oil certification programmes can help reduce environmental impacts and may help to improve market demand which will impact the palm oil industry directly. With various sustainable development goals outlined by the UN, this industry should strive to be more sustainable in an integrated approach rather than focusing on maximizing oil production or treating specific wastes alone.

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Bioconversion of Fruits and Vegetables Wastes into Value-Added Products

Sarita Shrestha, Janak Raj Khatiwada, Hem Kanta Sharma, and Wensheng Qin

Abstract

The increase in human population with the increase in nutritional awareness for fruits and vegetables consumption is forcing toward higher production and supply of fruits and vegetables. However, some sorts of food processing steps are involved before human consumption which is essential for preserving the properties of those fruits and vegetables. During these processes and till reaching the consumers, many fruits and vegetables wastes are produced. Although the emphasis was given to produce less waste and reuse the products as much as possible, utilization of those wastes in bioprocessing and production of different value-added products were less emphasized. Thus, in this chapter, we describe the major value-added bioproducts produced from fruits and vegetables wastes such as bioactive compounds, phenolic compounds, enzymes, pigments, flavoring compounds and aroma, dietary fibers, organic acids, bioenergy, bioplastics, exopolysaccharides, single-cell protein, etc.

Keywords

Value-added products • Bioconversion • Bioactive compounds • Single-cell protein • Bioenergy • Bioplastics • Exopolysaccharides

1 Importance of Fruits, Vegetables, and Their Waste

Human population of the world is continuously increasing with a growth rate of 1.05% per year reaching a population of over 7.7 billion and, by 2030, it is predicted to reach 8.5 billion (United Nations 2019). With the limited natural resources, it is difficult to supply food to the growing population. At the same time, due to the rising human population, there is a high demand for food production. Fruits and vegetables (FV) consumption is considerably increased with the increase in awareness of FV and their health benefits to humans. FV are fundamental for human nourishment as they contain significant amounts of minerals, vitamins, and fibers. The consumption of natural and high-quality FV is also increased for healthier lifestyles (FAO 2016). Moreover, the consumption of FV imparts in reducing the threat of stroke, some cancer, and coronary heart disease. Health welfare of these kinds is chiefly credited to natural micronutrients like vitamin C, carotenoids, tocopherols, polyphenolics, etc. The organic micronutrients are available in colored (yellow and green) vegetables and citrus fruits. Although a large population is conscious of their health problems connected with nutrition, they lack plentiful intake of FV and there is a need to find out the alternate option to get these micronutrients (Schieber et al. 2001). At the same time, most of the population do not consume raw FV in many cases and these FV need to undergo some kind of processing. Thus, during the processing of FV, large masses of wastes are generated. Regrettably, FV depletion rates are high and depend upon the types of fruits. Fruits from temperate zones produce less amount of waste compared to fruits from tropical and subtropical zones (Schieber et al. 2001; Kodagoda and Marapana 2017).

It is anticipated that 1/3rd of all food harvested is lost or dumped as waste in the world (FAO 2019) throughout the food supply chain. Global scenarios of some FV wastes production are shown in Table 1. Thus, there is a need to decrease food loss or waste along with the production as well

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as in different stages of food supply chain. In addition, a huge amount of food waste is also generated in different food processing industries (FAO 2019; Ravindran and Jaiswal 2016). These food wastes are classified into two major groups as the waste obtained from plants and the waste obtained from animals based on biochemical characteristics of food waste and origin. The wastes obtained from animals are mainly produced from the dairy, meat, fisheries, and seafood processing industries. Similarly, plant-derived wastes include different types of residues obtained from different crops including FV (Ravindran and Jaiswal 2016). These FV are produced seasonally and overproduction during the season must be stored properly for future use. However, the perishable nature of FV, inappropriate storage conditions mainly in tropical regions lead to increased production of waste. In addition, the remains of FV like stem, stalks, leaves, roots, and tubers impart in waste. FV processing waste includes pomace, peels, and seeds accounting for 25–30% waste. Thus, it is revealed that FV losses or wastes are mostly due to post-harvest grading quality standards of FV set by retailers. This type of loss and deterioration of crops mainly occur in hot and moist climates, the seasonality that results in insufficient access (FAO 2019).

According to FAO (2011) a combined data from Canada, New Zealand, the USA, and Australia nearly half the amount of the FV produced in the world annually end up as wastes (FAO 2011) in the garbage. Other factors like improper drying, storage, and transportation play important roles in the production of FV waste. FV processing industries generate a larger portion (30–50%) of fruits and vegetable waste (FVW) as by-products during different stages of processing, distribution, and consumption (Di Donato et al. 2011). Moreover, the fruit wastes are also generated during the production of pickle, puree, sauces, fresh-cut fruit, canned fruit, juices, dehydrated fruit, jams, etc. (Di Donato et al. 2011; Coman et al. 2020).

2 Potentials of FVWs in Production of Value-Added Products

FV are organic matter and contain macronutrients like proteins, lipids and carbohydrates, bioactive compounds, and phytochemicals. The high costs of drying, storing, and transportation of the organic wastes produced during different processes make them used as feed or composted to produce

Table 1 Global scenario of fruits and vegetables waste production adopted from Uçkun-Kiran et al. (2014), Caldeira et al. (2019), CEC (2017), Oelofse (2014), Tran and Mitchell (1995)

Wastes	Asia	South Africa	North America	Europe	Australia	References
Potatoes/tubers	12,912 KT	955000 T	244 MT	9.4 Mt	23.6 KT	Uçkun-Kiran et al. (2014), Caldeira et al. (2019), CEC (2017), Oelofse (2014)
Cereals	52,374 KT	2605000 T	317 MT	15.6 Mt	1380 KT	Uçkun-Kiran et al. (2014), Caldeira et al. (2019), CEC (2017), Oelofse (2014)
Oil crops	13,590 KT	NR	43 MT	12.7 Mt	3.9 KT	Uçkun-Kiran et al. (2014), Caldeira et al. (2019), CEC (2017)
Vegetables	59,949 KT	2020950 T	NR	31.3 Mt	54.1 KT	Uçkun-Kiran et al. (2014), Caldeira et al. (2019), Oelofse (2014)
Apples	4116 KT	NR	NR	NR	5.9 KT	Uçkun-Kiran et al. (2014)
Bananas	8544 KT	NR	NR	NR	5.4 KT	Uçkun-Kiran et al. (2014)
Pineapple/peel	579 KT	NR	NR	NR	400 KT	Uçkun-Kiran et al. (2014), Tran and Mitchell (1995)
Fruits	28,328 KT	2470050 T	NR	28.1 Mt	30.9 KT	(Uçkun-Kiran et al. (2014), Caldeira et al. (2019), Oelofse (2014)
Fruits and vegetables	88,277 KT	4491000 T	492 MT	59.4 Mt	85 KT	Uçkun-Kiran et al. (2014), Caldeira et al. (2019), Oelofse (2014)

Note T: ton, KT: kiloton, Mt: metric ton, MT: million ton, NR: not reported fertilizer or discarded in rivers or banks causing conservational hazard (Kodagoda and Marapana 2017; Coman et al. 2020; Wadhwa et al. 2013). Thus, lately many researches have been going and more attentiveness has been given on the recovery of value-added products like the bioactive compounds possessing health benefits for humans from industrial by-products (Coman et al. 2020). Additionally, FVWs contain high moisture, a good pool of lipids, complex carbohydrates, nutraceuticals, proteins, and fats. Therefore, these wastes are recycled to be used as feed resources or can be commercially utilized as the raw materials for the production of essential metabolites. FVWs are exploited by certain microbes and transformed into value-added products adding an economical value of FVWs. This approach of utilizing resources from wastes creates possibilities in the development and contributes in the justifiable improvement of livestock industries (Ravindran and Jaiswal 2016; Wadhwa et al. 2013; Panda et al. 2016). The effective and efficient utilization of FVWs will increase farmers' profits, reduce the cost of animal feeding, generate different profitable products, aid in waste management, and reduce pollution. Different FVWs such as cauliflower leaves, corn husk, cabbage leaves, pea pods, leafy waste of mustard, tomato pomace, citrus waste, carrot waste, mango peels, bottle gourd pulp, banana peel, etc., can be directly fed to animals or following drying or ensiling with crop straws. These dried or ensilaged animal feeds do not affect nutrient deployment, health, lusciousness, and functioning of livestock. The FVWs can be utilized in the production of edible oil, essential oils, pigments, polyphenols, enzymes, bio-methane, bioethanol, bioplastic, anti-carcinogenic compounds, single-cell proteins, and more (Wadhwa et al. 2013). The overall simple diagrammatic representation of converting the FVWs into products adding value is presented in the Fig. 1.

To fulfill the increasing demand of food for the growing population, valorization of food supply chain waste should be studied so that it helps to design different opportunities for the production of bioactive compounds, biofuels, bioplastics, enzymes, and more. The waste management problem is exaggerated due to ineffective waste management leading to slow actions on appropriate conduct, treatment, and disposal of waste (Ravindran and Jaiswal 2016). However, the common and easy waste management strategy is to prioritize lessening waste production and minimum importance on discarding.

3 Conversion Process

The FVWs and other by-products produced from food industries can be used in the production of different value-added products mainly by three processes; thermal conversion, chemical conversion, and biological conversion (Singh et al. 2019). The appropriate conversion method depends on the composition of wastes and by-products and the aim of the recovery process.

3.1 Thermal Conversion

This process includes incineration, hydrothermal carbonization, pyrolysis, and gasification. Incineration implicates the burning and alteration of waste constituents into heat and energy and also decreases the volume of solid waste up to 80–85%. This technique of combusting solid waste is antiquated, and food waste seems to be unsuitable for incineration due to moisture content in FVWs. However, this technique may be beneficial when used after drying of FVWs with respect to energy loss. The heat generated from the combustion process is generally consumed by steam turbines for producing energy or for exchanging heat (Pham et al. 2015). Thus, the thermal treatment of waste is applied with the precise aim of generating power (Singh et al. 2019).

Hydrothermal carbonization (HTC) is an aqueous carbonization process performed at a relatively lower temperature (180–350 °C) and autogenous pressure. This process is suitable for wet or high moisture containing wastes which alters the food trashes into an energy-rich valuable resource (Pham et al. 2015). This process has various advantages such as it is faster than biological processes, removes many organic impurities and pathogens, and reduces waste volume. HTC process results in the production of highly carbonized and energy-containing material known as hydrochar which is equivalent to lignite coal. The hydrochars can be used in removing dyes from polluted water (Singh et al. 2019; Pham et al. 2015).

Gasification and pyrolysis are also thermal processes that effectively work against food wastes containing carbon. Gasification is the process in which waste is converted into a mixture of combustible gas by partial oxidation at temperature 800–900 °C. Similarly, pyrolysis is the process which converts waste into bio-oil, solid biochar, and syngas. The produced combustible gas can be burned directly or can be used as a feedstock in methanol production (Pham et al. 2015).

3.2 Chemical Conversion

This process is commonly applied in food processing industries and includes hydrolysis, oxidation for producing value-added products from food waste (Singh et al. 2019). The chemicals (acid or alkali) help to disrupt the cell and extract the compounds. New and alternative solvents with enhanced physical properties are being used as extraction solvents such as propane, butane, dimethyl ether for extraction of natural products like oils, antioxidants, aromas.

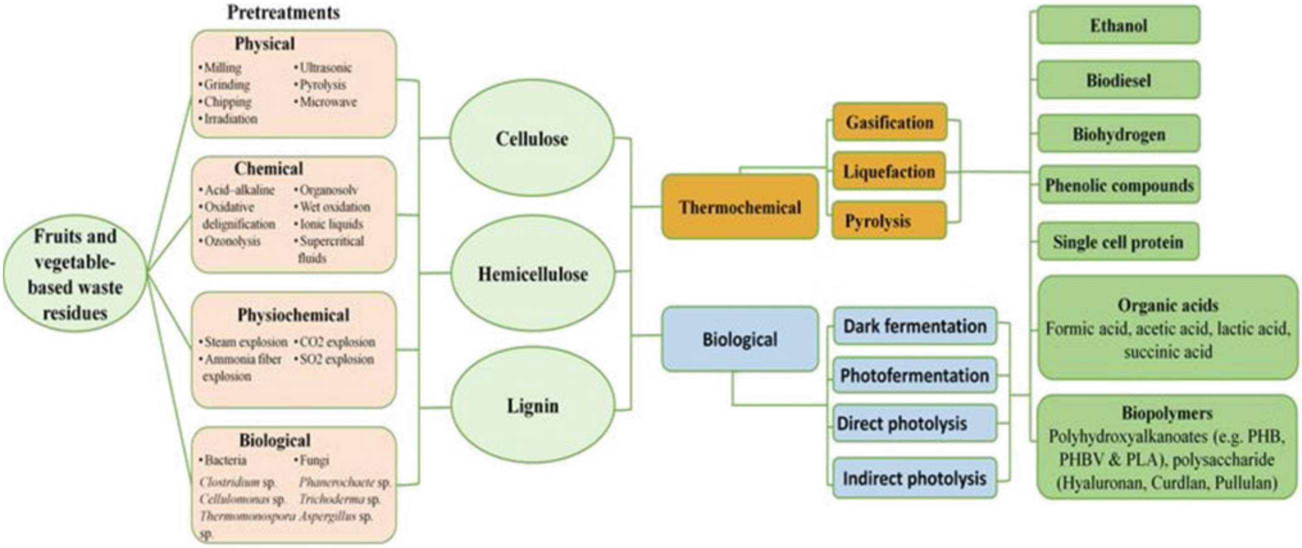

Fig. 1 Schematic demonstration of the conversion of fruits and vegetables wastes into value-added products

Valuable by-products and materials can be extracted by green extraction techniques like high-voltage electrical discharge and pulsed electric field technology. In both technologies, electroporation occurs, and cell permeability is increased so that extraction of intracellular compounds is enhanced (Chemat et al. 2020; Sarkis et al. 2015). Extraction of antioxidants from potato peels with ethanol was executed by Amado et al. The antioxidant extraction was related to the process conditions like temperature, time, and ethanol concentration (Amado et al. 2014).

3.3 Biological Conversion

This process is becoming more common and gaining interest throughout the world. Energy, bioactive compounds, and value making products can be recovered from organic wastes by the biological conversion involving anaerobic digestion and fermentation. Anaerobic digestion is the process of microbial catabolism in which organic wastes decompose and produce biogas mainly methane, and traces of nitrogen, CO_2, hydrogen sulfide in absence of oxygen. Fermentation process includes either solid-state fermentation (less water/moisture content) or submerged state fermentation (very less or absence of water/moisture content). Different factors such as pretreatment, kinds/quality of substrates, and microbes used play an important role. Biological conversion is eco-friendly, environmentally safe, protective to human health, and can minimize carbon dioxide, methane like gas emission (Singh et al. 2019; Awasthi et al. 2019). Vegetable wastes such as tomato, fennel, carrot, and more can be used as a cheap carbon substrate for microbial culture without chemical pre-treatment. These FVWs can be used as environment-friendly and low-cost substrates in culture media for the manufacture of biomolecules such as enzymes and biopolymers using some specific microorganisms (Di Donato et al. 2011).

4 Bioconversion of FVWs into Different Value-Added Products

As the fossil-based resources are diminishing, alternate feedstock for producing chemicals and fuels needs to be secured or explored out. Different biomass in a form of organic wastes produced are being an interesting subject for their exploitation as renewable resources. The organic wastes have been considered as a valuable feedstock in generating varieties of intermediates and products. For example, some furans and organic acids are usually used as chemical precursors to manufacture various products including polymers, biosurfactants, biolubricants, or nanoparticles (Esteban and Ladero 2018). Some of the value-added products produced from FVWs are listed in Table 2. These products have various uses in industries, due to their similar functioning as recognized products. The waste management systems begin with waste minimization. Therefore, to achieve waste minimization in the industry, it is beneficial to use further effective approaches such as in-house recycling of waste, reuse of waste products, and upgrading of waste property. FVWs are greatly rich in starch, inulin, hemicellulose, pectin, and cellulose like polysaccharides and thus can be used as resources for producing a wide array of products such as antibiotics, biofuels, vitamins, enzymes, pigments, livestock feed, and more (Sadh et al. 2018).

4.1 Bioactive Compounds

Bioactive compounds comprise a wide variety of natural compounds which can be found mainly in different colored FV and offer tremendous storage of food additives, nutraceuticals, and functional foods. Natural sources of bioactive compounds are plants, fruits, tea, olive, algae, bacteria, and fungi. Polyphenols like compounds can be discovered in the environment at extreme intensity relative to other compounds. So, to extract sufficient amounts of bioactive compounds improved and advanced technologies need to be applied. The common bioactive compound extraction methods are pressurized liquid extraction, solid–liquid, or liquid–liquid extraction, ultrasound-assisted and microwave extractions, enzyme and instant controlled pressure drop-assisted extractions, and supercritical and subcritical extractions (Gil-Chávez et al. 2013). The FVWs mainly contain sterols, tocopherols, carotenes, terpenes, polyphenols, dietary fibers like bioactive compounds which are value-adding compounds (Kumar et al. 2017). With an increase in food processing industries by-products and losses of FV, there is an increase in the amount of FVWs. Thus, the FVWs can be an alternative source to produce bioactive compounds which will help to make farmers financially stronger and cut the problem of managing waste.

4.1.1 Phenolic Compounds

Phenolic compounds are an assembly of diverse molecules categorized as secondary metabolites widely found in plants. The most commonly studied bioactive phenolic compounds from FVWs have health beneficial properties like cardioprotective, anticarcinogenic, antioxidant, and anti-inflammatory (Haminiuk et al. 2012; Balasundram et al. 2006). The phenolic compounds generally possess an aromatic ring having hydroxy substituents. Of various compounds, tannins, flavonoids, and phenolic acids have dietary functions. These substances are produced by plants throughout their ordinary growth and in response to different situations like biotic stress and UV radiation (Rispail et al. 2005). The type and number of phenolic compounds found in fruits depend on many factors; types and maturity of fruits, geographic location, soil composition, climate, storing conditions, etc. (Robards et al. 1999). Varieties of FVWs produced as a residue of asparagus, grape, olive, citrus, apple, onion, pomegranate, potato, mango, carrot, banana, etc., can be worthy sources of phenolic compounds (Kumar et al. 2017). The phenolic compounds act as antioxidants and asa substrate for oxidation reaction. The extraction and recovery of phenolic compounds are complicated because these compounds are highly reactive and are unevenly distributed in various forms. The soluble form of phenolic compounds is mainly located in vacuoles (Rispail et al. 2005). Extraction, as well as recovery of phenolic compounds, are done following submerged or solid-state fermentation methods. However, the most commonly used is solid-state fermentation due to high efficiency, high yield, shorter time, and less costly (Martins et al. 2011).

Phenolic acids include hydroxybenzoic acid (syringic, vanillic, gallic acid) plus caffeic, sinapic, ferulic acid like hydroxycinnamic acids. Flavonoids are the largest group of plant phenolics, having few molecular compounds. Tannins are the third important group of phenolics and have relatively high molecular weight and include hydrolyzable and condensed tannins (Balasundram et al. 2006).

Flavonols and flavones are commonly found in plants. One or more hydroxyl groups are bound to a sugar unit (most commonly glucose) with rhamnose and the disaccharide (Balasundram et al. 2006). Anthocyanins are another most common and widely found flavonoids which are accountable for blue, red, and violet colors of some FV, although red color of orange and tomato is due to carotenoid. In ripe berries, five classes of phenolic compounds such as phenolic acid, flavonol, flavones, flavanonols, and anthocyanins are well present. In different types of grapes, different phenolic compounds are found. For example, red grapes have anthocyanins, whereas white grapes have flavonols. The most common citrus fruits have only rutinosides that are non-bitter but pummelo and sour oranges have only flavanone neohesperidosides giving bitter taste. However, some citrus fruits like grapefruit include both neohesperidosides and flavanone rutinosides. Phenolic compounds like malvidin glycosides formed during wine maturation are unaffected by sulfur dioxide bleaching. Cinnamic acid is a foremost portion of phenolic compounds found in citrus fruits (Robards et al. 1999). The concentration of phenolics is different within plant tissues (Balasundram et al. 2006). Some simple food processing like peeling of FV can abolish a substantial share of polyphenols. In some fruits such as grapes, the high concentration of these substances is often present in the skin than in the pulp. For example, tannin is complex polyphenols commonly found in the skin and seed of grape berry. The concentration of tannins is not exactly the same in wine produced from grapes and in the fresh harvest fruit. Tannin is lower in wine produced from grapes compared to fresh grapes due to loss of these compounds during pressing and fermentation. Conversely, maximum of the main solutes existing in the grape berry at harvest time are present in wine composition. Limited digestion process, physical and thermal processing, and mastication help in the absorption of the phenolic compounds in the intestine. Sometimes, nutrients released during digestion may interact with other food components and form complex and colloidal structures which may affect in absorption (Parada and Aguilera 2007). Phenolic compounds are used as dietary

Table 2 Potential value-added products from fruits and vegetables wastes

Different wastes	Value-added products	References
Pineapple waste	Biogas, ethanol, hydrogen, lactic acid, citric acid, ascorbic acid, ferulic acid, furaneol, vanillin, fiber	Choonut et al. (2014), Dorta and Sogi (2017), Leong and Shui (2002)
Grape waste	Phenolic compounds, essential oil (Oleic and linoleic acid), tartaric acid, lactic acid, hydrolytic enzymes, Polyhydroxyalkanoates, anthocyanin	Teles et al. (2019), Follonier et al. (2014), Shinagawa et al. (2015)
Potato waste	Chlorogenic, ferulic acid, pullulan, lipid, cellulolytic enzymes, livestock feed	Wadhwa et al. (2013), Amado et al. (2014), dos Santos et al. (2012), Muniraj et al. (2015), Esparza et al. (2020)
Banana waste	Single-cell protein, polymers (lignin, hemicellulose, pectin), sterols, anthocyanin, carotenoids, phenolic compound, ascorbic acid, bioethanol, amylase	Unakal et al. (2012), Ingale et al. (2014), Malav et al. (2017), Leong and Shui (2002), Someya et al. (2002)
Pomegranate waste	Single-cell protein, phenolic compounds, ascorbic acid, dietary fiber, ferulic acid	Tilay et al. (2008), Malav et al. (2017), Li et al. (2006)
Orange waste	Single-cell protein, pectin, pectinase, ascorbic acid, ferulic acid, curdlan	Ahmed et al. (2016), Tilay et al. (2008), Esparza et al. (2020), Mondal et al. (2012), Malav et al. (2017), Leong and Shui (2002)
Watermelon waste	Single-cell protein, ascorbic acid	Malav et al. (2017), Leong and Shui (2002)
Sweet beet waste	Livestock feed, single-cell protein	Wadhwa et al. (2013), Malav et al. (2017)
Cucumber waste	Single-cell protein, flavonoids, flavanols	Mondal et al. (2012), Agarwal et al. (2012)
Coconut waste	Xanthan, curdlan, ascorbic acid, phenolic compounds	Esparza et al. (2020), Leong and Shui (2002), Dey et al. (2003)
Date palm waste	Xanthan, curdlan	Esparza et al. (2020)
Asparagus waste	Curdlan	Esparza et al. (2020)
Canola oil waste	Biodiesel	Lee et al. (2012)
Cassava waste	Curdlan, pullulan, animal feed, lipid, biodiesel	Ajila et al. (2012), Muniraj et al. (2015), Esparza et al. (2020), Lu et al. (2011)
Apricot waste	Succinic acid, lactic acid, polyhydroxyalkanoates	Follonier et al. (2014)
Cherries waste	Lactic acid, succinic acid	Follonier et al. (2014)
Sweet potato waste	Lipid, citric acid	Muniraj et al. (2015), Yu et al. (2017)
Corncob waste	Lactic acid, formic acid, citric acid, succinic acid, protease, amylase, protease, lipid, biodiesel	Di Donato et al. (2011) Kandasamy et al. (2016), Kong et al. (2019), Muniraj et al. (2015), Venkata and Venkata (2010)
Apple waste	Ascorbic acid, flavonoids, flavonols, pectin, anthocyanin, enzymes, single-cell protein, aroma compound, ethanol, organic acid, livestock feed	Wadhwa et al. (2013), Vendruscolo et al. (2008), Leong and Shui (2002), Wolfe and Liu (2003), Schieber et al. (2003)
Mango waste	Carotenoid, dietary fiber Ascorbic acid Furaneol Oleic and linoleic acid Livestock feed	Wadhwa et al. (2013) Pickenhagen et al. (1981), Leong and Shui (2002) Ajila et al. (2010), Kittiphoom and Sutasinee (2013)
Citrus waste	Pectin, pectinase, flavonol, phenolic acid, livestock feed	Wadhwa et al. (2013), Robards et al. (1999), Dhillon et al. (2004), Bocco et al. (1998)

(continued)

Table 2 (continued)

Different wastes	Value-added products	References
Tomato waste	Polysaccharides, polyphenols, ascorbic acid, livestock feed	Di Donato et al. (2011), Wadhwa et al. (2013), Leong and Shui (2002)
Avocado waste	Phenolic compound, ascorbic acid, carotenoid, fiber	Chemat et al. (2020), Leong and Shui (2002)
Papaya waste	Ascorbic acid	Leong and Shui (2002)
Bottle gourd waste	Cellulase, animal feed	Wadhwa et al. (2013), Verma and Kumar (2020)
Carrot waste	Biopolymers, polysaccharides, enzymes, polyphenols, livestock feed	Di Donato et al. (2011), Wadhwa et al. (2013)
Amla pulp	Polyphenol, flavonoid	Agarwal et al. (2012)
Lemon waste	Polysaccharides, enzymes, polyphenols, flavonoid	Di Donato et al. (2011), Agarwal et al. (2012)
Food processing waste	Hydrogen, bioethanol, biobutanol	Zhang et al. (2016)
Agro-industrial wastes	Pigments	Panesar et al. (2015)

supplements and food fortification for health benefits and prefer natural sources that are not able to synthesize chemically and need to be extracted from original plant material (Schieber et al. 2001).

4.1.2 Enzymes

Enzymes are biological catalysts, proteinaceous, and catalyze a number of metabolic processes. Enzymes are applied in different industries for the production of a wide variety of products. For instance, pectinases and amylases are used in food industries, cellulases in biofuel industries, and tannases in reducing the tannic acid amount in effluents. However, raw materials used for the production of different enzymes account for about 30% of the operation cost (Ravindran and Jaiswal 2016). Plant-related food wastes mainly contain cellulose, hemicellulose, lignin, starch, xylan, pectin, glucan, etc., depending upon the nature of waste products. Most commonly applied enzymes are amylases, cellulases, hemicellulases, ligninases, pectinases, tannases, proteases, lipases. Microorganisms can be utilized for the production of different enzymes and the rate of enzyme production varies with the organisms growing on dissimilar substrates and different methods of fermentation.

Enzymes Acting on Polysaccharides

i. Amylases: This group of enzymes composed of glucoamylase, β-amylase, and α-amylase which hydrolyze starch, oligosaccharide, and polysaccharides into glucose, fructose, maltose sugars. Amylases are classified in exo-amylase and endo-amylase based on the hydrolysis of starch (Panda et al. 2016). Many FVWs such as banana waste (Unakal et al. 2012), date waste (Said et al. 2014), apple pomace (Nigam and Singh 1994), and potato peel (Mushtaq et al. 2017) have been used in amylase production. Microorganisms like *Candida guilliermondii*, *Aspergillus niger*, *A. tamarii*, *A. oryzae*, *Bacillus licheniformis*, *B. subtilis*, *Thermomyces lanuginosus*, and *Rhizopus oryzae*are exploited for amylase production (Unakal et al. 2012; Said et al. 2014; Nigam and Singh 1994; Mushtaq et al. 2017; Metha and Satyanarayana 2016). Amylases are widely used in baking, brewing, and preparation of digestive aids such as for the production of sugar, paper, moist cakes, fruit juices, chocolate cakes, starch syrup, and more (Metha and Satyanarayana 2016).

ii. Cellulases: This group of enzymes is comprised of exoglucanase (cellobiohydrolase), endo-β-glucanase, and β-glucosidase which hydrolyze cellulose into glucose, cellobiose, and other oligosaccharides. The three main cellulases act synergistically to cleave the glycosidic linkage of cellulose and completely hydrolyze the cellulose present in plant wastes. Exoglucanase cleaves the long chain from endings (reducing or non-reducing), endoglucanase cleaves the long oligosaccharides into short oligosaccharide chain, and β-glucosidase further hydrolyze to glucose (Kuhad and Gupta 2011; Juturu and Wu 2014). Vegetable waste like bottle gourd peel can be the substrate for producing cellulase by *Neurospora crassa* and *Trichoderma reesei* (Verma and Kumar 2020), potato peel by *Aspergillus niger* (dos Santos et al. 2012). Cellulases are applied in animal feed, food, and brewery production, textile processing, detergent production, and pulp paper manufacture. Recently, the increasing demand for biofuels and chemicals recovered from renewable resources has made cellulases to be exploited for producing fermentable sugars in cellulose biorefinery (Kuhad and Gupta 2011).

iii. Hemicellulases: This group of enzymes integrates α-arabinofuranosidases, α-glucuronidases, mannanases, and α-d-galactosidases that attack the β-1,4-glycosidic bonds of hemicellulose in lignocellulosic biomass. Hemicellulases are efficient in breaking esterified side chain groups as well as glycosidic bonds.

Mannanases destroy mannan which is the basic part of the plant cell wall commonly in plant seeds and fruits. The group of enzymes included in mannanases is β-mannanases, β-mannosidases, and β-glucosidases (Malgas et al. 2015; Chauhan et al. 2012). Mannan plays an essential role as seed storage compounds and in an arabidopsis mutation where (gluco)mannan synthase lacks (Malgas et al. 2015; Goubet et al. 2003). *Bacillus* sp., *Aspergillus* sp., *Clostridium* sp., *Streptomyces* sp., *Trichosporonoides oedocephalis*, etc., have the ability to produce mannanases. They use apple pomace, plantain peels, mango peels, potato peels, passion fruit peel, etc., as substrates for mannanase production. Mannanases are applicable in industries like pharmaceutical, pulp and paper, food, oil, feed, textile and detergent industries, and coffee extraction (Chauhan et al. 2012).

iv. Pectinases: This includes a group of enzymes such as pectinesterase, polygalacturonase, pectin lyase, and pectate lyase which hydrolyze pectin. Pectin is a kind of polysaccharide which gives rigidity and structure and is present in the primary cell walls and middle lamella of plants. These classes of enzymes are most commonly used for the production and clarification of fruit juices. Pectinases can be produced from wastes of strawberry pomace, orange peel, cranberry pomace, apple pomace, citrus peel, sugarcane bagasse, etc., when used as a substrate by *Aspergillus niger* strains (Dhillon et al. 2004; Ahmed et al. 2016). Some pectinase-producing microbes are *Aureobasidium* sp., *Candida* sp., *Cryptococcus* sp., *Klebsiella* sp., *Kluyveromyces* sp., *Penicillium* sp., *Bacillus* sp., *Pseudomonas* sp., *Rhizopus* sp., *Rhizomucor* (Amin et al. 2019). Pectinases are being exploited in wine industries, paper and pulp industries, wastewater treatment, bioethanol production, extraction of DNA from a plant, and protoplast isolation from a plant. In addition, pectinases are expended in the production of animal feed, saccharification and liquefaction of biomass, oil extraction, bio-scouring of cotton fiber, retting and degumming of plant fiber, and tea and coffee fermentation (Kubra et al. 2018; Kashyap et al. 2001). Moreover, pectinases are also used in feed to remove all the antinutritional properties of pectin, augment the viscosity of plant products, and progress digestion in animals (Ajila et al. 2012).

v. Xylanase: Xylanases are a complex and very important group of carbohydrolases. This enzyme group consists of α-glucuronidase, ferulic acid esterase, endo-xylanases, β-xylosidases, p-coumaric acid esterase, and acetyl xylan esterase which breakdown xylan (an important plant polysaccharide) (Beg et al. 2001). Orange discards, apple pomace, sorghum straw, lemon pomace, pear peel, lemon peel, banana peel, soya bean hull, melon peel, and hazelnut casing are used to produce xylanase by *Trichoderma harzianum* (Seyis and Aksoz 2005; Couto 2008), and grape pomace used as substrate by *Aspergillus niger* to produce xylanase (Teles et al. 2019). Xylanases are employed in animal feed industries, food like bread and biscuit industries, wine and beer industries, textile and paper industries, biofuel production, deinking of waste paper. Some of xylanases-producing microorganisms are *Arthrobacter, Micrococcus, Bacillus, Paenibacillus*, *Staphylococcus*, *Streptomyces, Nonomura, Flavobacterium, Cellulomonas, Chaetomium thermophilum, Humicolainsolens, Thermoascus auranticus, Actinomadura, Microbacterium, Rhodothermus*, and *Pseudoxanthomonas* (Alokika 2019; Chakdar et al. 2016). Xylanase together with pectinase and cellulase are commonly used in extracting and clarifying fruit juices and liquefaction of fruits and vegetables (Alokika 2019). Similarly, xylanase with phytase and cellulase in animal feed enhance digestion and absorption of nutrients and xylanase with cellulase and laccase are applied to generate ethanol (Chakdar et al. 2016).

Enzymes Acting on Proteins

i. Proteases: These enzymes are the proteolytic enzymes that break down peptide bonds between amino acids in polypeptide chains. Proteases are one of the frequently significant industrial enzymes used in detergent, food, pharmaceutical, leather, textile, and silk industries. Based on the catalytic residues in the functional site, proteases are sub-categorized into metalloproteases, serine proteases, cysteine proteases, glutamic acid proteases, aspartic proteases, and threonine proteases (Singh et al. 2016). *Bacillus* sp. like *B. licheniformis, B. lentus, B. amyloliquefaciens,* are the most exploited in the industrial sector for protease production (Razzaq et al. 2019). *Aspergillus* sp., *Serratia liquefaciens, Flavobacterium balustinum, Penicillium* sp., *Rhizomucor* sp., *Rhizopus* sp., *Thermoascus aurantiacus, Trichoderma reesei,* etc., are also the proteases producers (Singh et al. 2016). Proteases formed *by Conidiobolus coronatus, Streptomyces avermectnus, and Bacillus subtilis* are used in photographic industries to retrieve silver (Razzaq et al. 2019). Plant also produces proteases which are broadly consumed in food industries and medicine. The varieties of plant proteases (bromelain, papain, ficin) are used in milk clotting, brewing, cancer treatment, meat softening, viral and digestion disorders (González-Rábade et al. 2011). FVWs like jackfruit seed powder, palm kernel cake, olive oil, corncobs, green gram husk, sesame oil cake, black gram husk, chickpea husk (Sandhya et al. 2005; Kandasamy et al. 2016; Prakasham et al. 2006), potato peel, pomegranate peel, karat peel, and mango peel (Panda et al. 2016) can be used as a substrate for proteases production.

ii. Transglutaminases: This collection of enzymes are transferase enzymes catalyzes the formation of isopeptide bonds between proteins. Transglutaminases are also known as protein–glutamine γ-glutamyl transferases. *Actinomadura* sp., *Bacillus circulans*, *B. subtilis*, *Corynebacterium* sp., *Enterobacter* sp., *Streptomyces* sp., *Streptoverticillium* sp. are some of the transglutaminase producers (Kieliszek and Misiewicz 2014). Transglutaminases are used to produce various dairy products, in processing of meat, producing bakery products, and edible films. Transglutaminase has noteworthy impending to enhance viscosity, firmness, water-binding capacity, and elasticity of food products (Kieliszek and Misiewicz 2014).

Other Enzymes

i. Tannase is also known as tannin acyl hydrolase which hydrolyzes tannin into glucose and gallic acid. Gallic acid produces propyl gallate and trimethoprim (Lekha and Lonsane 1997). Various agricultural residues; *Syzygiumcumini*, *Phyllanthus emblica*, *Acacia nilotica,* and *Eucalyptus glogus* (Kumar et al. 2016), *Acacia nilotica, Phyllanthus emblica*, *Syzygiumcumini*, *Zyzyphus mauritiana*, *Eugenia cuspidate* leaves (Selwal et al. 2011) generate tannase by specific organisms. Tannase-producing microbes are *Aspergillus, Penicillium* (Batra and Saxena 2005), *Rhizopus oryzae* (Hadi et al. 1994), *Bacillus licheniformis* (Das Mohapatra et al. 2006), *Klebsiella pneumoniae* (Kumar et al. 2016).

Tannin is present in many edible FV, but they are well-thoughtout as disadvantageous nutritionally because they form complexes with digestive enzymes, starch, protein, and decrease the nutritive significance of food. Tannases are considerably used as a clarifying agent in beer and wine, in producing instant tea, in reducing fruit juices astringency, decreasing anti-nutritional effects of tannins in animal feed, removing tannin from the effluent of leather industry, chemical, and pharmaceutical industries (Lekha and Lonsane 1997; Selwal et al. 2011).

ii. Laccases are the enzymes that have potential to oxidize both non-phenolic and phenolic lignin associated and very recalcitrant compounds. These are used in the reclamation of effluents produced from petrochemical and textile, pulp and paper industries, delignification of lignocellulose, in water purification systems, as a bioremediation agent in soil, tool for medical diagnostics, catalysts for producing constituents in cosmetics, and anti-cancer drugs (Couto and Herrera 2006; Wang 2013). Some of the microbes including *Pleurotusostreatus, Aspergillus, Coriolopsis, Pleurotuscinna barinus, Streptomyces cyaneus, Trametesmodesta, T. versicolor*, *T. trogii, Cladosporium* sp. are laccases producers (Couto and Herrera 2006; Yang et al. 2015). Different FVWs such as apple residues, sugarcane bagasse, apricot seed shell, corncob, etc., are used for laccase production (Yang et al. 2015; Birhanli and Ye silada 2013).

iii. Inulinases act upon inulin which is a polyfructose chain linked by β-2,1-linkage and ends with a glucose unit producing fructose. Inulinases are applied in manufacturing butanediol, lactic acid, citric acid, and bioethanol. Some known inulinases producer are *Actinomyces viscosus, Penicillium* sp., *Saccharomyces* sp., *Chrysosporium pannorum, Streptococcus salivarius, Aspergillus niger, Fusarium oxysporum*, and *Kluyveromyces fragilis* (Chi et al. 2009). Organic low-cost substrates applied for inulinase production are banana peel, orange peel and bagasse, sugarcane bagasse, etc. (Onilude et al. 2012).

4.2 Pigments

The food leftover has high values for biological oxygen demand causing problems in its collection, treatment, disposal, and losing the precious raw materials. The cheaply available FV residues can be used effectively for microbial pigment production that are helpful for making processes economic and eco-friendly. Microbial biotechnology has developed new possibilities for immense utilization of waste in the production of augmented products via fermentation process rather than conventional applications like making compost or feeding cattle as fodder (Panesar et al. 2015). The various synthetic colorants have carcinogenic and teratogenic properties. Thus, food containing synthetic colorants is being avoided and the stipulation for naturally and safely appearing eatable color has increased. Food industries are replacing them with natural pigments like betalains, carotenoids, anthocyanins, and carminic acid. Beetroot (both yellow and red beetroot), colored leafy or grainy amaranth, cactus fruits, and swiss chard contain water-soluble nitrogenous pigments known as betalains. Betalain is composed of yellow betaxanthin and red betacyanin. They act as antioxidants and counteract biological molecule oxidation. Betalains are extensively used in desserts, confectioneries, dry mixes, dairy and meat products like modern food industries (Azeredo 2009).

Carotenoid pigment is found in extensive colored FV like peach, papaya, citrus fruits, green leafy vegetables, carrot, spinach, squash/pumpkin, and more. Different chemical structures of carotenoid are lycopene, carotene, cryptoxanthin, lutein, zeaxanthin, astaxanthin, and fucoxanthin having different functions like performing as pro-vitamin A, and antioxidant. However, carotenoids are used commercially in the feed and food industries as additives, supplements, colorants, and in cosmetic and pharmaceutical industries for nutraceuticals purposes (Jaswir et al. 2011).

A broad array of FVWs such as pea pod powder, fruit pulp, taro leaves, grape waste, okra, soya, and green gram waste are computed as prospective sources of mineral, carbon, and nitrogen to produce microbial pigments (Panesar et al. 2015). Microbial pigments are produced from bacteria, yeasts, mold, and algae by fermentation processes (solid-state or submerged fermentation). However, the amount of exploitation of countless nutrients and production of pigment may vary depending on the fermentation process and organism used. This kind of pigments has functions in the dairy, textile, food, and pharmaceutical industries (Panesar et al. 2015). Some pigments have abilities to fight against protozoal, bacteria, fungi, and are inflammatory and cytotoxic. The pigments play a vital role in upholding optical health and melanins are incorporated in sunscreen creams to guard the skin from ultraviolet radiation (Soliev et al. 2011). Microorganisms like *Serratia marcescens, Penicillium purpurogneum, Monascus* sp. produce red pigment; *Rhodotorula rubra, Monascus* sp., *Bacillus subtilis, Fusarium* sp. produce yellow pigment; *Saccharomyces neoformans*, *Cryptococcus* sp. are black pigment producers, and so on (Panesar et al. 2015).

4.3 Flavoring Agent and Aromas

FVWs can also act as the source for the production of flavoring agents and aroma. Many natural flavoring agents are volatile compounds manufactured from litters using biological transformations. The demand for natural and familiar flavors like vanillin, strawberry flavor, pineapple flavor, etc., are increasing. Vanillin formed from vanillic acid gives vanilla flavor. This vanilla is extracted from *Vanilla planifolia* by microbial transformation, fermentation, and enzymatic reactions. The precursor of vanilla is ferulic acid that is present in pineapple peel, orange peel, pomegranate peel. Vanilla flavor is the leading flavor and vastly used in detergent, food, beverages, pharmaceutical, and cosmetic industries (Tilay et al. 2008; Sagar et al. 2018; Lun et al. 2014).

Furaneol is a critical flavor/aroma compound, developing a flavor of caramelized pineapple in fruits such as pineapples, strawberries, mangoes, raspberries, etc. It imparts fruity and strawberry flavor at low concentration, whereas at high concentration it gives caramel and burnt sugar flavor. Methyl ether is responsible for aroma (Pickenhagen et al. 1981).

Essential volatile oils can be obtained from FVWs like orange peels, citrus peel, lemon peels, fruit seeds, garlic residues, thyme remains, oregano waste, clove residues, basil remainders, cinnamon rests, coriander leftover, ginger coverings, rosemary residues, and peppermint remains. The numerous volatile compounds are existent in the essential oil that retain flavoring and antimicrobial properties (Kalemba and Kunicka 2003). The utmost volatile compounds are alcohols, organic sulfur compounds, terpenoids, and aldehydes (Berger 2007). These essential oils are added in producing fragrances, bath products, cosmetics, household cleaning products, and flavoring of drink and food (Berger 2007). For instance; essential oils extracted from oranges have medicinal values, so they are supplemented as a constituent in gastric, purgative, and flatus-relieving preparations and tea formulations. Additionally, orange oil is applicable in remedying piles, slipping or falling of rectum and uterus, and diarrhea. D-limonene present in lemon improves immunity, pledges irregular moods, stimulates, boosts and activates mind and body, and cares skin by reducing wrinkles (Wadhwa et al. 2013; Berger 2007).

4.4 Dietary Fiber

Nowadays, people are being more health concerned for a healthy lifestyle and are more interested in having fruits rich in minerals, bioactive compounds, dietary fibers, and low in calories, sodium, and fats in their food. Dietary fibers are the indigestible carbohydrates present in plant cell walls and show central responsibilities in human diet together with health (Palafox-Carlos et al. 2011). Plant carbohydrate polymers and other non-carbohydrate components like pectin, hemicellulose, hemicellulose, waxes, polyphenols, resistant protein are dietary fiber (Elleuch et al. 2011). FVWs and agro-industrial by-products are high in fibers thus used as food supplements (Kowalska et al. 2017). Intake of dietary fiber reduces obesity, diabetes, cardiovascular diseases, hyperlipidemia, hypercholesterolemia, and hyperglycemia (Mann and Cummings 2009). Dietary fiber helps in the absorption of antioxidants like carotenoids and phenolic compounds. Dietary fiber also regulates digestion, absorption, and metabolism of nutrients. In addition, dietary fiber increases the fecal bulk, excites colonic fermentation, lowers insulin and cholesterol levels. Dietary fiber serves as food additives and delivers commercial profits to the pharmaceutical, food, and cosmetic industries (Elleuch et al. 2011; Kowalska et al. 2017). Dietary fiber has good water and oil holding capacity, emulsifying or/and gel-forming capacity, and swelling capacity so that it helps in lowering cholesterol, modifying the viscosity of intestinal contents, and forming gel with bile in the intestine (Palafox-Carlos et al. 2011; Elleuch et al. 2011; Ayala-Zavala et al. 2011). The addition of dietary fibers aid to modify the stickiness, consistency, self-life, and sensual characters of the foodstuffs like bakery products, dairy, meats, jams, soups, etc. However, the addition of fiber must be in the appropriate percentage otherwise it may produce detrimental changes in shade, flavor, and quality of foods (Elleuch et al. 2011). In bakery products, dietary fibers prolong the freshness, retain water, loaf volume, and flexibility thereby enhance digestion. Similarly, in dairy products like ice cream, the addition of fiber develops texture and managing properties by hampering crystal progression while storing (Elleuch et al. 2011; Ayala-Zavala et al. 2011).

4.5 Organic Acids

Organic acids have weak acidic properties and are produced from various organic matter by microbial processing. Those organic acids are branded building block chemicals and are used in food administering, gas and oil stimulation units, feedstuff and nutrition industries, drugs, esthetic and chemical industries, etc. Lactic acid, acetic acid, and citric acid are some organic acids which are manufactured from FVWs (Panda et al. 2016; Sauer et al. 2008). The selection of organism used and carbon source that enhances the growth of organism influence by-product formation and costs of the organic acids production procedure.

4.5.1 Citric Acid

Commercially important bio-product, citric acid acidifies and enhances flavor in food, medical and brew products. FVWs like apple pomace, cassava waste, pineapple waste, and maosmbi waste are used in citric acid production (Couto 2008). Citric acid can be manufactured either by submerged or solid-state fermentations utilizing various molds, yeasts, and bacteria. Of total citric acid produced, approximately 99% is through microbial procedures. Most popularly known citric acid-producing microbes are *Yarrowia lipolytica, Candida tropicalis, C. catenula*, *C. guilliermondii*, *Aspergillus niger*, and *A. wentii* (Max et al. 2010).

4.5.2 Acetic Acid

Acetic acid can be produced from FVWs. It is most commonly used as vinegar in almost all countries although the concentration of acetic acid varies in vinegar. The vinegar contains 4.1–12.3% of acetic acid in Canada produced vinegar (Panda et al. 2016). Acetic acid bacteria family includes *Endobacter, Acetobacter, Gluconobacter, Acidomonas, Bombella, Commensalibacter, Gluconacetobacter,* etc. For vinegar production, *Acetobacter, Gluconacetobacter, Gluconobacter*, and *Acidomonas* are recommended because they can highly oxidize sugar, sugar alcohol, and ethanol into acetic acid. Those bacteria are unaffected by acetic acid produced in fermentation media (Gomes et al. 2018).

4.5.3 Lactic Acid

Lactic acid is a high-value organic acid, commonly being expended in beautifying, food, leather tanning, and pharmaceutical industries. About 70% of lactic acid produced is consumed in yogurts and cheese-producing industries as acidulant and preservative. Lactic acid acts as a precursor for synthesizing polylactic acid, biodegradable composites in bioplastic production. Polymers of lactic acid are biodegradable, biocompatible, and have moisturizing, antimicrobial, rejuvenating, emulsifying properties. Thus, lactic acid has the potential to be used in various industries (Martinez et al. 2013). Bio-production of this acid is aided by various microorganisms using no cost or less cost substrate like fruits vegetables by-products and FVWs. Microorganisms including *Bacillus sp., Rhizopus sp., Saccharomyces cerevisiae, Kluyveromyces lactis, Pichia stipites, Lactobacillus casei, L. delbrueckii*, *L. plantarum,* etc., are lactic acid producers. FVWs like green peas remains, sweet corn waste, mango and orange residues, cassava residue, and potato peel can be used as low-cost substrates to produce lactic acid (Sagar et al. 2018; Martinez et al. 2013; Kong et al. 2019).

4.6 Bioenergy

The decrease in fossil resources and feedstocks, the ecological problems associated with greenhouse gas emissions, and also the increase in oil price are forcing to search for alternative resources for the production of transport fuels, energy, and compounds. In such cases, organic wastes and their intrinsic chemical complication are possible to be utilized as important resources for the generation of bioenergy like hydrogen, ethanol, and biodiesel. The feedstock, i.e., FVWs undergo changes during various fermentation processes before production of final bioenergy (Uçkun-Kiran et al. 2014; Sanders et al. 2007).

4.6.1 Bioethanol

Bioethanol commonly known as ethyl alcohol is a colorless liquid, decomposable, less toxic, and is used to power automobiles. Bioethanol can be produced from fermentable sugars like glucose, sucrose, etc., of plant sources (fruits and vegetable wastes) using microorganisms. Bioethanol produced from plant sources is CO_2-neutral because CO_2 is released while combustion of bioethanol is equal to the CO_2 absorbed by the plant during the growing phase (Chin and H'ng 2013). One of the most common and well-known bioprocesses for bioethanol production is yeast-catalyzed production method. Bioethanol production from wastes comprises steps such as biomass pretreatment and saccharification followed by fermentation of sugars. Different researches have been performed by using different FVWs like potato peel, apple pomace, apple waste, banana peel, banana waste, pineapple waste, soybean litter, and soybean molasses for bioethanol production using *Saccharomyces cerevisiae*. Mushimiyimana and Tallapragada also used agro-waste including peel of carrot, onion, sugar beet, and potato to produce bioethanol. In this process, *Penicillium* sp. and *Saccharomyces cerevisiae* are used for hydrolysis and fermentation to produce bioethanol, respectively (Mushimiyimana and Tallapragada 2016). Ingale and friends synthesized bioethanol from banana discards after pre-treating with *Aspergillus ellipticus* and *A. fumigatus* (Ingale et al. 2014). Bioethanol is consumed in fuel industries, pharmaceuticals, cosmetics, beverages, and chemical industries. It has been used as adhesive in dyes and paints, raw materials for plastics, preservative, solvent for spirits industries, disinfectant, bleaching agent, and cleaning agent, etc. (Chin and H'ng 2013).

4.6.2 Biohydrogen

Biohydrogen is universally recognized as complementary to fossil fuels due to its non-polluting feature, less costly, and renewable source. Hydrogen gas includes 2.75 times greater energy yield than hydrocarbon fuels and it is carbon neutral. This can be considered as a clean fuel and energy carrier without CO_2 releases and can be easily operated in generating electricity (Kapdan and Kargi 2006). With the development of sustainable and minimization of waste policy, biohydrogen production is realized from renewable sources, also known as green technology. Hydrogen can be made by different processes; electrolysis of water, biological processes, and thermocatalytic reformation of hydrogen-rich organic compounds (Kapdan and Kargi 2006). Biological processes for hydrogen generation using microorganisms is an exciting approach and includes different methods including direct biophotolysis, indirect biophotolysis, dark fermentation, and photo fermentation. Biophotolysis refers to breaking water molecules by microbes like green microalgae and cyanobacteria into hydrogen and oxygen in presence of sunlight, whereas fermentation process refers to the production of biohydrogen by converting organic compounds as an energy source by microbes in the absence or presence of light (Levin et al. 2004; Rahman et al. 2016). Biohydrogen is produced as a secondary outcome during anaerobic alteration of organic wastes, whereas in photosynthetic processes microorganisms use carbon dioxide and water for hydrogen production (Levin et al. 2004). Different wastes like potato waste, pumpkin waste, fennel waste, olive pomace, leafy vegetables like cabbage, water celery, cauliflower, etc., can be a substrate for biohydrogen production (Ghimire et al. 2015; Lee et al. 2010). Some biohydrogen producers are *Clostridium butyricum, Bacillus sp., Escherichia coli, Rhodobacter sphaeroides, Rhodopseudomonas palustris, R. faecalis, Rhodospirillum rubrum*, etc. (Rahman et al. 2016). The principal application of biohydrogen is utilization as a fuel cell for generating electricity, however, during the production of biohydrogen other gas such as ammonia, methane, hydrogen sulfite may be produced (Levin et al. 2004; Rahman et al. 2016) which can be used for advantages.

4.6.3 Biomethane

Biomethane is a cheap form of bioenergy which can be produced from anaerobic digestion of biogenic wastes by different microbes. The practice of vegetable waste to generate biogas is environmentally friendly and resolves the residual disposal problem, air and water pollution, soil contamination, and lowers reliance on wood fuel. During anaerobic digestion, the acidogenic microbes are responsible to produce acetate, carbon dioxide, and hydrogen. This produced hydrogen along with acetate is digested by methanogens into water and methane. The charging rates of biodegradable organic FVWs should be proper to produce methane. For example, if loading of organic waste is high, the digestion by acidogenic microbes increases, while methanogenic microbes are unable to increase which results in the termination of methane production. Biomethane production involves hydrolysis, methanogenesis, and acidogenesis that are completed by a sequence of microbial interactions. However, the products differ with the type of bacteria involved (Singh et al. 2012). A previous study used vegetable waste like salad leaves, potato peelings, green peas, and carrots remains in a number of phase transitioning reactors and a focal reactor to produce biomethane (Raynal et al. 1998). Organic waste influences excessive production of methane and processed slurry formation. This processed suspension can be applied in conditioning soil or biofertilizer (Singh et al. 2012).

4.6.4 Biodiesel

Biodiesel is a renewable and clean-burning liquid biofuel which consists of low aliphatic alcohols and esters of alkyl groups having high fatty acids. Biodiesel can be considered as "carbon neutral" because this biofuel produces no net output of carbon dioxide. In addition, biodiesel is inexhaustible and perishable energy which reduces very fast (4×) than fossil fuel, has greasing assets that reduce engine wear, and is secure for storing and management due to low explosiveness and a high flash point of 100–170 °C (Ramirez-Arias et al. 2018). Transesterification is a commonly applied procedure of producing biodiesel, requires only low temperature and pressure, and produces 98% conversion yield (Muniraj et al. 2015). However, supercritical fluid extraction methods can also be applied to extract biodiesel from oilseed (Lee et al. 2010). In the transesterification process, triglyceride reacts with alcohol to form biodiesel and crude glycerol. Fruits and vegetable wastes rich in lipids or oil such as rapeseed, palm, soybean, and canola are used in biodiesel manufacture (Lee et al. 2010; Muniraj et al. 2015). The choice of feedstocks plays a critical role in regulating the cost of diesel (Singh et al. 2012). Vegetable oils are countered with ethanol in the existence of catalysts in biodiesel production (Stamenkovic et al. 2011). Approximately 100% of the yield of biodiesel was obtained by Lee et al. from canola oil waste employing supercritical fluid extraction methods. Biodiesel can also be recovered from microbial oils/lipids thus, oleaginous microorganisms (capable of accumulating lipids) including algae, yeast, and fungi can be probable feedstocks for manufacturing biodiesel (Muniraj et al. 2015; Zhang et al. 2016). In the study of Surendra et al., larvae of *Hermetia illucens* were used in efficient organic waste management, and the larvae were cultivated on food trash to yield fat plus prepupae rich in protein. These black soldier fly prepupae derived oil was converted into high-quality biodiesel (Surendra et al. 2016).

4.7 Bioplastics

Bioplastics are the biopolymers as plastic material having mechanical endurance, easy processability, chemical apathy, weightlessness, flexibility, and produced from renewable sources. Bioplastics are biodegradable and can be synthesized from FVWs. Biopolymers have obviously prevailing starch, cellulose, protein, lignin, natural rubber-like molecules. The main important component of bioplastic is polyesters and the biodegradable polyesters are in different commercial forms. The commercial biodegradable polyesters are as follows; polybutylene succinate adipate (PBSA), polylactic acid (PLA), polyhydroxyalkanoate (PHA), polyglycolic acid (PGA), polybutylene succinate (PBS), aliphatic–aromatic copolyesters (AAC), polybutylene adipate/terephthalate (PBAT), and polymethylene adipate/terephthalate (PTMAT). Among these, PLA and PHA are the most important synthetic bioplastics (de Moura et al. 2017; Esparza et al. 2020). PLA can be obtained from the processing of renewable carbohydrate sources like corn into dextrose and further followed by bacterial fermentation in which dextrose is converted into lactic acid. PLA is biodegradable, decomposing to give H_2O, CO_2, and humus (Drumright et al. 2000). Bacteria that are employed in the production of PLA belongs to *Lactobacillus* genus such as *L. acidophilus, L. amylophilus, L. casei, L. maltaromicus, L. salivarius, L. delbrueckii, L. bavaricus, and L. jensenii* (Nampoothiri et al. 2010). FVWs like sugarcane and cassava bagasse, potato wastes, tapioca, corn stover, carrot waste, beet syrup, sweet sorghum, etc., may be used for PLA invention. PLA is applied in releasing controlled drugs, fixing bone fixation, composites implantation, packaging, coating paper, releasing sustained pesticides and fertilizers, etc. (Nampoothiri et al. 2010; Castro-Aguirre et al. 2016).

PHAs are the second most essential synthetic bioplastics after PLA (Esparza et al. 2020). PHAs are polyesters that are synthesized from the polymerization of various hydroxy alkanoic acids by microorganisms. These microorganisms accumulate this biopolymer in the cytoplasm as stored energy. Some bacteria and filamentous fungi can produce enzymes to decompose PHAs. Pomace from fruits like apricot, cherries, grapes can be a carbon source and recycled culinary oil as a precursor for PHAs production (Follonier et al. 2014). PHA-producing microbes are *Ralstonia eutropha, Pseudomonas oleovorans, Chromatium vinosum, Thiocapsapfennigii*, etc., and these microbes have PHA synthase enzyme. Bioplastic has a wide range of applications like in manufacturing latex paints, in medical application with tissue engineering, to obtain enantiomeric pure hydroxyalkanoic acid, etc. (Steinbüchel 2001).

4.8 Exopolysaccharides (EPS)

EPS are polysaccharides secreted by microorganisms outside the cell or in the medium throughout the growth phase and occur as capsule or slime. EPS varies with exceptional physical and chemical characteristics. EPS manufactured by lactic acid bacteria are considered harmless and used as food additives or as functional food ingredients (de Vuyst et al. 2001). However, few EPS can provide infectious and immunogenicity which differs in different species of microorganisms (Weiner et al. 1995). EPS can be homopolysaccharides like D-fructose and D-glucose having indistinguishable monosaccharide units and heteropolysaccharides consisting of different monosaccharides in distinctive proportions (de Vuyst et al. 2001). EPS can be used as a corporal barrier, in cell/cell identification and cooperation, a rejoinder to conservational stress, and in biofilm expansion/adherence (Weiner et al. 1995). Some of the microbial EPS advantageous in industries are dextran, xanthan, pullulan, and gellan secreted by *Leuconostoc mesenteroides, Xanthomonas campestris,* and *Sphingomonas paucimobilis,* respectively. Microbial EPS are particularly used to improve the consistency, rheology, and flavoring properties of dairy products that increase both wellbeing and financial benefits (Esparza et al. 2020; de Vuyst et al. 2001). The Food and Drug Authority approved xanthan as a food additive biopolymer after that the insistence of xanthan has been increasing. Xanthan is used in cosmetics, pharmaceutical, textile, petroleum, and especially the food industry (Esparza et al. 2020). Pullulan is a decomposable polysaccharide found in the culture medium of *Aureobasidium* *pullulans*. This biopolymer is applied as covering in food, as a low-fat constituent, as a prebiotic, as surface-active and stabilizing agent, as denture adhesives, as drug transporter, vaccinations, and capsule coating, etc. (Esparza et al. 2020; Prajapati et al. 2013). Generally, synthesizing pullulan, xanthan like exopolysaccharides are relatively expensive because glucose and/or saccharose are used as the solitary carbon source for the growth of microorganisms. However, carbon source from cassava waste, potato waste, coconut waste, sugar cane waste, sugar beet waste, maize waste, orange waste, asparagus waste, etc., can be expended so as to reduce the production costs which further reduce the disposal problem and encourage the re-use of waste (Esparza et al. 2020).

Heteropolysaccharides are long-chain polymers when suspended or dispersed in water, display gelling characteristics. This thickening property is essential in the formulation of some food products. Such polymers are also applied for stabilization, emulsification, suspension of particulates, crystallization control, encapsulation, film formation, and syneresis inhibition (Vendruscolo et al. 2008). Heteropolysaccharides producing bacteria are *Lactobacillus* sp., *Streptococcus thermophilus, Lactobacillus lactis, L. helveticus, L. delbrueckii,* etc. Different wastes like apple waste, soy waste, etc., are utilized by microorganisms in producing heteropolysaccharides (de Vuyst et al. 2001). The most common natural heteropolysaccharide found in FV peels and used in different industries for the production of various products is pectin (Tan et al. 2018). Pectin heteropolysaccharide is a normal food element for jellies, jams, and marmalades, for treating diarrhea with calcium salts due to its gentle decline in the intestine, has prebiotic effect stimulating belly health by regulatory microbial inhabitants (Tan et al. 2018). Pectin produced from different sources varies in properties, for example, apple pectin solidifies superiorly to citrus pectin. However, apple pectin has inferior properties to mango pectin (Adi et al. 2019). Thus, heteropolysaccharides like pectin can be produced from organic wastes so that it assists in declining the production cost, pollution, and environmental cleanliness.

4.9 Single-Cell Protein (SCP)

SCP is a protein that originated from microorganisms such as algae, bacteria, fungi, and yeast. Those microorganisms can utilize various carbon sources for SCP synthesis. For human consumption, SCP is commonly produced from filamentous fungi and yeast. However, bacterial SCP is generally used in feed industries (Ritala et al. 2017). Different FVWs can be used as cheap or no cost carbon source for the growth of microorganisms and SCP production (Najafpour 2007; Mondal et al. 2012). These substrates include pineapple waste, banana peels, pomegranate peel, watermelon waste, beet pulp, papaya waste, corn cob, soybean waste, orange peels, cucumber peels, etc. SCP producing expertise is an appropriate practice for transforming unwanted materials into useful protein. *Aspergillus oryzae, A. flavus, A. niger, Fusarium semitectum, Rhizopus oligosporus, Saccharomyces cerevisiae, Trichoderma harzianum, T. reesei, Penicillium javanicum, Kluyveromyces marxianus*, etc., can be used for SCP production (Malav et al. 2017). The production of SCP relates to the type of substrate availability, constituents present in media (Mondal et al. 2012), and environmental conditions (Reihani and Khosravi-Darani 2018). There are few steps for SCP production. General steps are (a) preparation of culture media, (b) cultivation, (c) extraction and intensifying SCP, and (d) final processing of SCP. SCP initially was popular during war times in human nutrition, when conventional protein sources were not sufficient. It is again becoming important to fulfill the protein demands of an increasing population, and can also be used in livestock feed as a protein source. Algal SCP offers omega-3 fatty acids, vitamins, carotenoids along with protein, and thus SCP is used as food supplements. Production of SCP utilizes methane as a carbon source and helps to reduce greenhouse gas emission as well (Ritala et al. 2017).

5 Conclusion and Future Prospects

The increase in population, as well as fruits and vegetable consumption with increase in nutrition awareness, is generating a huge amount of FV wastes. However, some nutrients and compounds existent in FV wastes can be potential sources for feeding animals, making organic fertilizer, or for producing value-added products. On the whole, it can be concluded that FV wastes can be reused as cheap or no cost substrate in yielding various value-adding products like biologically active compounds, enzymes, pigments, bioenergy, etc. Those valuable compounds are helpful to lessen the overall production cost. For example, producing enzymes or biopolymer from fruits processing waste and essential oils from fruit peels are value-adding products that may reduce the entire production cost. In addition, appropriate utilization of food sources minimizes the production of food trashes and disposal problems and also helps in solving hunger problems of increasing population. Moreover, the sustainable utilization of resources from FVWs can reduce greenhouse gas emission, and finally, waste can be converted into wealth.

With the adoption of advanced techniques such as protein and/or genetic engineering, molecular biology, and bioinformatics the researchers can generate improved microbial strains to consume FVWs and prevent losing valuable compounds from wastes. Thus, effort has to be made in the development and adoption of efficient microbial strains, for example, plethora of enzyme production in heterologous hosts and their reformation by protein engineering or chemical resources can achieve dynamic and effective enzymes. Such strains can be utilized in the commercial production of different value-added products from wastes by reducing the investment cost and minimizing the waste production.

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Biological Methods for Carbon Dioxide Conversion and Utilization

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Abstract

Over recent decades, massive greenhouse gas (GHG) releases in the environment by anthropogenic activities have contributed to global warming. It is also important that additional pollutants are reduced, or emerging solutions are created to prevent repeated CO_2 accumulations. Biological processes in nature can evaluate ambient CO_2, but the biological mechanism cannot absorb and use all CO_2 in metropolitan and commercial environments where a large concentration of CO_2 production is observed. Specific chemicals and plastic goods with CO_2 absorption properties are not environmentally friendly or rather pricey. The usage of CO_2 as a raw material at an industrial level is less important than the excess. Mechanisms for the production, aggregation, and utilization of carbon have developed in nature. The photosynthetic and organic species assimilate and eventually transform CO_2 into complex molecules. Over the last three decades, extensive work has been conducted to identify chemical and ecosystem transformations of CO_2, over numerous biological and synthetic materials including lactones, exopolysaccharides, bioplastics, microbial alcohols, carboxylic acids, esters, and biodiesel polymers.

Keywords

CO_2 • Conversion • Climate change • Greenhouse gases • Emissions • Pollution

1 Introduction

The latest trend of strong human-induced anthropogenic carbon dioxide (CO_2) pollution has risen to 35.7 billion tons a year (Olivier et al. 2012). The resultant emissions of ambient carbon dioxide, along with methane and nitrous oxide in at least 800.000 years, were unparalleled and were considered to be the main source of global change as per the Intergovernmental Panel on Climate Change (IPCC). As a result, the 1983–2012 period was potentially the mildest 30-year period in the Northern Hemisphere over the past 1.400 years (Pachauri et al. 2014). CO_2 emissions are mainly induced by the burning of fossil fuels and the disposal of steel mills, thermoelectric power stations, cement stations, and refineries. A worldwide deal has recently been signed at the 2015 United Nations climate change conference, COP 21 in Paris, France (Sutter and Berlinger 2015) to decrease pollution from zero net greenhouse gasses and to restrict temperature changes to an average of 1.5 °C over the twenty-first century.

In addition to implementing greenhouse gas mitigation steps, CO_2 is also an effective method to minimize CO_2 pollution. CO_2 is used as a feedstock to manufacture chemicals and electricity. Methods would also be addressed

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for the safe transfer of CO_2 to chemicals and products with little or even negligible pollution. Indeed, carbon dioxide may be specifically scavenged (or with time possibly absorbed by the air) from industrial greenhouse pollution systems, turned into essential chemicals and fuel chemicals, otherwise extracted from the petroleum production with fossil oil. The safe low-temperature solution for such transformations is biocatalytic conversion. A variety of biological cycles include the fixation of enzyme CO_2 or the conversion step, as the most prevalent of natural CO_2 transformations is the Kelvin cycle (Shi et al. 2015), but there is no serial reduction of the CO_2 enzyme to methanol (CH_3OH) in nature. Kuwabata et al. (1993, 1994) confirmed, in 1993 and 1994, that CO_2 can be biocatalytically transformed to CH_3OH in the solution of a CO_2-saturated phosphate buffer. The dehydrogenase (EC 1.2.1.2) type and the dehydrogenase methanol (EC 1.1.99.8) existence as an electron mediator, they used electrolysis to transform by formaldehyde.

Recent studies based on the concepts, redox chemistry, processes, and enzyme energy for the processing of CO_2 including analysis of key pathways of metabolism in cells (Alissandratos and Easton 2015; Sultana et al. 2016; Long et al. 2017) and the consideration of methodologies and materials for enzyme immobilization have arisen due to their substantial and growing importance in carbon-reduction technology. But the difficulty in implementing a cascadic dehydrogenase enzyme reaction mechanism for CO_2 conversion into CH_3OH can be overcome by the usage of powerful and reliable enzymes and the construction of a workable, stable, and highly successful reaction mechanism. Therefore, the mechanism will ensure that the biocatalytic productivity rate of enzymes and the quality of usage of cofactors are maximized. Enzyme immobility is in attention since Obert and Dave (1999), Mushtaq et al. (2014a) verified enhancement in the production of methanol in a porous silica solution by embedding the three dehydrogenases in NADH with porous silica gel solution and being exposed to CO_2-bubbles to increase biocatalytic efficiency by optimizing frequent enzyme usage and containment (Sagir et al. 2014a).

2 Chemistry of CO_2 Utilization in Biorefineries

To reduce CO_2 released from the emission from the asnthropogenic source into the atmosphere, carbon capture and utilization (CCU) technology is being tested. Through highly efficient technology, CCU can overcome energy scarcity and direct processing under moderate conditions of the industrial CO_2 pollution into useful goods and chemicals (Sagir et al. 2014b, 2016). This approach is of immense significance to capture and transform CO_2 into added-value chemicals or intermediates at the same time as it provides a new waste disposal technique. Various methods for transforming carbonates, poly (carbonates), carbamate derivatives, and carboxylic acids into usable products have been developed (Peters et al. 2011; Yoshida and Ihara 2004). Using carbonates of CO_2 and epoxy cycloads and transformations, cyclic carbonates are known as excellent polar aprotic solvents and strong chemicals (Beckman 2004; Thakur et al. 2018). Many metal complexes (e.g., Mg, Al, Ca, and In) as well as transforming metal complexes (e.g., Zn, Fe, Cr, Co) and organo-catalysts were developed to quantify such reactions (Beckman 2004). There are certain limitations in a large number of catalytic systems that require high (>100 ° C), high (>10 bar), or broad catalyst loadings (>5 mol%). Owing to the usage of energy and rising environmental issues, chemical CO_2 fixation is extremely desirable (Talebian et al. 2015; Shahzad et al. 2018). Various catalytic routes can use CO_2 in the manufacture of valuable industrial chemicals and fine goods. Nevertheless, it was important to increase the yield of the product and its molecular weight copolymers. Through turning the C–O, C–N, C–C, and C–H bonds into useful goods and oils, CO_2 may be chemically converted. Bond formation includes the development of oxazolidinone, quinazoline, urea derivatives, carbamates, isocyanates, and polyurethanes; bond-forming requires the processing of carboxylic acids and their derivatives; bond creation involves methanol and the formic acid derivatives; and bond creation includes the synthesis of C–O and polycarbonates (Mushtaq et al. 2014b; Azam et al. 2014; Thakur et al. 2018).

2.1 C–O Bond Formation

CO_2 is used as a raw material in cyclic carbonates synthesized into epoxides after injecting CO_2 and then processed cyclic carbonate in five components that can be used by electrolytes in secondary batteries, aprotic polar solvents, raw chemicals preparation, polycarbonate, and polyurethane precious monomers (Ju et al. 2007; Yang et al. 2012). Many catalytic systems (homogeneous or heterogeneous) have been developed from this reaction in recent years. In the production of polycarbonate and some other chemicals, as a stable, non-corrosive, and environmentally sensitive structure, the synthesis of Dialkyl carbonates is done with the use of CO_2 for raw material, particularly dimethyl Carbonates (DEC). The DMC synthesis method relies on the reaction of methanol and CO_2 to water which causes the balance to change to DMC in the presence of dialkyl tin oxide as a catalyst and acetal. Including the reaction, chemical agents such as metal oxides, metal carbonates, metal hydroxides, metal alcoholics, polymer products, or active polymer complexes, such as polyoxometalates and carbodiimides, are also catalyzed. Polycarbonate synthesis by utilizing metal catalyzing CO_2 and epoxide copolymerization is a convenient path to use CO_2 (Mushtaq et al. 2014c; Sagir et al. 2014c; Thakur et al. 2018).

2.2 C–H Bond Formation

Formic acid is an important intermediate chemical and essential agricultural, commonly used industrially. The organic synthesis is closely linked to the current phenomenon in green chemistry, through catalytic hydrogenation and CO_2. As a novel substitute for the current fuel option, methanol is now an essential component of the chemical industry due to its high-octane level. At the same time, methanol can be used as a preponderant or intermediate raw material to manufacture other fuels and valuable products in industries (Himeda et al. 2005).

2.3 C–N Bond Formation

Heterocyclic compounds such as oxazolidinones are important chemicals that demonstrate various applications as intermediate and chiral auxiliaries for organic compounds in their synthesis. Cyclic carbamates such as 5-substituted oxazolidinones are used commonly as components of biologically active substances for the preparation of medicinal and agricultural substances. The processing of oxazolidinones is primarily assisted by five synthetic paths. It can be synthesized through the use of C1 feedstock by carbonizing amino alcohols into phosgene, carbon monoxide (CO), CO_2 injection into the aziridine process, CO_2 reaction through amino alcohols, CO_2 reaction with acetylene amines and three-step propargylic alcohol processes, and amines and CO_2 usage as an important raw material. Urea derivatives may be specifically synthesized through the catalytic process of CO_2 and amines. Amine carbamation is widely used for the production of organic carbamates in the area of medicinal products such as medicines, pre-drugs, and intermediate medicines. In the presence of tin compounds, amine and CO_2 chemically combine with alcohol as a catalyst, by dehydrating acetal, to capture water in this cycle to recycle the alcohol. The conventional industrial route of isocyanates include either CO or phosgene as a carbon source is a striking approach to isocyanate chemical synthesis (Liu et al. 2017).

2.4 C–C Bond Formation

A substituting source of carbonyl provides greener pathways for potential possibilities for the chemical processes, with the valuable industrial transitions that are used as reference molecules for the carboxylic acid derivatives. In the method of green chemistry, the inclusion of CO_2 in certain organic substrates will provide useful products for the creation of new C–C bonds in catalytic successions. Acrylic acid and its derivatives are synthesized on a large scale through the oxidation of many precursors such as propylene, acrolein, and acrylonitrile hydrolysis (Lin 2001). The most compelling and upcoming simple method for processing acrylic acids is carboxylation of an alkene by explicitly utilizing carbon nucleophiles and CO_2 because the usage of CO_2 as a safe and repeatable C1 fuel will avoid the use of insensitive reaction conditions. Carboxylation of CO_2 heterocyclic aromatic compounds creates essential molecules and organic chemicals for medicinal purposes (Fischer et al. 2006).

3 Potential of Biological Conversion of CO_2

The Bio-fixation of CO_2 by microorganisms is a way to prevent climate disasters. Carbon sequestration through bacteria is not just a renewable yet safe solution for the prevention of global warming. The major advantage of the usage of carbonic anhydrase (CA) microbes to transform CO_2 is that CO_2 is processed through a broad variety of metabolism pathways. Several bacterial generations generate active CA, transforming CO_2 into bicarbonates and $CaCO_3$ in the presence of Ca^{2+} ion (Bermúdez et al. 2013). $CaCO_3$ is the component that can quickly be isolated and used for different industrial applications such as cement, pottery, sugar grinding, glass, iron, and steel (Shi et al. 2015; Thakur et al. 2018; Bhagat et al. 2018; Yadav et al. 2014). CA is either extracellularly present in bacteria in conjunction with periplasm or within the cytoplasm (intracellular) (Leung et al. 2014). In the presence of zinc, copper, and cadmium, Sharma et al. (2009) washed out the extracellular CA from *Pseudomonas fragi*. Much of the microbial CA rely on metals and its behavior is mainly related to divalent metal ions. The literature survey also showed the capacity for the development of calcium carbonate precipitates of microbial CA in CO_2 conversion. In a previous study, an estimate of the number of calcium carbonates produced in the presence of calcium ions was used to evaluate the CO_2 conversion capacity of *Aerobacillus pallidus* and bovine carbon anhydrase (BCA). In the recorded experiment, the flue gasses were initially cooled to 60 °C. A more effective CO_2 conversion by *A. pallidus* than BCA has been published (Bose and Satyanarayana 2017a). *A. pallidus* was stable between the temperature range of 40–60 °C, in contrast to the BCA which tolerates temperatures between 35–40 °C, tolerating harsh conditions required for the industrially controlled cycle. The CA from *Lactobacillus delbrueckii* was reported and the calcium carbonate synthesized by Li et al. (2015)

was 50. At 50 bars with a half-life of 177 h, this AC was highly stable. Moreover, the sequestration by thermo alkotolerant CA from *Bacillus sp.* has been recorded by Thakur et al. (2018). The enzyme was stable to 90 °C with a half-life of 25.36 min, allowing cooling costs and time-saving more valuable for industrial CO_2 conversion. Moreover, Jo et al. (2014) have confirmed that recombinant enzymes have a half-life of over 70 days, at 50 °C, of the *Perse-phonella Marina* and *Thermovibrio Ammonificans* clones and their expression. Also, under elevated temperatures, this CA rapidly accelerates $CaCO_3$ mineralization from CO_2. Such experiments have shown concretely the usage of CA as a successful CO_2 conversion candidate. These biological catalysts are able to survive extreme environments over a prolonged period of time and are also technological obstacles for their use (Sagir et al. 2014d) (Fig. 1).

4 Mechanism and Catalytic Activity of Biological Methods

CA has been classified based on the protein sequence into five structurally distinct classes: α, β, γ, δ, and ζ. Such groups vary in oligomeric status and total fold. The ion is zinc in α, β, γ, and δ form, but the cadmium as metal ion is in the ζ class. In the b, d-CA, zinc is linked with three ligands of histidine and water, while three histidine and two cysteine molecules have been substituted in the b-CA. However, the alignment of metal ions in z-CA is identical with b-CA apart from cadmium metal ions (Kim et al. 2019; Lionetto et al. 2016). In the presence of metal ion(s) attached in the active region, CA is catalytically active (Sagir et al. 2014a; Ullah et al. 2015; Kisker et al. 1996). Using the PyMOL as given in (Fig. 2), a comprehensive three-dimensional structure of *Methanosarcina thermophila's*

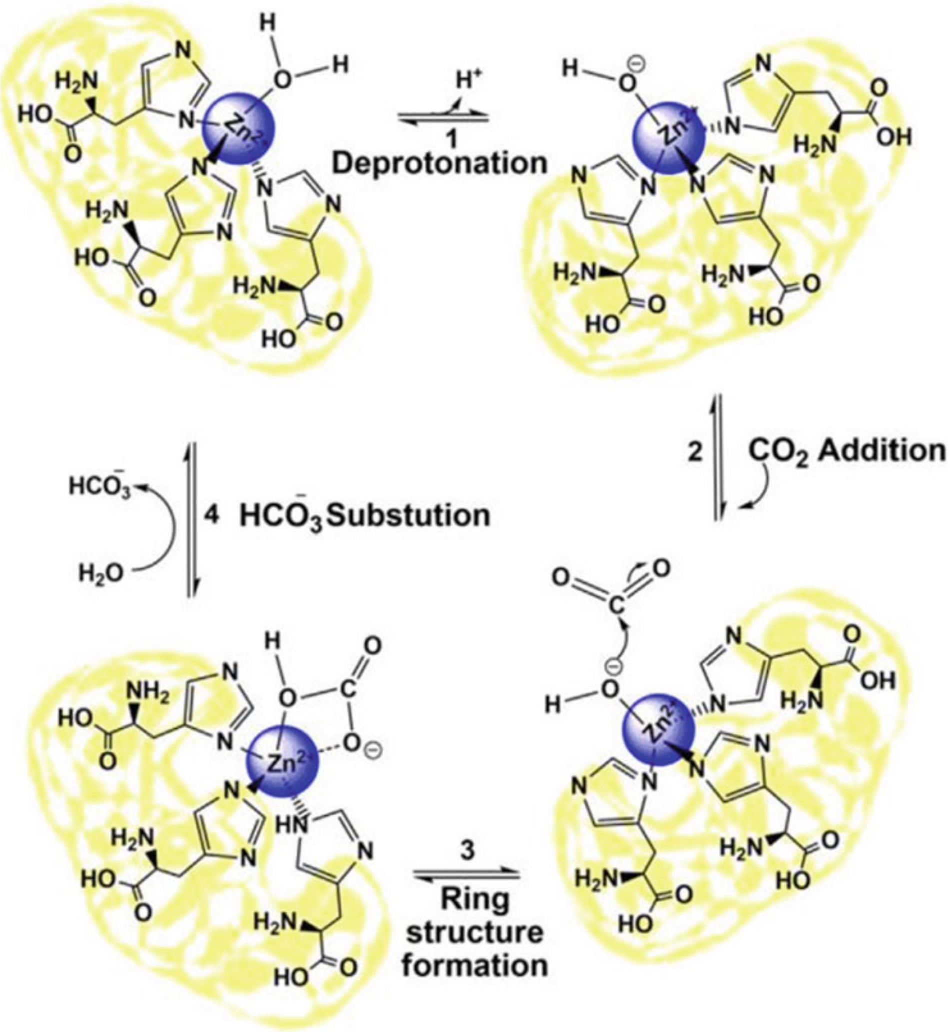

Fig. 1 CA process for the oxidation of CO_2 to carbonates in the environment (Sharma et al. 2020)

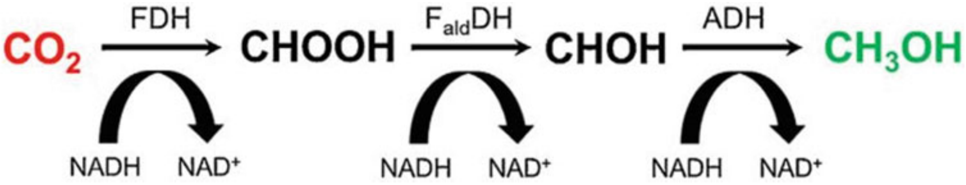

Fig. 2 CO_2 transformation to CH_3OH via the biocatalytic process

CA class is seen. CA kinetic study has shown that both groups have the same iso-mechanism in two phases (Smith et al. 1999; Syrjänen et al. 2010). A structural CA analysis reveals that the active site of the enzyme varies according to the form of CA. The catalytic triad is mainly constituted by three amino acid waste and water/hydroxide molecules that create a coordination relation with the metal ion (Mushtaq et al. 2015; Talebian et al. 2018; Sagir et al. 2018; Somalinga et al. 2016). The active CA site has two dominant regions, one hydrophobic area and the other half the hydrophilic zone. Hydrophobic amino acids (Val 207, Leu-198, Val-121, Thro-199, Val-143, and Trp-209) play a significant function for the CO_2 molecule in its trapping, while those that are induced by hydrophilic amino acids (Asn-67, Asn-62, Thr-200-Og1, His-64, Tyr-7, and Thr-199-Og1) are responsible for proton movement and generation of bicarbonate from CO_2 via hydration reaction (Ullah et al. 2019a; Domsic and McKenna 2010; Miscione et al. 2007; Sahoo et al. 2018). The first step is the proton release from zinc bound to water to produce Zn-hydroxide ion; (2) hydroxide ion attacks atomic CO_2, (3) the product (bicarbonate tetrahedral intermediate) formation occurs; (4) in the last point, the insertion of a water molecule and the completion of a catalyst process replace the zinc-bound carbonate (Ullah et al. 2019b; Tahir et al. 2019; Aggarwal et al. 2015; Jiang et al. 2003).

5 Biological Transformation of CO_2 to Methanol

Three NADH moles are taken per mole CH_3OH formed by the use of the CH_3OH enzymes in the forward cascade reaction (Fig. 2). By using three dehydrogenases (Obert and Dave 1999). Besides, CH_3OH outputs were determined based on the inserted original NADH. For example, the number of moles CH_3OH generated for a production of 100% is equal to the number of 1/3 of the original NADH. The overall performance of the enzymatic cascade reaction, which converts CO_2 to the CH_3OH solution, was seen early on if the reaction was carried out in a solution with the enzymatic sol-gel systems (Sagir and Talebian 2020; Sagir et al. 2020).

It was likely attributed to improved local reactant concentrations in sol-gel nanopores, which tended to result in containment results for every enzymatic phase of the process and thereby enhanced substrate supply. Since that time, a vast variety of different techniques have been tried to immobilize enzymes to maximize their beneficial effect and to enable full reuse of enzymes. The work mentioned included planning and testing suitable carriers for immobilizers and evaluating the subsequent kinetic reactions and limitations of mass transfer (Jiang et al. 2003; Xu et al. 2006; Sun et al. 2009; Shi et al. 2012; Wang et al. 2014). More recently, additional changes were made as the real estate program has required cofactor regeneration (Ji et al. 2015; Cazelles et al. 2013; El Zahab et al. 2008; Davé 2002; Luo et al. 2015).

5.1 Enzymes

5.1.1 Dehydrogenases

Two forms of shape dehydrogenase (FDH, EC 1.2.1.2) are present; (1) Type 1: a metal-independent enzyme that irreversibly catalyzes the CHOOH–CO_2 reaction with the use of cofactor of nicotinamide adenine dinucleotide (NAD^+); (2) Type 2: A metal-dependent FDH (Mo) or tungsten-driven (W) enzyme that catalyzed CO_2 reduction to CHOOH reversibly. In FDH form I, the catalytic stage includes the shift of hydride, from the C atom of the CHOOH to the C4 atom of the NAD^+ ring of pyridine (de Bok et al. 2003; Moura et al. 2004; Hartmann et al. 2015; Beller and Bornscheuer 2014). The process of FDH type 2 (the first article on the use of *Candida boidinii* FDH for this reaction, from 1976 Reda et al. (2008) used in the conversion of enzyme CO_2 to CHOOH continues to be explored in detail as to how the enzyme's response with CO_2 is performed (Schütte et al. 1976; Mondal et al. 2015; Bassegoda et al. 2014). Currently, it is therefore thought that CHOOH oxygenated from the C H-bonds in FDH form 2 catalyzes collateral with a proton transfer from the Mo/W centers into Selenocysteine or Histidine enzyme residues.

Several efforts in protein engineering have been undertaken to produce an enzyme with improved action of carbon reductase than the wild dehydrogenase type existing. Clostridium carboxidivorans, which are produced and processed with the use of an E. coli host cell, are effectively catalyzed to transform CO_2 to CHOOH. Furthermore, the

FDH Clostridium carboxidivorans had a 10-fold lower NAD^+ binding affinity and a lower 30-fold CHOOH binding affinity concerning the FDH of the Candida Boidinii. This function makes for a better FDH option for the CO_2 processing of the Candida Boidinii. Formaldehyde dehydrogenases were used to catalyze the CHOH transition to CHOOH, and the alcohol transformation into Aldehyde/Ketone (NAD^+ reduced to NADH) was catalyzed by ADH (Alissandratos et al. 2013).

5.1.2 Carbonic Anhydrase

It catalyzes the solubilization of CO2 in liquids utilizing carbonic anhydrase (CA, EC 4.2.1.1). The catalysis by employing the CA is recognized as very rapid and capable of 10^6 k_{cat}, a pace that is approximately 10 million times rapid compared to the uncatalyzed natural response (Khalifah 1971). CA efficiency may be compromised by temperature and the existence of other pollutants. Indeed, after combustion, the CO_2-rich exhaust stream will hit more than 100 °C, which is an excessive temperature of CA. Even inhibiting enzyme function were strong amine amounts, residues of heavy metal, and nitrogen oxides (Daigle et al. 2009; Ramanan et al. 2009; Supuran et al. 2003; Bond et al. 2001), as was the case. In the Indus test CO_2 sorption columns, CA as well as susceptible to the extreme alkaline conditions, where the occurrence of peptide-hydrolysis and denaturation could happen (Floyd et al. 2013).

To report those confines, the nitrile CA from the extremophilic *Desulfovibrio vulgaris* has been used to render it extremely heat resistant and vigorous nature in high pH and thereby allowing the enzyme designed to sustain operation and stability up to 107 °C in a 4.2 M (pH > 10) amine solvent (Alvizo et al. 2014). A CA method on a pilot scale was used to extract 60% CO_2 (30–500 L per minute) from a continuous stream on flue gas with a CO_2 proportion of 12%. Working for 60 h in five successive days, the CA was no failure for enzyme activity (Alvizo et al. 2014). A liquid membrane device comprising enzymes was applied to another large-scale patent utilizing CA with real flow gas. A fluid layer was confined to two membranes (permeable gas) working at varying pressures to move CO_2 through the membranes in this device. The membrane can be immobilized with CA or the solution may be open. The downside of this method, although a liquid film prevents the entrance of certain gasses such as nitrogen and oxygen, is that CO_2 is readily consumed by a fast conversion to bicarbonate. The study of the Desulfovibrio vulgaris by the CA team in protein engineering indicates more precisely that these enzymes could be engineered to withstand over 100 ° C and to tolerate the use of alkaline in harsh environments (Alvizo et al. 2014).

5.2 Enzymatic Conversion of CO_2 to Biomaterials

For biofuels and biorefineries, the future bacteria, which can use CO_2 by cooperation, connect the different biological, physical, and chemical disciplines. We illustrate here how CO_2 chemistry can be used to turn low-valuation substances into useful chemical goods in chemoautotrophic prokaryotes. The combined introduction of electron donors to convert carbon capture and storage (CCS) reservoirs into the bioreactors is a vital possibility for the future, of genetically trained or engineered prokaryote or nanoscience. It is currently unclear if in one body, several bodies, or a group of species or a transformed ecosystem, this is successful or how capable these strategies would be. Besides, too little awareness about how biomolecules are generated in a reservoir influences the microbial dynamics of local microbial species and therefore how the local microbes influence the development and fate of bio-conversion. Further methods are essential, such as risk assessment. For starters, on the laboratory stage, experiments and assessments should be conducted for the microbial dynamics in imminent bioreactors to prevent unintended results (Thakur et al. 2018).

5.2.1 CO_2 Conversion to Biopolymer and Bioplastics

Greenhouse gases (GHGs), for example, CO_2, are rising and leading to climate change with methane nitrous oxide (N_2O, Chlorofluorocarbons (CFCs)). Around the same moment, the production of non-degradable objects, for example, plastics, triggers the deterioration of the ecosystem. Ultimately, the production of oil-based plastics increased by 299 million tons worldwide, a 3.9% raise over the 2012 timeframe (Yan et al. 2006; Kumar et al. 2016a). Polyhydroxyalkanotes (PHAs) are biological polymers with biodegradable, biocompatible, and thermostable characteristics. It is deposited in various entity classes as intracellular reservoirs, particularly while carbon content is abundant and a restricting nutrient state in media (Kumar et al. 2018; Gupta et al. 2017). PHA aggregation of microbes is a survival strategy in order to reduce climate strain on microbes residing in numerous ecological habitats including microbial fields, artificial habitats, rhizosphere, aquatic sediments, and marble mines (Kumar et al. 2017a). *R. Eutropha* retains PHAs as a carbon substitute generally referred to as bioplastics in its cytoplasm (Yu 2014). PHA grains comprise typically of poly 3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) chains and short poly 3-hydroxybutyrate (PHB) chains (Kumar et al. 2016b). Genetic engineering development has been the source and use of a broad variety of carbon products, for example, bicarbonate sodium, glucose, plant oils, and fructose to generate PHA Copolymers which show better mechanical durability compared to HPB (Guo et al. 2018). Intracellular PHA from inorganic carbon caught, identical to *Serratia sp*, is stated to be deposited. ISTD04 utilizes 48% of the dry biomass of sodium bicarbonate as a source of carbon and polyhydroxy valerate (PHV).

5.2.2 CO_2 Conversion to Biofuel

Biofuel with carbon capture and storage (BECCS) ability is an emerging greenhouse gas reduction technique that creates negative CO_2 emissions intending to reduce greenhouse gas emissions. The term biofuel is usually liquid fuels, for example, biodiesel and ethanol which serve as a replacement for combustibles such as gasoline, diesel, and jet fuel (Singh and Thakur 2015; Tripathi et al. 2015). Oil often contains oils including pellets of wood and biogas or syngas as well as stable and gaseous fuels. The biofuel cycle involves procedures for thermochemical, biochemical, and chemical transformations.

Chemolithotrophic bacteria are the major biomolecules in cell biomass and could accrue up to 2–60% in lipids present in the dry bacterial biomass. This cycle is based on fatty and triglyceride acids as the main part of microbial lipids and oils and could also be converted into alcoholic esters (Bharti et al. 2014a). Lipid extraction from chemoautotrophic bacteria is difficult because it requires the enhanced processing processes and higher energy consumption and lesser biomass yield. Developments in chemical and physical technology to extract and purify lipids from dry bacterial biomass offer an economical alternative to manufacture biofuel from chemical-autotrophic bacteria. Biodiesel chemist's key chemistry is very fast and is normally done in the transesterification of triglycerides (lipid) in the existence of catalysts (acid or base) with an alcohol, for example, methanol or ethanol (Kumar et al. 2017b; Madhavan et al. 2017). Alkalinized transesterification is the most popular form of biodiesel production; thus, the transformed substance is glycerol and fatty acid methyl esters (FAMEs). If there are significant amounts of free fatty acid (FFAs) in the ingredients (oils), the use of acid catalysts is preferred whereby FFAs are esterified concurrently and converted into fatty acids (Kumar et al. 2016c). The primary consistent catalysts for lipids transesterification are sulfonic acid, sulfuric acid, phosphoric acid, hydrochloric acid, and boron trifluoride (Ma and Hanna 1999).

Recently, owing to their excellent adsorption and simple to work with, recovery, low operating cost, and widely used in a persistent reactor, heterogeneous catalysts became increasingly attractive. Heterogeneous strong catalysts such as zeolites, metal-doped silica, titans, sulfate zirconia, tungsten zirconia, sulfonated stain oxide, and Nafion NR50 have so far been used (Madhuvilakku and Piraman 2013). NR50 was the most popular form of a substance used in the field (Shen et al. 2013). Using intracellular and extracellular lipase as a biological catalytic is yet another option for the development of enzymatic diesel, with strong supports including biochar and activated charcoal being immobilized by both (Intracellular and Extracellular) biological catalysts (Khosla et al. 2017; Singh et al. 2015). Compared to the usage of free enzymes, these methods are highly specialized because their decreased measures include downstream processes and processing operations. Very little detail is accessible mainly related to the development of Chemolithotrophic lipids. (Chemolithotrophic condensed CO_2 *Serratia sp*.) The bacterial culture filtrate ISTD04 formed 466 mg/L extracellular lipids and dry biomass intracellular lipids 64.7% (Bharti et al. 2014a, b). The portion of fatty acid plays a significant role in the manufacture of good-quality biodiesel. Higher saturated fatty acid content in biodiesel compared to unsaturated fatty acids is problematic in the wintertime as fuel injector pipes are blocked but at the same time, they are more resilient to oxidation and increase the fuel's energy efficiency.

5.2.3 CO_2 Conversion to Biosurfactants

Various classes of bacteria and yeasts could be able to generate active biological materials called biosurfactants, for example, bacteria and fungi (Beller and Bornscheuer 2014). *Bacteria sp.* are the most abundant. *Bacillus sp., Pseudomonas sp., Acinetobacter calcoaceticus, Serratia esp., and Rhodococus sp*. have been recorded for the development of biosurfactants (Maheshwari et al. 2017). Thanks to their biological degradability, greater precision, and diversified use, these compounds have strong advantages over chemically synthesized surfactants (Rosenberg 1984). Related biological compounds made up of mycolic acid, glycolipids, a polysaccharide–lipid matrix, phospholipid, lipoproteins, and structural materials, are biosurfactants. Four groups of biosurfactants including (1) lipoproteins or lipopeptides, (2) phospholipids, (3) glycolipids, and (4) polymers (Healy et al. 1996) can be classified based on the chemical structure of their biosurfactants. Among the two classes of biological surfactants in these four types, the first one is the rhamnolipids that fall under the glycolipid subclass.

It helps to reduce alkanes and numerous hydrophobic substances chiefly formed via *Pseudomonas sp.* (Tracy et al. 2012). The second biosurfactant group consists of lipopeptides, primarily lipopeptides, which possess certain imperative applications and action against various groups of microorganisms in biological fields. (CLPBS). The broad spectrum of action of this drug is supported by its antibacterial, antiviral, or antifungal properties, cytolytic function, fibrin clot-forming inhibition, and macrophage stimulating operation (Kim et al. 2004). Hydrocarbons have generally been the preferred sources of carbon for the production of biologics with hydrophobic and water-soluble substrates (molasses). In other business sectors, including milk, cosmetics, and pharmaceutical companies, hydrocarbons are often abhorrent to processing and use as carbohydrates. The chosen biosurfactant carbon substratum for the processing of fats, vegetable oils, glycerol, and carbohydrates. Nonetheless, bacteria *Bacillus sp* absorb CO_2. Biosurfactants may be generated, but very little documentation occurs on the usage of CO_2 by bacteria in their development (Sundaram and Thakur 2015).

5.2.4 CO_2 Conversion to Chemicals

Biomaterials formed by CO_2 microbes have been developed in different items such as acetone, isoprene, iso-butyraldehyde, microbial acid, and salicylic acid. with progression in the field of protein and genetic engineering (Lee et al. 2012). The cyano-bacterium synechocystis species, which previously expressed heterologous isoprene synthase, has reported rises in isoprene production in a heterologous gene combination of *Enterococcus faecalis* and *Streptococcus pneumoniae genes* (Lindberg et al. 2010). The gram-negative soil bacterium is *R Eutropha* also recognized as *Cupriavidus necator*. Depending on the kind of carbon supply in the market, it could be produced mixotrophically, autotrophically, and heterotrophically and. *R. Eutropha* uses H_2 in the deficit of biological substrates as its primary sources of energy for CO_2 fixation through the CBB process. CA has enormous value for the enhancement of the fixation beyond the Rubis CO in autotrophic CO_2 fixation. Four CA genes have also arisen in R. The H16 genome sequence review analyzed *Eutropha*, which is capable of trapping and utilizing CO_2 to generate useful chemicals.

The other useful materials that can be generated by genetically modified R are ferulic acid, precursor biomolecules for vanillin biotransformation, and 2-methylcytric acid (Brigham et al. 2012; Bi et al. 2013). While the significant creation of R imminent biochemical numeral is critical. In Eutropha, primarily organic compounds are used as a carbon source rather than CO_2 by the approaches mentioned (Fukui et al. 2002). With the use of HCO_3-inorganic carbons, such as those present in the *Metalosphaera, Sulfolóbus, Archaeoglobus, and Cenarchaeum*, CO_2 is used to generate a succinyl-CoA that ultimately constitutes two acetyl-coA molecules in a 4-HB loop (Budde et al. 2011; Huber et al. 2008) by 3-hydroxypropionate-4-hydroxybutyrate(3HP-4HB) process. The product of heterological expression in hyper-thermophilic archea *Pyrococcus furiosus* was five genes accountable for fixing CO_2 in the archea of *Metallosphaera sedula* which effectively incorporated carbon dioxide into a key building block (Keller et al. 2013).

5.2.5 CO_2 Conversion to Bio-composite Materials

$CaCO_3$ is a convincing mineral present in the atmosphere and is well known to be precipitated by chemolithoautotrophic bacteria (Srivastava et al. 2015a; Bose and Satyanarayana 2017b). Calcite, aragonite, and vaterite in the non-hydrated polymorphic type of Calcite (Srivastava et al. 2015b). CCS is one of the advanced solutions to reduce carbon pollution from human activities and upsurge the energy gain by the current infrastructure to deal with the expected climate change (Sheikh et al. 2014).

Biomineralization of CO_2 occurs mainly by $CaCO_3$ precipitation and is an important global carbon cycle mechanism in the environment as a whole, including aquatic, freshwater, and terrestrial habitats. *Bacillus sp:* microorganisms such as *cyanobacteria, eukaryotic microalgae,* and *Serratia sp.* Calcification and precipitation of calcite have been documented to be abusively spread in the atmosphere (Kumar et al. 2017b; Bharti et al. 2014b; Bar-Even et al. 2010).

Bacterial species including *Pseudomonas sp., Vibrio sp.*, and bacteria that reduce sulfates were well known for the calcification phase, but their physiological function is still unclear (Ercole et al. 2007). Calcium injection and outflow of calcium in the cell are very significant as calcium is considered as one of the key subordinate signals that assist to communicate the cell's mechanisms. The cell wall of bacteria possesses an S-layer which is a nucleation location in which $CaCO_3$ is produced and maybe a controlling reaction to the atmosphere of microbes (Messner and Sleytr 1992). This has been observed in many bacterial and archaeal organism organisms.

In *bacillaceae*, s-layers are potentially able to differentiate between cell periplasmic space and thus to regulate exoenzymes secretion. The class of biological molecules with substantial properties that are essential to CCU is peptides that have been selectively produced for carbon capture (Comotti et al. 2013; Li et al. 2014). This coating form, engineered artificially, is a plausible alternative for the existing CO_2 separator technologies (Rittmann et al. 2015), with partial absorption of CO_2 over N_2 and CH_4. Hexapeptide-based amyloid fibers have specific carbamate separation properties developed to bind up CO_2 via the creation of carbamate. It is believed to be the next indication of biological materials for CCU applications, planned or engineered peptides, and proteins (Li et al. 2014).

5.2.6 CO_2 Conversion to Exopolysaccharides

Calcium carbonate precipitation biomineralization of CO_2 by microorganisms and effective point source CCS techniques (Bose and Satyanarayana 2017b) have been developed. The excretory materials of humans secreted into their atmosphere are the extracellular polymeric substances (EPS) (Guo et al. 2018; Subramanian et al. 2010). The microbial EPS consists mainly of carbohydrates and components of noncarbohydrates that microbes secrete during cell lysis or not available in the surrounding environment from a carbon source (More et al. 2014). The current and essential strategy is to recognize the pathways for EPS development in microorganisms and to identify the mechanisms of development (Kumar et al. 2017a; Singh et al. 2014). Diverse groups of organisms may be generating EPS which comprises eukaryotes, archaea, and bacteria, and whose temperature, molecular composition, pH, nutritional load, and carbon source of molecules varies according to their rheological, biological, physical, and chemical characteristics (Shen et al. 2013; Gupta and Thakur 2016).

The synthesis of EPS is widespread in the majority of Gram-negative bacteria, for example, *Azoarcus sp., Rhizobium sp., Agrobacterium sp., Azotobacter vinelandii, Haemophilus sp., Xanthomonas campestris, Pseudomonas sp.,* and *Zoogloea sp.* The grams were also recorded belonging to bacteria such as *Streptococus Bovis, Leuconostoc mesenteroides, and Lactobacillus sp.* for the development of EPS (Jiang 2011). This latest biological material has possible use in several areas, including bio-flocculants, substance cementing, fibers, detergents, microbial oil recovery, pharmaceuticals, food additives, metal processing, and wastewater disposal, as a consequence of its special characteristics such as flexibility, biocompatibility, and biodegradability, EPS allows microorganisms to overcome their environmental limits, such as metal toxicity, nutrient restriction, feeding exposure to food, energy shortage, and preserves the microorganism in unfavorable climate (Kumar et al. 2017b).

6 Issues and Challenges in Commercialization of Biological Conversion Methods

The rise in CO_2 amount in the atmosphere causes global warming and thus climate change, which poses a challenge to the survival of earthly life. Specific methods are now applicable to CO_2 reduction and control, such as chemical, physical, and biological. The released CO_2 may be actively pumped into deeper waters or directly through the earth's atmosphere by anthropogenic practices. In reality, technologies such as CCU and CCS are extremely energy-exhaustive techniques that influence the whole commercial use of CCS in the network. For typical operation, there are no primary technical fences to catch CO_2. The total costs of introducing CCS in plants are projected to be not a cost-effective strategy, relative to those without CCS. The higher expense of carbon captures is the biggest problem with the adoption of CCS technologies, primarily from gas fuels and industrial combustion practices. An accepted selection of technical solutions, including the introduction of CCS, may be considered to fulfill the carbon footprint mitigation objective. Deeply based on the environment and form of gas supply the CCS system used was, thanks to its lower c), the most powerful device for coal-fired power stations. CO_2 capture system after combustion at a low cost. Thanks to its high performance and small construction costs, the CO_2 absorption technique is the modern strategy of separation. The CO_2 capture by land or microorganism biologically. CO_2 capturing. Because of this, biological methods convert CO_2 into microbial waste products, organic fuels, and essential chemicals, however, the geological and chemical techniques of CCU posse some limitations. When complex CO_2 fixation enzymes exist, these microbes engage in plant-like operations throughout the global carbon cycle. Because CO_2 is the only source of carbon for these bacteria, they adapt and establish pathways to sequester and utilize the CO_2 from various sources. The appliance of organic CCUs at industries for concurrent usage of CO_2 and the processing of organic materials is also a difficult technique because of lower biomass output, contamination-prone, high fermenter repair and maintenance costs, and costs inherent in the selection and storage of biomass materials are key concerns. Throughout the processing of value-added items like biodiesel, PHA, EPS, biosurfactants, and many more, extracted microbial biomass has been used further. As an alternative to current commercial goods, biomaterials derived from Chemolithotrophic are rising reliance on synthetic materials.

7 Conclusions

CO_2 processing is a challenging area of science and until now the large-scale extraction of CO_2 did not attain an optimal approach. Several CO_2 conversion processes utilizing chemicals, materials, and biological molecules have nevertheless been published. Yet each of these CO_2 catches or transforming machines has its drawbacks, which complicates its industrial use. There are also drawbacks to CCU as a method for CO_2 sequestration. An alternate solution will be to reduce and recycle CO_2 from stable CO_2 reactions with catalyst instead of depending upon a bioenergy storage method to turn CO_2 into bioenergy. To order to meet the objective of environmental stability and its economic viability, the combined CO_2 sequestration and bio-valorization strategy must be enforced. But the economic situation must be closely examined so that the solution to bio-fuel-led biorefinery is feasible. In order to make significant progress to CO_2 reduction, changes in CO_2 recovery are therefore required to mitigate possible climate change.

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Potential Utilisation of Fruit and Vegetable Waste: An Overview

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Abstract

Reducing food waste by maximum resource utilization creates good impacts for food security, environment, and climate. Fruit and vegetables are among the most commonly used commodities of all horticultural crops. Therefore, all wastes could be considered as a desirable byproduct if sufficient technological means are used to increase the value of subsequent goods to outweigh their processing costs. Fruit and vegetable wastes have a strong bioconversion potential into useful industrial, biotechnological, bioenergy, and biocontrol products. This waste can serve as a valuable source of organic carbons, essential oils, pigments, and enzymes that can be used to produce valuable chemicals and compounds of high value. The chapter discusses the strategies adopted for bioconversion like recycling, reprocessing, and eventual use of their discharge into the environment which could cause adverse effects on the environment. A variety of valuable materials produced by the bioconversion of fruit and vegetable wastes are also enlisted to highlight the food waste management prospects.

Keywords

Bioconversion • Value-added product • Pigments • Bioplastics • Bioethanol

1 Introduction

In the modern world, driven by an increase in economic advancement and global population, demand for fruits and vegetables has increased, and this trend is likely to lead to the development of valuable products from its residues in the coming future (Wadhwa et al. 2015). Massive research works have been conducted in recent years to use fruit and vegetable wastes (FVW) to develop highly significant bio-products. The sustainable bioconversion of fruit and vegetable into useful goods not only provides economic benefits and moreover reduces the pollution caused by the decomposition of fruit and vegetable in the landfill sites and surroundings. The main solid wastes from fruits and vegetables are potato and tomato waste, grape and apple pomace, and peels. FVW contain more cellulose, starch, monosaccharide, and lignin compared to liquid fruit and vegetable in which nutrients are in diluted form. During the last few years, biofuel production using alternative feedstocks to traditional fossil raw materials has attracted considerable interest. FVW are considered to be a raw material with low procurement costs that contribute to the creation of an innovative paradigm.

The Food and Agriculture Organization of the United Nations (UN-FAO) stated that at least one-third of the world's food products are wasted each year and among this, horticultural commodities are the maximum (Fidelis 2018). The waste to wealth approach is currently being implemented in most of the developed countries that led to solve their waste management problems. The key challenges for the conversion of FVW to valuable products are their heterogeneous nature and high moisture content. On

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the basis of source and structure, certain modifications can be done to promote microbial growth for developing desirable products of interest in an economically and environmentally benign route. A specific policy for the management of all types of FVW cannot be implemented because of their varied composition by source (Sindhu et al. 2019). This chapter gives an overview of potential applications of bioconversion processes for the generation of energy as well as numerous other valuable products from various FVW.

1.1 Current Bioconversion Processes

Bioconversion methods have been developed on the basis of the characteristics of the FVW. A number of bioconversion processes namely fermentation, extraction, and anaerobic digestion can be utilized for the production of biofuels, enzymes, biopolymers, heat, electricity, etc. The current bioconversion processes for producing valuable materials from FVW are depicted in Fig. 1. The biochemical transformations involve anaerobic digestion and composting. A number of processes like thermal treatments, fermentation, or combined processes are used for the production of different industrially significant products. Thermal conversion normally involves pyrolysis, incineration, or gasification. Fermentation using some microorganisms is difficult due to the FVW's heterogeneous nature. FVW are biodegradable and contain high moisture, and are therefore suitable for anaerobic digestion to produce bioenergy. Such drawbacks of FVW's anaerobic digestion led to the reduction of pH value during the digestion process of fatty acids. It would prevent the development of methanogen microbes. This challenge can be resolved by adopting integrated or alternative methods. Earlier studies have shown that focusing on a single FVW is not profitable for bioconversion. Many other works are being carried out around the world to turn heterogeneous FVW into many useful products, contributing to the creation of a viable, economical, and sustainable approach to FVW bioconversion (Sindhu et al. 2019). To achieve these objectives, a variety of chemical, physical, biological, mechanical, and alternative processes have been reported. There were numerous studies reported for the pretreatment of FVW, including acid, alkali, ultrasound, sequential, and surfactant-assisted pretreatments. Among such processes, sequential pretreatment followed by alkali treatment was observed with the highest reduction in sugar yield. There was a generation of inhibitors in the case of acid and alkali pretreatments. On comparing with other pretreatment methods, sequential pretreatment was considered to be good for sugarcane bagasse to yield reduction of sugar with better removal of lignin and hemicelluloses. The choice of the pretreatments will be on the basis of economic viability and the desired product. Pretreated sugarcane bagasse is used as an effective inert support material for microbial growth in the simultaneous saccharification and fermentation (SSF) methods. Several pretreatment methods have been recorded for bagasse, namely alkali, acid, organo-solvent, organic acid, and physical treatments. Developing a suitable pretreatment would reduce the capital and production costs. Many industries use acid pretreatment, and the benefit of this technique is the development of two main processing streams namely pentose and hexose streams. The conversion of value-added compounds is through the pentose stream and the hexose process is utilized for bioethanol production (Sindhu et al. 2016).

1.2 Applications of Bioconversion Processes

The bioconversion of FVW into value-added products is really attention-grabbing and has wider applications in the medical, pharmaceutical, and allied sectors. The key value-added products that can be derived from FVW include enzymes, ethanol, reducing sugars, proteins, furfural, organic acids, phenols, activated carbon, carbohydrates, degradable plastic composites, amino acids, lipids, biosorbent, cosmetics, medicines, resins, methane, biopesticides, fertilizer, biopromoters, surfactants, and other miscellaneous products (Wadhwa et al. 2015). Applications of bioconversion of FVW into value-added products in various sectors are presented in Fig. 2.

In recent years, the advent of emerging technologies for product developments has led to a sustainable economy in various manufacturing sectors. There are four main industrial enzyme sectors: household, technological, food, and feed enzymes. FVW in industry are an underutilized raw material and is a key sector of emphasis in the global economy that can be processed into valuable items. The use of immobilized biocatalytic enzymes for bioconversion could improve the ecological sustainability of production. In terms of waste stream conditions, the absence of an appropriate immobilization system among the many available methods coupled with specific process requirements is a significant challenge for FVW stream valorization. Besides the differential nature of different enzymes during immobilization, the cost poses another major barrier to the adoption of immobilized biocatalytic waste recovery systems. Usage of processed enzymes rather than raw extract potentially increases the production cost. The cost of the biocatalytic immobilized method for the recovery of FVW into commercial products depends on the market price of raw materials and the implementation of systematic methods for valorization. Implementation of synthetic biological strategies that allow site-driven immobilization enhances the stability of enzymes in non-ideal ecosystems or leads to sub-unit stabilization.

Fig. 1 Various bioconversion processes of fruit and vegetable wastes for the production of value-added materials

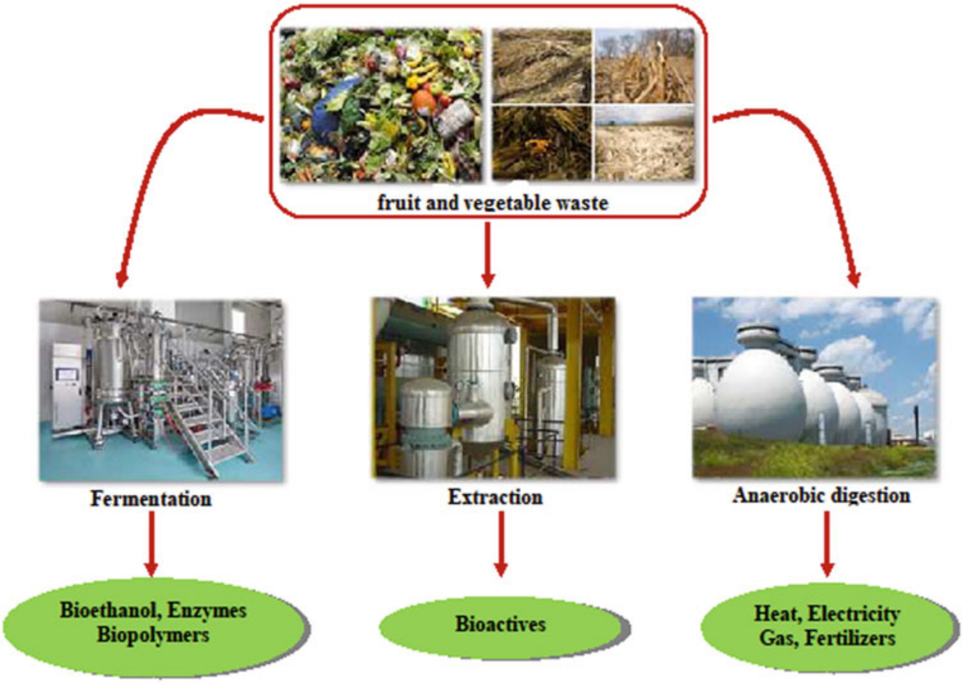
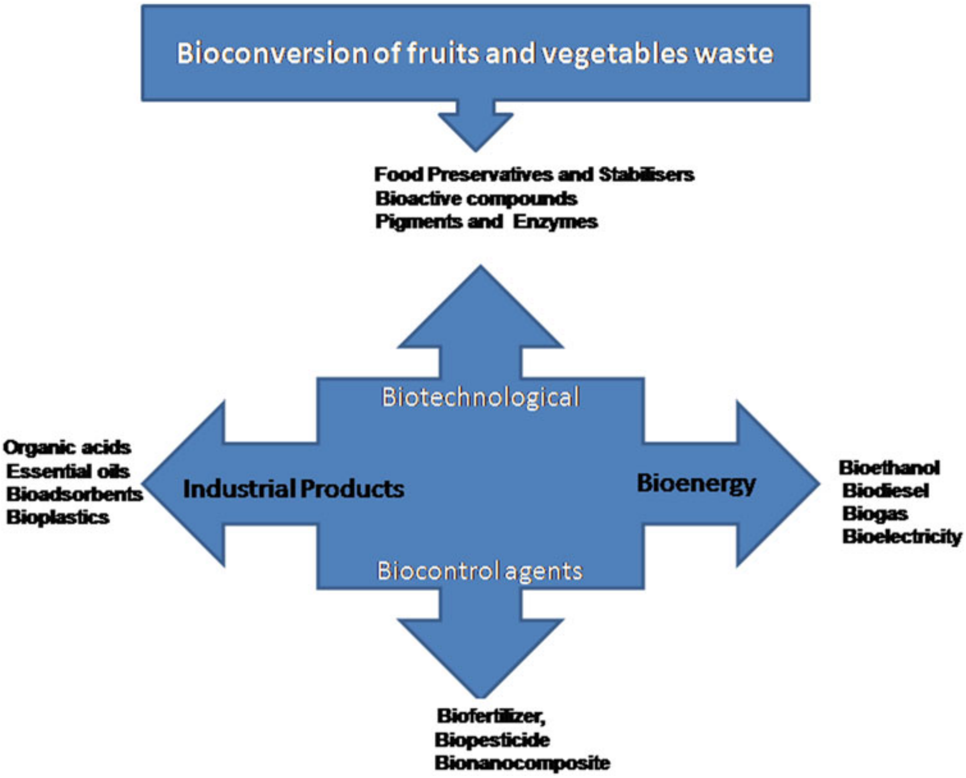


Fig. 2 Application of bioconversion of fruit and vegetable wastes in different fields



Although several researchers developed biocatalysts with potential repeatability and high activity, retention after several consecutive cycles reduced their activity after numerous successive cycles. The proper control of the immobilized enzyme to adjust both leaching and loss of activity is critical for discovering their actual performance in industry. Both the single-enzyme and multi-enzyme biocatalytic systems are highly promising in terms of increasing conversion efficiency and enabling a more effective catalyzing of value-added bioconversion process. The detailed characterization of the diffusion-reaction mechanism and kinetics of immobilized enzyme will access the essential apprehension of immobilized enzyme systems for useful applications. Furthermore, the complex industrial conditions also have a significant impact on the stability of enzymes and their performances. In the case of multi-enzyme systems, the stability of the whole system depends on sensitivity to solvents, inhibitors, and their co-substrates of each enzyme. Rational designing of enzymes provides a profound ability for the production of a variety of valuable bioproducts and thus favoring the management of FVW accumulation. In addition, genetically engineered enzymes may prove superior catalytic performance in food packaging applications. Interdisciplinary researches in various fields namely food sciences, agricultural economics, molecular biology, biochemistry, genetic engineering, and food regulators are required to support enzyme-assisted applications for commercial waste stream recovery.

2 Bioconversion of FVW

2.1 Biotechnological Products

Biotechnology has gone through a maturation process in which the uses of biocatalysts in the food, pharmaceutical, and chemical industries have been established for research and development. The progresses in biotechnology have contributed to a new era for enzymes because of their capability to respond to a variety of reactions under different environmental and experimental conditions. Furthermore, enzymes are contributing a crucial role in the bio-based economy to replace harmful chemical reactions by developing cleaner technologies for new processes and products to the market. Enzymes support the processes in different angles by lowering the cost of production, reducing waste, and lowering energy for the production of green end materials. The first report of the use of enzymes in an industry was reported in 1960 for the production of glucose syrup through starch hydrolysis using glucosidase as a catalyst. The major advantages of starch hydrolysis using glycosidase were increased yields, improved purity, and simpler crystallization. Later in 1973, immobilized glucose isomerase was implemented in the production of fructose syrup on an industrial scale. Another advancement in biotechnology includes the development of a variety of natural solid supports in the field of agro-industry that led to key nutrients innovations for better crop production. Corn and sugarcane bagasse were the most commonly studied among a series of crop residue using these natural solid supports (Valdo et al. 2017).

2.1.1 Food Preservatives and Stabilizers

Mango seed kernel extract is a natural antioxidant used in the food industry as preservatives. These extracts have improved the oxidative stability of sunflower oil at ambient temperature and also during cooking. This also improves the qualities and stabilities of fresh and stored potato chips and the shelf life of the ghee. Antimicrobial substrates are effectively used as food preservatives to prolong the shelf life of beverages where heat treatment can affect their delicate malty taste. Today, a number of FVW are used to prepare more powerful preservatives in foods than other natural antimicrobials. The best examples are MSK methanol extract and methanolic, ethanolic, and aqueous extracts of pomegranate peels and papaya seed waste.

2.1.2 Bioactive Compounds

Bioactive substances have several health benefits like anti-hypertensive, antidiabetic, anticoagulant, antimicrobial, anticancer, hypocholesterolemic agents, etc. The use of waste streams for processing creates it economically feasible (Sindhu et al. 2019). FVW are a valuable source of phytochemicals and has now been researched for the production of dietary fibers, phenolic compounds, and other bioactive materials. For most vegetables and fruits, only the pulp is used, but researches have shown that large quantities of phytochemicals and vital nutrients are available in peels, seeds, and other parts that are not generally consumed. For example, about 15% more phenolic compound concentration is found in grape, lemon, orange peels, mango, avocado, and jackfruit seeds than their fruit pulp. In general, waste should be treated using either thermal or non-thermal methodologies that may affect phytochemicals and nutrients (Sagar et al. 2018). Carotenoids, flavonoids, phenolic acids, and their derivatives are examples of bioactive components that can be extracted from solid FVW. These compounds can be utilized in the pharmaceutical, cosmetic, and nutraceutical industries.

Dry citrus peel waste is a source of D-limonene and a number of flavonoids such as aseriocitrin, nariturin, naringin, and hesperidin that are nowadays applied in the food, pharmaceutical, and cosmetic sectors. Grape pomace is a valuable source of polyphenols and has numerous health benefits, including cancer treatments, anti-inflammatory, free radical scavenging, and anti-proliferation properties. Grape peels contain large quantities of tannins (16–27%) and other polyphenolic compounds (2.0–6.5%), including resveratrol, quercetin, proanthocyanidins, ellagic acid, anthocyanins, and catechins. The polyphenol content of grape seeds is approximately 60% more compared to whole grapes and has high concentrations of catechins, flavanols, and epicatechins. Apple pomace and their peels also contain flavonoids and polyphenolic compounds. It includes hydroxycinnamates, phloretin glycosides, quercetin glycosides, catechins, and procyanidins. Olive pomace contains approximately 98% of the phenolic compounds which include tyrosol, hydroxytyrosol, cinnamic acid derivatives, flavonoids, and secoiridoids. An environmentally friendly strategy namely enzyme-assisted ultrasound hydrolysis was developed for the isolation of antioxidant phenolic compound from olive waste. Coffee byproduct extracts show outstanding anti-inflammatory, anti-allergenic, and antioxidant functions due to the existence of chlorogenic acids. The use of cellulolytic and pectinolytic enzymes improved the extraction of lycopene from tomato peel waste by eight to 18-fold (Cho et al. 2019). The study by Rodríguez et al. confirmed potato waste as an excellent source of antioxidants that can successfully reduce the oxidation of oils (Rodríguez et al. 2014). Barba et al. reported a number of green approaches for the extraction of antioxidant bioactive compounds (especially vitamin E) from grape waste. Such innovative approaches tend to be superior to traditional approaches in terms of processing time and energy consumption (Barba et al. 2016). Adinarayana et al. studied numerous substrates such as wheat rava, wheat bran, barley bran, rice bran, corn cob, peanut shell, and sugarcane bagasse for the synthesis of different types of antibiotics (Adinarayana et al. 2003).

2.1.3 Pigments

Biopigments produced from microbial sources have several advantages over synthetic pigments. *Monascuspurpureus*, a fungus, produces pigments with a number of therapeutic properties, such as cancer treatment, coronary heart disease, and hypertension. A number of reports are accessible on the use of FVW as a substrate for the production of carotenoids such as kinnow peel powder and pea pod, apple pomace, grape juice, grape must, date, sweet potato, tomato peel, and carrot pomace. The quality of meat products can be improved by adding lycopene and fiber-containing tomato peel. Beetroot is known to be an important source of water-soluble nitrogen pigments and xanthins that can help with oxygen-induced or free radical-mediated oxidation of biological molecules. The pigment betalain found in beetroot is widely used as a natural colorant in the modern food system. Dry carrot pomace can be used in 5% wheat bread to make high-fiber biscuits, cakes, dressings, and pickles in addition to carotenoids, fiber, and minerals and in functional drinks. Onion pomace is used in snacks as a natural source of high-quality functional ingredients such as dietary fiber, primarily insoluble fractions, and in total phenols and flavonoids with high antioxidant activity (Wadhwa et al. 2015). The high production cost of carotenoid can be reduced by improved nutrient production using better pigment strains (Sindhu et al. 2016).

Coffee husk and pulp have been used in the production of flavors using the *Ceratocystis fimbriata* mould (Adinarayana et al. 2003). Microbiological bioconversions of FVW into various pigments are cost-effective compared to other synthetic approaches for the production of natural aromas. Various microorganisms, including bacteria, yeasts, and fungi, have been shown to be capable of producing different aroma compounds. Vanillin is produced by bioconversion of ferulic acid which is extracted from FVW using liquid cultures of fungi. Ferulic acid can be recovered from wheat bran and barley spent grains using *Aspergillus niger*(*A. niger*) (Stabnikova et al. 2010). The recent increase in the interest in the use of coloring agents contributes to a rise in the incidence of cancer. Cheng and Yang reported carotenoid manufacturing using *Rhodotorulamucilaginosa* waste and grape waste for the effective pigment production by *Monascuspurpureus* (Sindhu et al. 2019).

2.1.4 Enzymes

Waste processing using enzymes is a newly established stream in terms of environmental and economic aspects and can be easily disposed of or recycled. The advantages of using enzymes in industrial-scale productions are the processing requires minimum purification with maximum yield and recovery of the enzymes without cell-disruption. Biosynthesis of most proteins is controlled by cellulose induction followed by catabolic suppression, thus permits limiting the amount of enzyme produced in non-defined media. Recombinant DNA techniques can be extended to the cloning and production of industrially essential enzymes (Gacesa and Hubble 1998).

Amylases are enzymes used to reduce starch to smaller carbohydrate units and are an appropriate enzyme in paper, fiber, detergent, biofuel, and milk processing. The FVW can be used as an alternative source for the economical production of amylase. Hasan et al. reported amylase produced by *Bacillus* and *Chryseobacterium* using FVW. Another bacteria namely *A.niger*(NCIM 616)is used for the production of amylase from banana peel (Hasan et al. 2017).

Cellulases are a class of enzymes used for the complete hydrolysis of cellulose. It has an essential role in the hydrolysis of biomass and is used in various fields such as biofuels, paper, textiles, detergents, and food. Julia et al. examined the use of soya hulls using solid-state fermentation for the production of cellulose by *A.niger* and found it to be highly efficient at shorter periods that reduces the overall process economy (Julia et al. 2016). Alkali pretreated FVW residues are found to be a suitable substrate without an additional supply of nutrition for improved cellulase production.

Protease is an enzyme that catalyzes protein hydrolysis. Applications are identified in the medical, food, and detergent industries. Ahmed et al. reported the production of pectinase from citrus peel containing soluble carbohydrates using *A.niger* (Ahmed et al. 2015). Botella et al. investigated the feasibility of grape pomace for the production of xylanases by *A. awamori*. Maximum invertase production under optimized conditions using fruit peel as a substrate has been reported. In the same way, *A. niger* was combined with a number of carbon sources, like fruit peel, lactose, fructose, and invertase. Among them, fructose has been considered as an important carbon source for the extraction of extracellular invertase. Various agro-industrial residues have been extensively studied for the production of proteases along with FVW (Bharathiraja et al. 2017). In the other study of alkaline protease using chickpea waste and various agro-industrial waste produced by *Bacillus* sp. (Sagar et al. 2018; Prakasham et al. 2006).

2.2 Industrial Products

The fruit and agricultural sectors are growing at a rapid rate; the resulting waste generation embodies major environmental challenges. Fruits and vegetables constitute the highest rate of waste but are high in nutrients. The underutilized waste may produce disease-causing microbes if the residue is left unprocessed. These wastes can be used as raw materials for the production of valuable products or as a source of renewable energy. Consistency in the availability of cheaper raw materials is essential to reduce the cost of production and to manage the efficient operation. During the twentieth century, the thriving use of agricultural waste as carbon and nitrogen sources for antibiotic fermentation emerged. Linking waste streams from several sectors to agro-based enterprises for efficient recovery would help to solve the problem of waste accumulation. This calls for realistic studies on the recovery of FVW for the manufacture of value-added goods.

2.2.1 Organic Acids

A number of organic acids can be extracted from FVW. Dry apricot waste is used as a base for the processing of citric acid using *A. niger* by fermentation. It was observed that SSF of *A.foetidus* using dried apricot waste as a substrate produced a high quantity of citric acid compared to other FVW like apple pomace, wheat, or rice bran. Most citric acids are produced mainly by SSF of starch or molasses exclusively by *A.niger*. As substrates for citric acid production, several types of FVW, molasses, and cassava bagasse have been examined. The apple waste is found to be an effective substrate for the production of citric acid. It was also produced from the date extract/molasses using *A.niger* ATCC 6275 and 9642 and from the date waste using *A.niger* ANSS-B5. Lactic acid has a crucial role in the carboxylic acid family due to its use in both the food and non-food commodities. This is used as a preservative and as an acidulant in the food industry. However, the commercial production of lactic acid is costly because of the high cost of the raw materials used. It can be saved through the use of biological waste. Pineapple waste can also be used for lactic acid production by using SSF. Sanada et al. have developed a bioprocess for the production of lactic acid that has various applications in the cosmetic, food, chemical, and pharmaceutical industries. The potential of mango peel as a substrate for the low-cost production of lactic acid has also been investigated. In this study, mango peel was fermented directly using bacteria with amylolytic and lactic acid production capabilities. Maximum production of 17.48 g/l of lactic acid was achieved by optimizing fermentation conditions. The mesophilic microbial system that can work at 35 ° C has been used in this study and appears to have a practical advantage due to its low cost. In another study, a lactic acid concentration of 63.33 g/l of fermentation media was obtained from the fermentation of mango peel by *Lactobacillus casei*. In order to minimize the cost of lactic acid production, low-priced raw materials, e.g., FVW such as banana, sapota, papaya, corn cob, and potato have been reported. All the substrates tested assisted the growth and development of lactic acid. An efficient concentration of lactic acid (72 g/l) was achieved with the fermentation of sapota peel. Nancib et al. used the date juice as a substrate for the production of lactic acid using *L. casei*subsp*rhamnosus* or *Lactobacillus delbrucki*. Ferulic acid is the most common hydroxyl cinnamic acid present in the walls of the plant cells. This phenolic antioxidant is widely used in the food and cosmetics industries. Pineapple, orange, and pomegranate peels have been used for ferulic acid extraction. Gallic acid, catechin, epicatechin, and ferulic acid were found to be the major polyphenols in pineapple peels. Ferulic acid is beneficial for the viability and motility of sperm in both fertile and infertile individuals, and the reduction of lipid by oxidative damage to sperm membranes and increased intracellular cAMP and cGMP may be associated with these benefits. It is possible that ferulic acid may be used to cure asthenozoospermic infertility. Acetic acid, another organic acid, can be produced from carrots and white radish leaves. Carrot leafage was used as a substrate for the two-stage hydrothermal production of acetic acid resulting in a high yield. Organic acid production by the use of vegetable waste thus serves two purposes: to reduce the cost of raw materials and to recycle waste, thus reducing the pollution problem (Wadhwa et al. 2015).

Sugarcane bagasse powder was found to be suitable for the fermentation of itaconic acid. Among the various fungi tested for the production of itaconic acid, *A. niger* produced the highest amount in SSF (Ramakrishnan et al. 2014). Succinic acid is commonly used in industries for the manufacture of green solvents, biodegradable plastics, and ingredients used to promote plant growth. The production of succinic acid from sugarcane bagasse hemicellulose hydrolyzate using *A. succinogenes* was reported (Ribeiro et al. 2011). The study found that the use of sodium bicarbonate, magnesium sulphate, and yeast extract improves the production of succinic acid. Sugarcane bagasse hemicellulose hydrolyzate was utilized to design a greener and economical process for succinic acid production (Dai and Xu 2013). Ultrasound-assisted dilute acid hydrolysis was reported to be a cost-effective, time- and energy-saving method for the hydrolysis of sugarcane bagasse. Wei et al. reported the butyric acid production by fermentation of sugarcane bagasse hydrolyzate using *Clostridium tyrobutyricum*. The acid pretreatment followed by enzymatical saccharification of sugarcane bagasse was demonstrated as the first feasible study for producing butyric acid without any detoxification. Gluconic acid is a dehydrogenation form of D-glucose and is produced by surface fermentation methods and is used in the milk, pharmaceutical, textile, cement, and chemical industries (Sindhu et al. 2016). The production of fumaric acid using waste biomass from the apple industry by *Rhizopus oryzae* was assessed by Das et al., in 2015. The result showed high fumaric acid yields by SSF compared to submerged fermentation. Also, the better yield of fumaric acid was recorded using small fungal pellets than larger pellets.

2.2.2 Essential Oils

The essential oils derived from lemon and lime peels often have a value of 20 times the value of their juice. Citrus terpenes, mainly D-limonene, are extracted from the peel oil. D-limonene is used for the preparation of hand cleaners and thinners. Citrus peels are considered as a potential source of essential oil and about 0.5–3.0 kg of essential oil/tone of fruit can be extracted. Essential oils from the citrus peel are usually used in soft drinks, alcoholic beverages, confectioneries, perfumes, cosmetics, soaps, and household goods due to its aromatic fragrance. It is also used to mask the bitter taste of drugs in pharmaceuticals. It increases the shelf life and nutrition of fresh fruit, skim milk, and low-fat milk. It also has a wide range of antibacterial action. Bitter and sweet orange oils are utilized in tea formulations as well as in carmin and laxative preparations. D-limonene extracted from lemon essential oil enhances immunity, counteracts feeling depression, improves the clarity of thinking and intention, energizes and strengthens the mind and body, activates and removes emotional barriers, encourages skin health, and decreases the appearance of wrinkles. Dry bitter orange oil is used in the treatment of uterine and rectal prolapse, diarrhea, and piles. Banana peel contains 2.2–10.9% lipids that are rich in polyunsaturated fatty acids, in particular linoleic acid and a-linolenic acid. Such fatty acids contribute to the prevention of atherosclerosis, cancer, heart disease, and diabetes. The Canadian black currant oil is a good source of essential fatty acids, tocopherols, and phytosterols. Dry tomato seed contains approximately 17% sugar, rich in linoleic and oleic acids, followed by linolenic and palmitoleic acids. Dry tomato peels contain 2.7% oleoresin, which in turn contains 7.2% lycopene. Oleoresin may be incorporated into the oil in quantities appropriate to the level of enrichment desired by the lycopene. Grapes seed oil is rich in unsaturated fatty acids, particularly linoleic acid. Passion fruit seed oil is edible and rich in unsaturated fatty acids namely linoleic and oleic acids. Fuel has free radical scavenging practices. Peach seed oil may also be used as edible oil. It contains 8.0% palmitic acid, 0.3% stearic acid, 55.1% oleic acid, and 36.5% linoleic acid. This can also be used for the manufacture of soap. Peach seed oil is richer in oleic and linoleic acids than in tomato seed oil (Wadhwa et al. 2015).

2.2.3 Bioadsorbents

Bio-adsorption is known to be an effective and low-cost method since it uses low-cost and abundant biomaterials, usually wastes to remove heavy metals and dyes from water. It also reduces the release of biological or chemical sludge in the atmosphere and allows for the recovery of biosorbents capable of recovering metals. Nawirska and Kwahave suggested chokeberry and apple pomace as heavy metal biosorbents. Mango peel was used as a biosorbent to extract Cd and Pb from an aqueous solution. A rapid biosorption rate, i.e., reaching stabilization at 60 min, was observed for both metals. A similar study reported the effective removal of Cu^{2+}, Ni^{2+}, and Zn^{2+} from constituted metal solutions and the actual wastewater electroplating industry using mango peel waste. Ahmed et al. examined the ability of activated carbon derived from date pits to eliminate contaminants such as heavy metals, phenolic compounds, dyes, and pesticides. Date ash pits had a noticeably higher efficiency of boron (71%) and phenol removal from contaminated drinking water relative to power plant ash and pine ash. Peach stone particles have the ability to biosorp mycotoxin under in vitro conditions due to their rather high cellulose content (58.5%). The biological polymers namely lignin, cellulose, and hemicellulose in peach shells contain numerous hydroxyl and phenolic groups that can be chemically modified to create adsorbent materials with excellent adsorbent properties. Powdered stem and leaf of pineapple can be used as cheaper adsorbents to adsorb methylene blue from aqueous solution. Effective biosorbants have been produced from pineapple fruit residues to remove toxic metals like copper, mercury, zinc, lead, nickel, and cadmium. Some researchers reported chemical modification of

FVW residue by the introduction of phosphate groups improved the adsorbent potential at lower pH levels. Heavy metals (Cr, Pb, and Ni) could be removed from polluted sewage sludge using citric acid derived from pineapple waste fermented with *A. niger* before their disposal sites. Pineapple waste water was also used as a low-cost nutrient substitute for *Acinetobacter haemolyticus*, which was used to minimize the concentration of chromium VI. Orange peels can also be exploited as cost-effective and environmentally responsive adsorbents to absorb dyes from contaminated water. Citrus fruit oil (D-limonene) shows detoxifying and antioxidant properties by increasing the level of glutathione S-transferase in the liver. The citrus fruit oil could be used as a feed additive to partly ameliorate aflatoxicosis (Wadhwa et al. 2015). Saygili et al. reported the bioconversion of grape processing waste for the production of activated carbon and are applied in anionic and cationic dye adsorption. The adsorption capacity was found to be comparatively high than commercial and agro-waste-based carbonaceous materials (Sayğılı et al. 2015).

2.2.4 Bioplastics

Biopolymers currently have a wide variety of applications in the automotive sector; they are biodegradable and non-toxic in nature. The residues left after the extraction of coconut water, papaya juice, and muskmelon juice have been used as a substrate (carbon source) in the production of bacterial cellulose, which can then be used for bioplastic development. In recent years, FVW have been used for the manufacture of polyhydroxybutyrate (PHB), a biopolymer that can be used as a biodegradable thermoplastic. It is commonly used in various areas, such as food, pharmaceuticals, chemicals, and cosmetics industries. Omar et al. 2001 used the date syrup as a base for the synthesis of PHB using *Bacillus megaterium*. Rusendi and Sheppard identified the use of potato waste from the potato chip manufacturing plant to generate PHB. Corn starch or potato waste is first hydrolyzed to produce glucose using high-temperature amylase and glucoamylase. *Lactobacillus* is used to ferment glucose into lactic acid, and then lactic acid(equal quantities of hydroxyl and carboxyl forms) can be self-condensed to form linear thermoplastic polyester polylactic acid (PLA), a biodegradable material. These can be used as time-consuming release coatings for fertilizers, pesticides, and agricultural mulch films that decay in the soil. Another useful use of polysaccharides derived from industrial waste tomatoes and granadilla peels is the production of a biodegradable film.

A green approach for the preparation of biopolymer polyhydroxybutyrate from potato waste originated from processing units has been investigated. This process includes the enzymatic conversion of potato starch into a condensed glucose solution (glucose concentration–208 mg/mL) followed by fermentation. Potato waste was utilized as a starch source while barley malt was used as an amylase source for bioplastic production. Lactic acid can be effectively used as a raw material for the industrial production of polylactic acid. The properties of PLA are significantly improved if only L-shaped lactic acid is present. Microbiological synthesis of lactic acid is preferred in this situation. The cheaper substrates for the production of lactic acid are agricultural waste containing starch, cellulose, and hemicellulose, which may be first enzymatically converted into soluble sugar, and then microbial L(+)-lactic acid is synthesized (Stabnikova O, Wang J, Ivanov V. Value-Added Biotechnological Products from Organic Wastes. vol. 10 2010). The production of bioplastics from urban FVW particularly tomato waste was reported. The composite film was produced by formulating polyvinyl alcohol with post-harvested tomato waste powder (Ramos and Swart 2017).

2.3 Bioenergy Products

In the fruit and vegetable industry, the normal advancement like minimization, recycling, feeding, composting, closed-loop growth, or conversion could be accomplished. Currently, there are only a few options for recycling these materials, so that it contaminates the environment to a great extent. Transportation costs and distribution issues of these materials have resulted in bulk wastage of fruit and vegetable. These FVW can be utilized for producing alternative bioenergy for future generations.

Biomass can also be transformed into bioenergy through a biorefinery technology enhancement approach. This biomass upgrade approach involves initial isolation and fractionation, liquefaction, pyrolysis, hydrolysis, fermentation, and gasification. Bioenergy is commonly referred to as solid, liquid, or gaseous fuels, which emerge to be used as an energy source, e.g. bioethanol or biodiesel, and are primarily derived from biorenewables. For bioenergy processing, biorefineries should have several advantages because of diverse biomass and they produce a variety of specific end products. Due to environmental concerns, the development of biodiesel through an integrated biorefinery approach has gained high interest in recent years (Arevalo-gallegos et al. 2017).

2.3.1 Bioethanol

Many studies are available on the production of bioethanol from different FVW using *S. cerevisiae*. FVW can be directly used for microbial growth or after sufficient treatment with biocatalyst for bioenergy production. The commodities derived from perishable waste may be processed into liquid and gaseous forms of biofuels. FVW containing high pectin, cellulose, and hemicellulose are used as an appropriate fermentation substrate. Among the various wastes used for bioethanol processing, potato peels, apple pomace and apple waste, banana peel and banana waste, beet and beet pomace waste, kinnow mandarin (*Citrus reticulata*) waste, and peach and peach waste have shown promising results. Pineapple pulp contains large quantities of sucrose, starch, and hemicellulose. These can also be used for the production of bioethanol. Production of bioethanol from pineapple, orange, and sweet lime fruit peels and powdered avocado seed waste has also been reported. Shilpa et al. reported that bioethanol yields for pineapple, banana, orange, and pea peels were 8.34, 7.45, 3.98, and 2.58% after seven days of fermentation. Among the four extracts of peel, the highest bioethanol production was obtained from papaya peel extract followed by banana and apple peel extracts (5.90–4.94%) and the lowest yield was from turnip peel extract (1.5%). On average, 20% of crop is grown, which can be used for the production of bioethanol. Approximately 174 kg/ha or 220 l/ha of ethanol will be extracted from these ground watermelons. Peach waste is used for the production of brandy; 6 L of brandy with 43% alcohol can be obtained from 100 kg of peach waste. Date extract was used as a substrate for the production of ethanol using the brand *S. cerevisiae* ATCC 36858 and *S. cerevisiae* STAR from date waste using *S. cerevisiae*. Spoiled date fruit was used as a substrate for methanol production using *Clostridium acetobutylicum* ATCC824 and *B. subtilis* DSM 4451 (Wadhwa et al. 2015). The disposal of potato peel waste is a major challenge in the vegetable processing sector and that also can be utilized for the economical and environmental friendly production of bioplastics (Devi et al. 2015).

Sugarcane bagasse was utilized for bioethanol production via simultaneous saccharification followed by fermentation. Bioethanol from the cultivation waste of cassava has been reported by several researchers. It is significant to convert complex carbohydrates into fermentable sugars before fermentation for the production of bioethanol from cassava bagasse. Padmaja has demonstrated various pretreatment methods followed by the use of a cellulolytic enzyme complex to effectively break down complex carbohydrate molecules of cassava waste to reduce sugars. Hydrothermal treatments followed by microwave-assisted dilute acid treatments were reported as an effective processing method for breaking down the carbohydrate molecules. The alcohol dehydrogenase gene acts primarily during the conversion of acetaldehyde to ethanol in *S. cerevisiae*. Zhang et al. showed a minimum energy consumption method for the extraction of ethanol from uncooked fresh sweet potatoes. The enzymatic fermentation of sweet potato produced about 14.4 g of ethanol from 100 g of fresh roots (Zhang et al. 2013; Panda et al. 2017).

2.3.2 Biodiesel

Biodiesel is a less volatile fatty acid that consist of long-chain mono-alkyl esters linkages. In order to avoid freezing at a very low temperature, B20 blending process is used. Lee et al. developed a rapid synthesis of biodiesel from pepper seed waste. The study found that the majority of the lipids can be easily turned into biodiesel. Thushari and Babel examined the use of waste palm oil and sulphonated carbon acid catalysts extracted from coconut meal residues for the production of biodiesel. Only a low-cost catalyst has been used for the processing of biodiesel. The biodiesel output from waste palm oil residues in the open reflux catalytic system is 92.7%. The fuel characteristics have been concluded to be compatible for high scale production. In this process, the catalyst used was very stable and was reusable and recyclable for four more cycles. Hu et al. developed a novel and effective technique for biodiesel production from waste oils with high acid value using an ionic liquid catalyst sulfobutylmethylimidazolium. Numerous process parameters namely reaction time, temperature, catalyst concentration and cycle of use, the molar ratio of conversion, etc. will influence the production of biodiesel. Rattanapoltee and Kaewkannetra reported biodiesel production from pineapple peel and sugarcane bagasse as low-cost agricultural residues for lipid accumulation. The study concluded that there would be a 2.13-fold rise in lipid content during the sugarcane bagasse bioconversion which reduces the cost of production. So, agricultural wastes such as sugarcane bagasse are ideal for the production of high-end biodiesel (Sindhu et al. 2019).

2.3.3 Biogas

This natural gas is a combination of carbon monoxide, methane, hydrogen sulfide, and siloxane. It is formed by the anaerobic digestion of the various wastes. When these gases are oxidized, they can release energy and will work as fuels (Panda et al. 2017). FVW are a significant problem, and theiranaerobic processing for the production of biogas is an emerging field of research. Deepanraj et al. examined that the pretreatment of substrates had significant effects on the production of biogas from FVW. Various pretreatments such as autoclave, microwave, and ultrasound of waste have been performed, and anaerobic digestion with compost has been performed. Ultrasound pretreatment is used to maximize the biogas production. Wu et al. reported an advanced method for the manufacturing of biogas from FVW by co-digestion with deoiled fat trap waste. The research was performed in a variety of digesters such as mesophilic digester, anaerobic temperature-phase digester, and anaerobic temperature-phase digester with recycling (Wu et al. 2015).

Among the sources of energy for the production of biogas, FVW are the most relevant because of their abundance and heterogeneous compositions having high contents of energy. Hang et al. carried out a batch study on fruit and vegetable methanization for a period of 10 to 28 days to optimize the maximum CH_4 yield. FVW are a rich source of several valuable ingredients, but the high salts and cations contents may impede the digestion process. In addition, the rich source of organic and nitrogen content in feedstocks releases a high concentration of free ammonia that may possibly be toxic to methanogens (Chen et al. 2008). Co-digestion of waste containing less nitrogen and lipid content is preferably used to manage these problems. Alvarez and Lidén reported different compositions of FVW under mesophilic anaerobic conditions for biogas production. The use of organic components for the processing of biomethane enhances the cleaner environment and provides a quality life in rural areas and diminishes the risk of water contamination (Fidelis 2018).

2.3.4 Bioelectricity

Organic components in FVW can be converted into electricity using microorganisms. Microbial fuel cells (MFCs) are effective electrochemical technologies for waste treatment by supplying renewable energy. The key benefits of MFC for wastewater treatment include the safe, clean, productive, and direct production of electricity, along with the elimination of organic wastewater components. The MFC consists of a partition of anode and cathode chambers by an active proton exchange membrane. Bacteria oxidized organic components and release a number of electrons and protons. The electrons are passed through the external circuit and protons move to the proton exchange membrane. Mediator-less MFCs were constructed for the bioconversion of orange peel to bioelectricity and up to 0.59 V can be produced under optimized conditions (Miran et al. 2016). Jia et al. investigated the production of bioelectricity from FVW using MFC. This study revealed that the rate of FVW loading has a major impact on MFC output (Jia et al. 2013). Microbial population research confirmed that fermentative bacteroides and exoelectrogenic *Geobacter* are the leading species that promote the transformation of organic FVW to bioelectricity. Rikame et al. reported the production of electricity from acidic FVW leachate with the aid of a dual chamber mediator MFC. The maximum yield of the power density of 15 W/m3 was observed under optimized conditions with an open circuit voltage of 12 V, and 90% COD elimination was also observed (Rikame et al. 2012). Goud et al. used canteen-based FVW composite as a proper substrate for the generation of bioelectricity using MFCs. The energy conversion rate was improved with an irregular loading due to the efficient usage of the substrate (Goud et al. 2011).

2.4 Biocontrol Agents

Biocontrol agents help to preserve and balance plant species together with their natural enemies. These are environmentally friendly, easy to use, effective throughout the season, and do not cause any side effects. This helps reduce the use of chemicals and other pesticides. Microbial biocontrol agents can be developed and used in one of three ways, depending on the type and number of applications needed. Strategies are classified into a classical approach consisting of a single, inoculative introduction; an incremental approach consisting of regular releases; and an inundative or biopesticide strategy. The epidemiological, density-dependent relationship between the biological control target and the biological control agent can be used to identify and differentiate these strategies (Charudattan 1999).

2.4.1 Biofertilizer

FVW can be easily composted with up to 6–22% nitrogen recovery and utilized as a substitute for a large proportion of nitrogen fertilizer. Plots fertilized with biocompost provide considerable yields compared to chemical fertilizers. Long-term applications of FVW compost will result in carbon accumulation at the topsoil and improve soil nitrogen levels over the years. Sarkar et al. used two amylolytic and three cellulolytic thermophilic bacteria (*Geobacillus* strains) for the composting of vegetable waste. A major reduction in the C/N ratio was recorded after 10 days of incubation. Vermicompost is a rich source of beneficial microorganisms and nutrients and is used as a soil conditioner or fertilizer. This includes the bio-oxidation and stabilization of organic matter by the collective activity of earthworms and microorganisms under aerobic and mesophilic conditions. Aerobic treatment can be successfully integrated with the implementation of legislative measures and technical and managerial support for the management of vegetable waste (Wadhwa et al. 2015). The aerobic thermophilic treatment has been suggested to turn sewage sludge, agricultural waste, or FVW into biofertilizer. This process involves the treatment of organic wastes under controlled aeration at 60 ° C with stirring at neutral pH. In order to preserve neutral pH for bioconversion, 5% of the total organic waste was added to $CaCO_3$ at the beginning. By adding artificial or natural bulking agents, the bioconversion and stability of the final products can be improved. The addition of starter bacterial culture like *Bacillus thermoamylovorans* enhances the bioconversion of the sewage sludge, but there is no need of starter culture for aerobic bioconversion of FVW to organic fertilizer. The end products included stable organic matter, phosphorus, nitrogen, and potassium. Its application to subsoil promotes the faster growth of agricultural plants (Stabnikova et al. 2010).

2.4.2 Biopesticide

The lack of large-scale production of biopesticides is one of the major constraints in the wider application of many biopesticides. The aqueous extracts of carob pulp have been reported as a carbon source in the manufacture of *Pantoeaagglomerans* PBC-1, which is used as a biopesticide. A 78% reduction in pathogen incidence was achieved with PBC-1 at 1-108 cfu/ml of fermentation media. Extracts of cucumber plant waste (leaves, stem, and roots excluding flowers and fruit) have been investigated to slow down the germination and growth of barnyard grass under laboratory and greenhouse conditions. It is a potent weed in rice fields that has caused enormous losses in rice production. Two active growth inhibitors, hydroxymegastigmadienone and trihydroxymegastigmadienone, were extracted from the aqueous methane extract of cucumber processing waste. Another antifungal compound was isolated from the pumpkin rind and labeled Pr-1 promoter that inhibited potentially the growth of a variety of fungi (Wadhwa et al. 2015).

Several classes of organisms, mainly parasitoids, predators, and microorganisms, are used as effective pest controls. The application of mycoparasitic and entomopathogenic fungi has received special notification for the biocontrol of insects and pests in agriculture. Global demand for biopesticides was constantly increasing at a rapid rate from 2012. Naturally occurring *B. bassiana* strains were isolated for massive biopesticide production using a dry cassava bagasse as a substrate. This methodology is very simple, cost-effective, and has been adopted by many farmers and their families. This has also been shown that the fungus is harmless to humans and wildlife. Entomopathogenic fungi produce some toxins that can be used as an insecticide. *B. bassiana* is also known to effectively produce significant amounts of toxins such as brassinolide, beauvericin, and beauverolide in the host body.

2.4.3 Bionanocomposite

The researches in the field of edible coatings (ECs) are nowadays a developing area because of the inherent hazardous effects of synthetic coatings. ECs can be used to shield fruit from fungal growth under post-harvest conditions using different matrices and active compounds (essential oils and food preservatives). Antagonistic microorganisms bearing ECs are used in both pre-and post-harvest levels area less explored. To develop ECs on the surface of the fruits or vegetable, a homogeneous dispersion of polymeric materials of film-forming solution is required. Coatings with food-grade polymers or ingredients are edible along with the whole fruit and vegetables which can be directly consumed. It is compulsory to satisfy the food regulatory policies while developing composition for ECs. The basic components of ECs include hydrocolloids and lipids, which can be used either separately or in composite forms. Composite coatings possess improved flexibility, extensibility, and stability. These formulations can also serve as a carrier of a broad range of other antioxidants, antimicrobials, vitamins, flavorings, or colorants. A layer-by-layer technology is used to produce multilayered coatings and provide effective enhancement of fruit quality during storage (Poverenov et al. 2013). Normally, ECs on fruit and vegetables can improve their conservation by using diverse polysaccharides or proteins. Polysaccharides have the ability to improve physical and microbial stability, especially in relatively high humidity environments. Lipids with low water vapor permeability are also used in fruit ECs. TALProlong and Semperfresh are examples of ECs that are currently available in the market based on carboxymethylcellulose, sodium salt, sucrose fatty acid ester, and emulsifier. The ECs developed from FVW are now used to extend the shelf life of bananas and other fruits. Extensive work has been carried out on ECs to improve shelf life and the quality of fruits. Muangdech developed ECs from aloe vera gel, carnauba wax, and chitosan to improve mango post-harvest shelf life. The microbial decay cannot be effectively controlled by using biopolymer components alone in ECs. Therefore, the incorporation of food-grade antimicrobial agents into the formulations can provide better coating characteristics. The developed ECs with antimicrobial properties are found to be more effective compared to the direct use of antimicrobial agents, because the migration of active compounds from ECs to the surface of the fruits is slow. An ideal EC is engineered to act as a carrier of biocontrol agents throughout the storage of the final product, both in terms of nutritional point of view and durability (Marín et al. 2017).

3 Conclusion and Future Perspectives

The optimization and development of biochemical parameters to improve the performance of biorefinery systems with reduced costs are currently a booming area of research in order to introduce the current outcomes to industries. A variety of processing methods including simple pretreatment to enzymatic saccharification protocols followed by microorganism fermentation are currently using to produce valuable products from FVW. Biotechnological approaches favor the production of genetically modified enzymes for use in industrial processes directly. Progresses for implementation and use of bacterial hosts in bioconversion processes will depend on the adaptability and performance of this biocatalyst to large bioreactors and the operating conditions. New techniques are to be developed for genome editing in fungi that will help for multiple modifications which allow easy metabolic engineering fitting them as efficient chassis. It is possible to utilize FVW as feedstock for the development of numerous valuable chemicals and goods, resulting in economically viable biorefineries. The sustainable development based circular economy has been playing a major function on the global market that is focused on waste minimization, resource conservation, regeneration, and recycling.

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Bionanocomposites Derived from Polysaccharides: Green Fabrication and Applications

Shadpour Mallakpour and Mina Naghdi

Abstract

Go-green is one of the most important issues in the current century. In the field of bionanocomposites, polysaccharides could be proper alternatives for the oil-based materials. Apart from their natural abundance and low costs, polysaccharides are non-toxic, biocompatible, and present extraordinary features. Their biodegradability is of great importance as well. Along with their merits, wide usage of polysaccharides may be restricted because of some shortages. Some disadvantages may come into play when polysaccharides are used alone. Here, the role of some materials at nanodimensions is highlighted. For this reason, a new generation of bionanocomposites derived from polysaccharides has been introduced with the potential to be employed in different sectors from biomedical and healthcare sectors such as wound dressing, tissue engineering, and drug delivery systems to water treatment and so on. In this chapter, the attempt was to discuss the imperative role of polysaccharides as either matrix or nanofiller in the preparation of bionanocomposites. The most important applications of the mentioned bionanocomposites related to their special features are also revealed in detail.

Keywords

Tissue engineering • Water treatment • Solution casting • Hydrogel • Antibacterial • Scanning electron microscopy • Food packaging • Reducing agent

1 Introduction

Nowadays, plastics with the base of petrochemical have entered to all aspects of life. Their role in the packaging sectors, automobile industry, construction and building, and almost all consumer goods and products cannot be denied (Amin et al. 2015). Following their vast usage, their accumulation in environment and landfilling has arisen global concerns. Each year, 150 million tons of plastic wastes are added to the environment and their major accumulation is in the landfills and oceans (Beydoun and Klankermayer 2020). It has been estimated by United Nations Environment Programme, if this trend of production and disposal of these wastes continues, the total production of plastics will be more than 2000 million tons by 2050 (Liu et al. 2020). One may propose recycling as an alternative for this issue, but most of the recycling protocols are not cost-effective and the recycled polymer does not meet all the quality requirements to be reused (Beydoun and Klankermayer 2020). Several other strategies have been suggested such as burning and producing petrol from plastic wastes, but they are not much effective to be used in a vast domain (Shahnawaz et al. 2019). So, using polymers and their derivatives, which are biodegradable and obtainable from sustainable resources, i.e., biopolymers seems to be one of the reasonable and best ways to solve these problems.

2 Biopolymers

Biopolymers are a class of synthetic or naturally occurring polymers that are degradable using enzymes, bacteria, or fungi (Mousa et al. 2016). Nowadays, there are diverse routes to supply biopolymers and they are generally classified as follows (Turan et al. 2018):

(i) Using biomass as the resources including proteins (such as gelatin, collagen, casein), polysaccharides

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(such as carrageenan, chitosan, starch, alginate), and lipids (such as wax and fatty acids).

(ii) Chemical synthesis by using biomass and even oil such as poly(ε-caprolactone), polylactic acid, and poly(vinyl alcohol) [PVA].

(iii) Microbial fermentation such as bacterial cellulose and poly(β-hydroxybutyrate).

Many of these polymers have the advantage of being biodegradable, highly available, cheapness, and consequently are proper candidates to be applied in different fields including food packaging technology, medical areas, electronics, etc. (Ibrahim et al. 2019). In another classification based on their constituent monomer, they are categorized as follows (Ibrahim et al. 2019; Gowthami and Angayarkanny 2019):

(i) Polynucleotides with nucleotides as the monomer.
(ii) Polypeptides with amino acids as the monomer.
(iii) Polyphenols or polyhydroxyphenols with the large phenolic structures as the monomer.
(iv) Polysaccharides with monosaccharides as the monomer.

Among the mentioned four groups of biopolymers, the later stands out. Polysaccharides are the most abundant biopolymers within the biosphere (Bagal-Kestwal et al. 2019). Hitherto, many attempts have been made to make this class of biopolymers more appropriate for the specific uses. Their usage as the matrix for the preparation of a wide range of bionanocomposites has been addressed in a lot of studies. On the other side, polysaccharide-based nanomaterials such as nanocellulose, nanochitin, and nanostarch are supposed as the new and favorable generation of nanoreinforcements in the preparation of bionanocomposites. In the rest of this chapter, the focus will be on different synthesis strategies for the bionanocomposites derived from polysaccharides and evaluation of their applications.

3 Polysaccharides

Polysaccharides are macromolecules composed of monosaccharides connected via glycosidic bonds and their degree of polymerization is commonly more than 100 (Ibrahim et al. 2019). They could be monofunctional or contain plenty of functional groups such as –OH, –$CONH_2$, –SO_3, –NH_2, and –COOH and are capable to be in different forms, e.g., films, microspheres, membranes, hydrogel, and gel (Gowthami and Angayarkanny 2019; Pooresmaeil and Namazi 2020). There are several ways for classification of the polysaccharides; they could be sorted by their structure (linear or branched), their monomeric units (homoglycans, diheteroglycans, triheteroglucans, tetraheteroglycans, pentaheteroglycans), and finally by their charge (neutral, anionic, or cationic) (BeMiller 2018). As an advantage, they have higher thermal stability in comparison to other biopolymers (Gowthami and Angayarkanny 2019). Polysaccharides are diverse in source and a brief review has been done in Table 1.

Figure 1 shows the number of published documents per year from 2000 to 2021 recorded from the Scopus website with keyword of applications of polysaccharides.

4 Bionanocomposites

Bionanocomposites, which are composed of bio-based materials have been introduced to the world as a new generation of hybrid nanostructures and are commonly known as a proper replacement for the petroleum-based nanocomposites (Visakh 2019; Ilyas et al. 2020). Apart from taking into account of the sustainability issue (Ma et al. 2016), they have the advantage of biocompatibility and biodegradability (Visakh 2019). Bionanocomposites can be divided into different categories; they may have a petroleum-based polymer embedded with renewable nanoparticles; in another case, a biopolymer may be used with incorporation of synthetic or inorganic nanoparticles, and finally in the third case both polymer matrix and nanoparticle may be provided from renewable resources (Arora et al. 2018).

Apart from their outstanding features, polysaccharides may present some shortcomings like limited barrier and mechanical properties in their unmodified form. These problems could be solved by their usage in the form of bionanocomposites (Mallakpour and Khodadadzadeh 2020). They are known as the group of natural materials, which are mostly addressed in the preparation of bionanocomposites. These types of bionanocomposites have a wide range of applications. In the following, the synthesis of bionanocomposites using polysaccharides along with their applications will be discussed.

5 Synthesis and Applications of Polysaccharide-Derived Bionanocomposites

5.1 Packaging

In recent years, green packaging has become an important topic of both academic and industrial research. Herein, biodegradation and mineralization are among the most important criteria to choose materials for different packaging purposes (Ilyas et al. 2020). A wide variety of biopolymers are used in this regard including lipids, proteins, and

Table 1 Some of the most used polysaccharides along with their sources and important applications

Polysaccharide	Source(s)	Applications	Reference(s)
Cellulose	Wood and cell wall of plants, cotton	Packaging, paper industry, biomedical sectors adsorbents in water treatment, sensors, and actuators	Guleria et al. (2020), Lizundia et al. (2017)
Cellulose nanocrystal	Acid hydrolysis process of cellulose fibers	Food industry, cosmetic, medical sectors, water treatment, and electronics	Grishkewich et al. (2017)
Agar	Red seaweeds	Packaging, culture medium	Kumar et al. (2019)
Chitosan	Deacetylation of chitin	Medical sectors such as tissue engineering, adsorbents in water treatment, agriculture, edible films, preventing dehydration of meat, drug delivery, biosensors, and catalyst support	Arasukumar et al. (2019), Yadav et al. (2020), Javaid et al. (2018)
Pectin	Fruit waste	Wound recuperating materials, tissue engineering	Govindaraj et al. (2018)
Tragacanth gum	Astragalus gummifer stems	Medical sectors such as bone tissue engineering, wound dressing, controlling pesticide release	Mallakpour and Abbasi (2020)
Xanthan gum	Aerobic fermentation of glucose, sucrose, etc. by Xanthomonas campestris	Coatings, film tablets, drug delivery, food industry, cosmetics, and water treatment	Iftekhar et al. (2020), Makhado et al. (2017)
Sodium alginate	Brown seaweed	Medical applications such as drug delivery, tissue engineering, etc., textile yarns, biosensors, enzyme mobilization	Macedo et al. (2020)
Guar gum	Cyamopsistetragonoloba seed	Food industry, drug, mining, textile engineering, and petroleum	Palem et al. (2019)
Chitin	Shrimps, crabs, and lobsters	Biomedical applications like wound dressing, drug delivery, etc., cosmetics, biosensors, water remediation	Rameshthangam et al. (2018)
Starch	Corn, potato, cassava, and cereal grains	Drug delivery, barrier coating/films, water remediation, paper sizing	Chi et al. (2020)

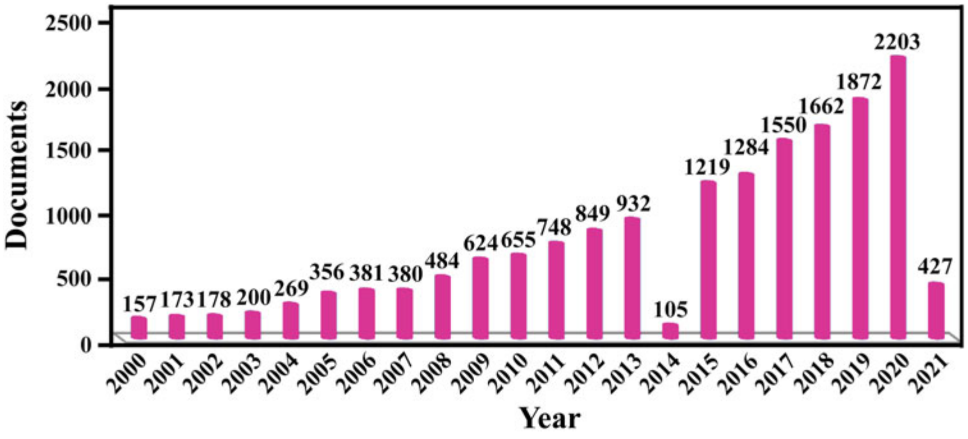

Fig. 1 Bar chart gathered from the Scopus website with the keyword of "applications of polysaccharides" (Feb 12, 2021)

polysaccharides. The main limitations in usage of unmodified polysaccharides are weak moisture barrier properties (Yadav et al. 2019) and inadequate mechanical acting, which could be solved by using them in the form of bionanocomposites (Hou et al. 2019). Meanwhile, in some cases, antibacterial activity may be donated to the packaging by incorporation of some nanomaterials like Ag nanoparticles (Ma et al. 2016).

Yadav et al. (2019) prepared cellulose nanocrystal/Ag/sodium alginate bionanocomposite film to be used for packaging. In their work, sodium alginate was used with a dual function; it was used as a reducing agent to convert $AgNO_3$ to Ag nanoparticles and as a polymer matrix. As demonstrated by red arrows in Fig. 2a, needle-like cellulose nanocrystals are well dispersed within the sodium alginate matrix. In addition to that, Fig. 2b shows that Ag nanoparticles are formed and good distribution of both nanocrystals and Ag nanoparticles in the sodium alginate matrix could be observed.

In another study (Ma et al. 2016), a nanohybrid composed of nanocrystal cellulose and Ag nanoparticles was prepared, and then it was used as a nanofiller to improve the properties of the poly(lactide) and poly(butylene adipate-*co*-terephthalate). However, the toughness of the resulted nanocomposites was decreased compared to the neat poly(lactide)-poly(butylene adipate-*co*-terephthalate), but significant improvement was observed for the thermal stability, storage modulus, and antibacterial performance. The resulted green nanocomposite can be a promising material to be used in food packaging.

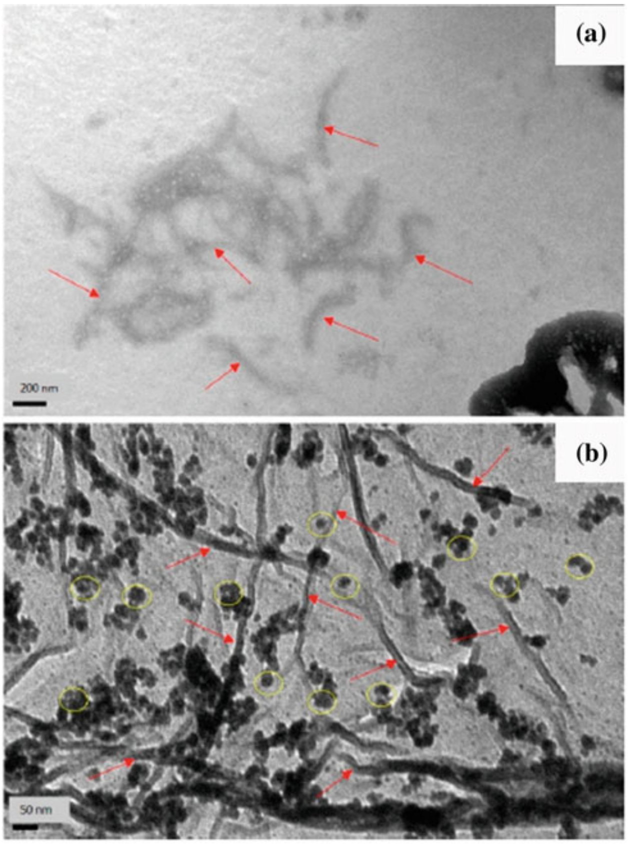

Fig. 2 Transmission electron microscopy (TEM) images of **a** CNC/Alg and **b** CNC/Ag/Alg composite films. Reprinted from Yadav et al. (2019) by permission from MDPI (CNC: cellulose nanocrystals, Alg: sodium alginate)

Bionanocomposites based on sugar palm starch embedded with nanofibrillated cellulose were prepared through a solution casting method (Ilyas et al. 2020). The sources of both of the counterparts were agro-wastes. The prepared bionanocomposites have the advantage of being biodegradable and water resistant with higher thermal endurance and could be used in the packaging industry.

Tedeschi et al. (2020) proposed a green alternative for the petroleum-based plastics. They used different weight percentages of cellulose, xylan, and hydrolyzed lignin, and the bionanocomposites were prepared during a solution casting. Finally, they observed that enhancing the lignin content leads to improvement in antioxidant and antibacterial properties and decreases oxygen barrier ability.

Li et al. (2019) used cellulose nanocrystals grafted with polyethylene glycol as the nanofiller to enhance features of poly(L-lactic acid) and make it proper for packaging applications. Cellulose nanocrystals functionalized with lower molecular weight poly(ethylene glycol) led to reduction in the oxygen permeability coefficient and had a reinforcing effect on the poly(L-lactic acid) matrix, while the case was grafted with long-chain poly(ethylene glycol) yielded a rather ductile product. They offer this strategy as a green approach to prepare packaging films with tunable properties.

A green approach was used by Yadav et al. (2019) to prepare chitosan-based bionanocomposites for food packaging. In this regard, they used cellulose nanocrystals to enhance mechanical and thermal features. They added different weight percentages of the cellulose nanocrystals to a chitosan solution and films were prepared by the solution casting. However, the cellulose nanocrystals dispersion within the chitosan matrix was weak, but the prepared films showed ultraviolet blocking ability. In addition, incorporation of cellulose nanocrystals in the polymer matrix prevents the dissolution of bionanocomposite films in water to a high extent and it was more effective in higher amounts of the cellulose nanocrystals.

Kumar et al. (2019) designed a series of bionanocomposite films based on agar and containing ZnO nanoparticles with different weight percentages and investigated their capability to enhance the shelf life of green grapes. The appearance of the green grapes wrapped in the prepared films after 7 days of storage is demonstrated in Fig. 3. As can be seen, the fruits preserved in the plastic (polyethylene)

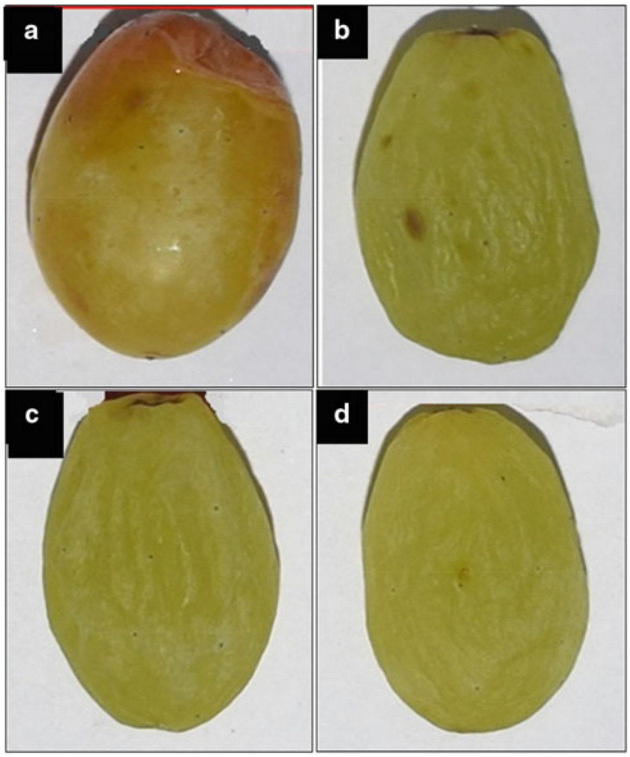

Fig. 3 Images of the green grape wrapped in: **a** Plastic (polyethylene) film, **b** Control film, **c** Film with 2% (w/w) Agar-ZnO, and **d** Film with 4% (w/w) agar-ZnO after 9 days storage at 37 °C. Reprinted from Kumar et al. (2019) by permission from Elsevier

film as well as pure agar film are rotten, while those preserved in the agar/ZnO films show a fresh appearance. They acclaimed that ZnO nanoparticles have a vital role to enhance the shelf life of the fruits, while bionanocomposite films containing 2 and 4 wt% of the ZnO nanoparticles were capable to preserve the green grapes for 14 and 21 days, respectively.

A similar study was done by Emamifar and Bavaisi (2020) to enhance the shelf life of strawberries using an edible film of sodium alginate embedded with ZnO nanoparticles with different ratios and it was observed by using 1.5 w/v of sodium alginate and 1.25 g/L of ZnO nanoparticles, the shelf life of the fruit could be enhanced up to 20 days. It was mentioned that this bionanocomposite showed the highest titratable acidity and lowest total soluble solids with the least microbial growth.

In a study, Zhao et al. (2020) tried to evaluate two methods for the preparation of alginate and chitosan-based bionanocomposite films reinforced by cellulose nanofibers with different contents and find out which method is better. In the first technique, they tried layer by layer to prepare bionanocomposites and then they used blending as the second method. They compared several results obtained from two methods and used some advantages and disadvantages to make the best decision about the routes which led to better features for the packaging applications. In the differential scanning calorimetry, alginate-based bionanocomposite containing 7 wt% of the cellulose nanofibers showed shifting of the exothermic peak to higher temperature and confirmed enhanced thermal resistance compared to the pure alginate. For chitosan-based bionanocomposite 7 wt%, the sample prepared from layer by layer showed shifting to higher temperature, which is a result of homogeneous dispersion of cellulose nanofibers within the chitosan matrix. In the case of alginate, blending was more efficient but for the chitosan-based bionanocomposites layer by layer demonstrated better results. These observations are more verifiable with the cross-section field emission scanning electron microscopy [FESEM] images, which showed homogeneity for the alginate-based bionanocomposites prepared by the blending route and in the case of chitosan layer-by-layer route led to more homogeneity.

A series of gum karaya/Cloisite Na^+ nanocomposite films with the potential to be used in food packaging have been designed by Cao and Song (2019). They acclaimed that addition of 0.75 wt% of cinnamaldehyde to the nanocomposite film formulation endues the film antimicrobial feature. What is more, owing to its plasticizing effect, incorporation of the cinnamaldehyde leads to improvement in the elongation of the resulted films; however, it reduced the glass transition temperature of the films to some extent.

SiO_2 nanoparticles were used to enhance features of agar/sodium alginate and make it potential materials for food packaging in a study by Hou et al. (2019). They discussed briefly the gelation mechanism and it is schematically shown in Fig. 4. As shown, agar contains hydroxyl groups along with some sulfate moieties, while sodium alginate contains hydroxyl functionality along with some carboxylate groups. Consequently, hydrogen bonding is responsible to form intermolecular hydrogen bonding. However, incorporation of 2.5 wt% of SiO_2 nanoparticles within the polysaccharides blend, reduced water vapor permeability dramatically, and mechanical features did not show tangible changes. But the bionanocomposite films containing 10 wt% of the SiO_2 nanoparticles showed significant improvement in tensile strength and elongation at break.

Junior et al. (2018) proposed starch/PVA-based bionanocomposites embedded with 6.5 wt% of cellulose nanofibrils derived from bamboo as an alternative for the petroleum-based packaging materials. A mechanical defibrillator was applied to prepare cellulose nanofibrils with different diameters as a result of different passes. Melting and crystallization enthalpy of the bionanocomposite were dramatically enhanced in the presence of nanofibrils prepared by 30 passes through the defibrillator. In addition, water absorption decreased compared to the control blend. This behavior may be a result of several types of interactions

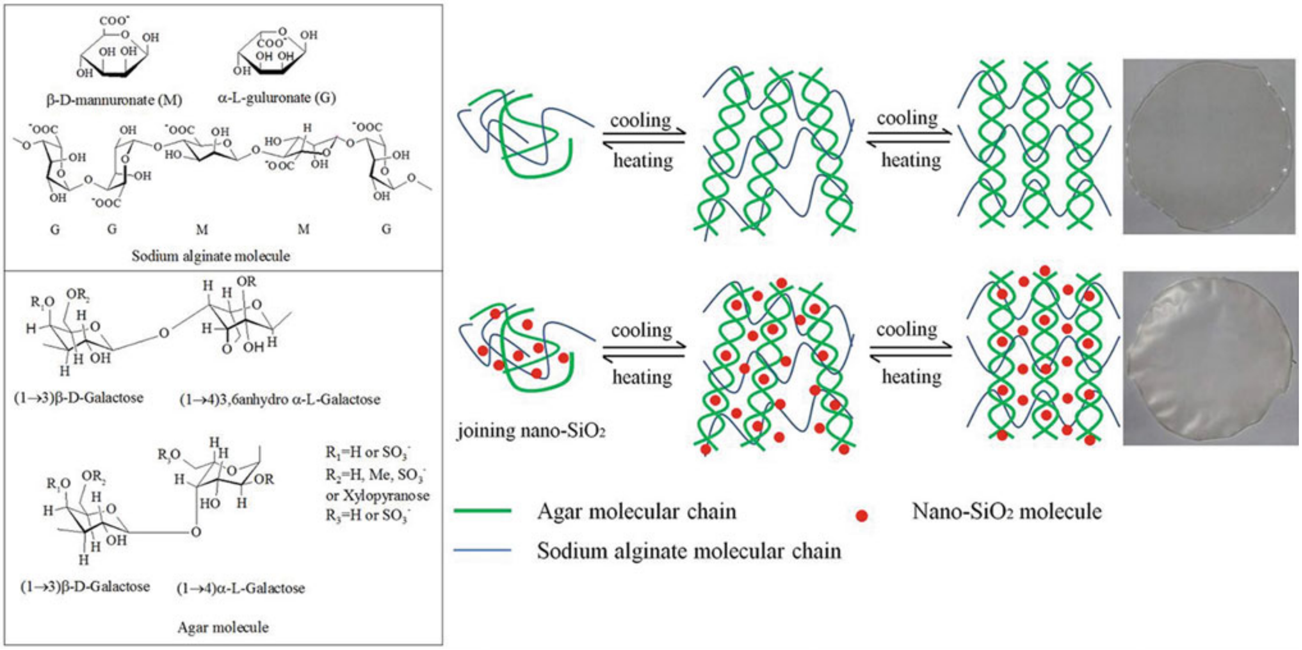

Fig. 4 Molecular structure of AG and SA and their ideal gelation mechanism diagram. Reprinted from Yadav et al. (2019) by permission from Elsevier (AG: agar, SA: sodium alginate)

between –OH functional groups of the nanofibrils and polymer matrix, which leads to the rather compact orientation and consequently less vacant spaces.

5.2 Water Remediation

Polysaccharides are vastly addressed in water treatment. They are highly abundant, cheap, and have a lot of functional groups in their structure and could be proper candidates for this aim (Badruddoza et al. 2013). Razani and Tehrani (2019) designed a bionanocomposite containing a hybrid of cellulose nanowhisker and layered double hydroxide. Following this purpose, cellulose nanowhiskers were first prepared during acid hydrolysis of cotton linter and then modified via polymerization of acrylic acid monomers in the presence of layered double hydroxide. The prepared bionanocomposite hydrogel was applied for the uptake of several cationic dyes and it seemed presence of layered double hydroxide dramatically improved the adsorption capacity.

A blend of sodium alginate (2 w/v) and guar gum (1 w/v) has been used as both reducing agents for the preparation of Ag nanoparticles and then as the polymeric matrix in the preparation of a bionanocomposite (Hasan et al. 2020). The calculated bandgap energy for this bionanocomposite was 2.5 eV and it was capable to degrade methylene blue under visible light.

Chitosan has been used for the preparation of chitosan/graphene oxide with magnetic properties with the capability to be used for Pb^{2+} removing from wastewater (Fan et al. 2013). They acclaimed the several functional groups in the chitosan backbone including free –OH and –NH_2 groups are important factors for this observation.

Mallakpour and Tabesh (2019) designed a biosorbent hydrogel based on tragacanth gum to remove methylene blue from aqueous solution. They also used different percentages of $CaCO_3$ nanoparticles to enhance the features of the tragacanth gum. An enhancement in the thermal stability of the bionanocomposites compared to the neat polysaccharide was observed and the maximum adsorption capacity for the bionanocomposite containing 5 wt% of $CaCO_3$ nanoparticles was reported to be 468.62 mg/g.

Mallakpour and Madani (2016) used chitosan as the matrix to prepare adsorbent for the Pb^{2+}. Owing to the high surface area and its tunnel structure, α-MnO_2 nanorods were used to enhance the adsorption capacitance of chitosan. Following this purpose and to better dispersion, α-MnO_2 nanorods were first modified using L-valin and then inserted within the chitosan with different percentages. It was observed by incorporation of 3 wt% of modified α-MnO_2 nanorods, the maximum adsorption capacity enhanced from 82.65 mg/g for pure chitosan film to 163.93 mg/g.

Chitosan/Fe_3O_4 nanocomposite films were proposed as biosorbents for the adsorption of Congo red (Kloster et al. 2019). Two different methods were used to prepare chitosan/Fe_3O_4 bionanocomposites; once Fe_3O_4 nanoparticles were synthesized in situ within the chitosan matrix. In the second protocol, Fe_3O_4 nanoparticles were first

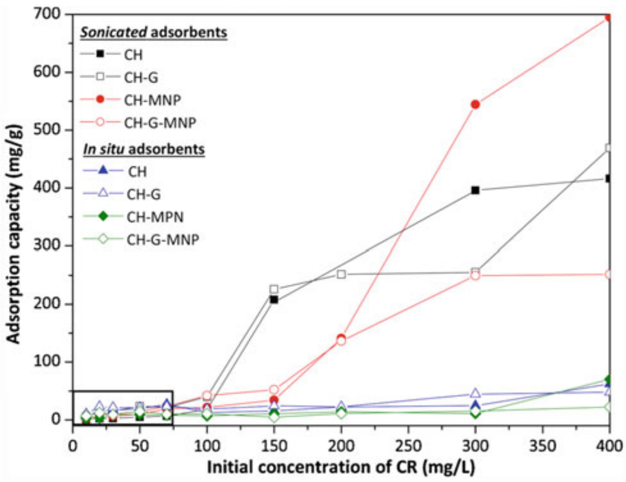

Fig. 5 Sorption capacity of chitosan-based films as a function of the initial concentration of adsorbate (CR) solution. Reprinted from Kloster et al. (2019) by permission from Elsevier (CR: Congo red, CH: Chitosan, G: Glycerol, MNP: Iron oxide nanoparticles)

synthesized and then they were added to the chitosan solution and after ultrasonic irradiation of the resulted suspension, bionanocomposite film was prepared by the solution casting technique. Glycerol was used as the plasticizer and the amount of Fe_3O_4 nanoparticles within the polymer matrix was 10 wt%. The performance of the pure chitosan, chitosan containing glycerol, and chitosan/Fe_3O_4 with and without glycerol in the adsorption of Congo red with different concentrations was studied and the resulted graphs are demonstrated in Fig. 5. As can be seen, in concentrations up to 100 mg/L, all the adsorbents behave similarly. But in higher concentrations, adsorbents prepared from the sonication route seem to be more efficient than those prepared during an in situ protocol. A part of this observation is due to the vast pH changes in the case of sonicated biosorbents compared to the in situ prepared samples. After adsorption of Congo red, the pH has changed from basic to acidic for the sonicated cases, which is due to their preparation procedure. The other factor is strong interactions among the polymer matrix and Fe_3O_4 nanoparticles, which disturbs the interaction with the Congo red dye. Also, it was pointed out to the partially dissolving of the sonicated biosorbents and consequently enhancing the adsorption area. Finally, presence of glycerol has a positive effect on the adsorption of dye by the biosorbents.

Chitosan-based biocomposite and bionanocomposite were used for the removal of methylene blue from wastewater (Sohni et al. 2019). Bulk lignin and lignin at nanosize attained from agro-industrial wastes were incorporated within the chitosan matrix. Owing to the presence of several functional groups in the lignin structure, the prepared biocomposite and bionanocomposite showed more adsorption compared to the pure chitosan. However, lignin at the nanoscale was more effective. Applicability of the prepared bionanocomposite as the biosorbent for spiked real aqueous samples was also studied and good performance was observed.

Nano-CaO and copolymer of 2-hydroxyethyl methacrylate as well as acrylic acid have been used to modify chitosan as a superadsorbent (Sethy et al. 2019). Due to high porosity, hydrophilicity, and plenty of functional groups, it showed high ability in the adsorption of Cr^{6+} and the maximum adsorption capacity from the Langmuir isotherm model was reported to be 149.70 mg/g at 25 °C.

Hosseinzadeh and Abdi (2017) proposed in situ synthesis of SiO_2 nanoparticles to prepare ideal adsorbent for methylene blue. In this work, firstly poly(acrylic acid) grafted sodium alginate was attained during a free-radical copolymerization reaction and then different volumes of tetraethylorthosilicate were added to prepare SiO_2 nanoparticles inside the polymeric network. The resulted materials demonstrated high porosity and surface area, potent electrostatic interactions, and consequently high adsorption capacity.

Yang et al. (2020) designed a multi-component system to be used for the wastewater treatment. In this regard, bacterial cellulose was used as the substrate and TiO_2 nanoparticles to prepare bionanocomposite with photocatalytic activity. In order to create more functionality and proper dispersion of TiO_2 within the polymer matrix, bacterial cellulose was first coated by polydopamine. As can be seen from Fig. 6, pure bacterial cellulose appeared in the form of nanofibrous and their diameter was 40 nm on average. The diameter of the nanofibrils was enhanced to 50 nm after coating the bacterial

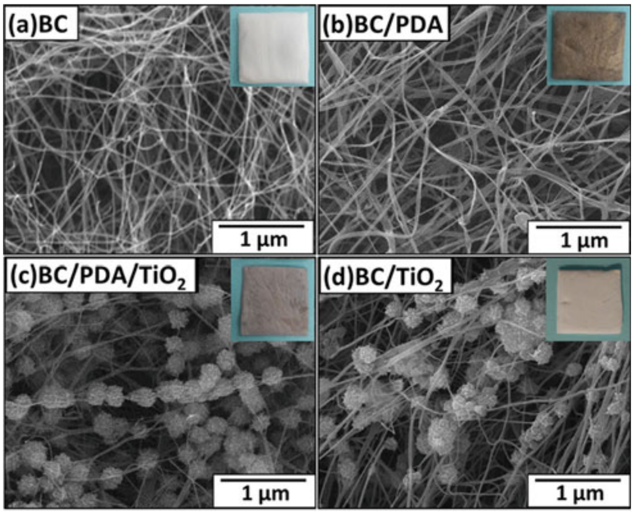

Fig. 6 Representative SEM images of **a** pristine BC, **b** BC/PDA, **c** BC/PDA/TiO_2, and **d** BC/TiO_2. Inserts are optical images of corresponding samples. Reprinted from Yang et al. (2020) by permission from Elsevier (SEM: scanning electron microscopy, BC: bacterial cellulose, PDA: polydopamine)

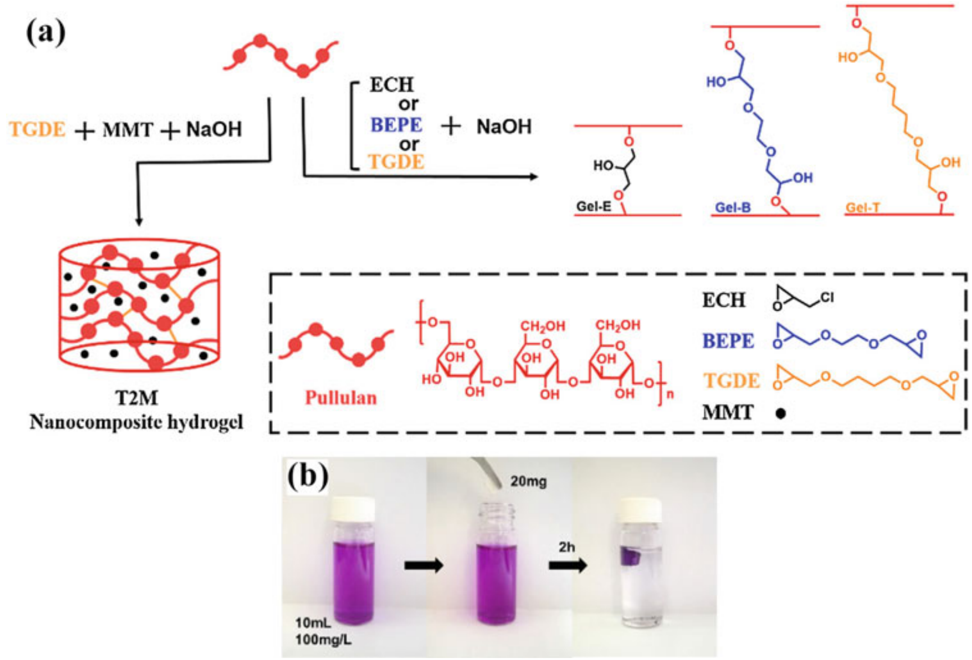

Fig. 7 **a** Schematic representation of the formation of the pullulan-derived hydrogels, **b** Image of the adsorption process (20 mg of dry T2M was immersed in 10 mL ofa 100 mg/L CV solutions for 2 h). Reprinted from Ref. (Su et al. 2019) by permission from Elsevier (T2M: Sample with 5% w/v of montmorillonite and 10% w/v tetramethylene glycoldiglycidyl ether, CV: Crystal violet, ECH: Epichlorohydrin, DEPE: 1, 2-bis (2, 3-epoxypropoxy)-ethane, TGDE: Tetramethylene glycol diglycidyl ether, MMT: Montmorillonite)

cellulose with polydopamine. By comparing Fig. 5c and d, they concluded that the presence of polydopamine within the nanocomposite leads to better dispersion of TiO_2 nanoparticles within the polymer matrix. The prepared nanocomposite showed efficiency in both photocatalytic degradation and removal of methyl orange, methylene blue, and rhodamine B. Presence of active sites and high surface area as a result of fine dispersion of TiO_2 nanoparticles is effective factors on the removal process. The photocatalytic activity of the prepared nanocomposite was compared with commercial P25 and showed superiority. Using photoluminescence spectra, it was confirmed that presence of polydopamine resulted in the separation of electron–hole moieties created at the interface of TiO_2 and polydopamine, and consequently improved the photocatalytic performance.

Li et al. (2020) applied Al_2O_3-hydroxyapatite composite to modify chitosan and make it a proper adsorbent for the water remediation purposes. Following this purpose, hydroxyapatite was synthesized in situ in the presence of Al_2O_3 nanoparticles. The specific surface area and pore volume gathered from Brunauer–Emmett–Teller analysis showed significant improvement for the prepared chitosan/Al_2O_3-hydroxyapatite beads compared to the neat chitosan. The performance of the prepared nanocomposite beads in the elimination of estradiol and chrysoidine from aqueous solution was examined and its efficiency was compared with pure chitosan. The maximum adsorption capacity dramatically enhanced by incorporation of the Al_2O_3-hydroxyapatite within the chitosan matrix. In the case of estradiol removal, it enhanced from 29.04 to 39.78 mg/g, while for the chrysoidine adsorption, it improved from 8.60 to 23.26 mg/g. However, no optimization on the amount of the adsorbent was done.

A series of pullulan-based nanocomposite hydrogels embedded with montmorillonite were used as the adsorbents of crystal violet (Su et al. 2019). Effect of different parameters including montmorillonite content and type of the crosslinker on the features of the end product as well as adsorption efficiency was studied. Tetramethylene glycol diglycidyl ether, 1, 2-bis(2, 3-epoxypropoxy)-ethane, and epichlorohydrin at varied concentrations were applied as the crosslinkers and it was observed that the longer chain crosslinker leads to pores with smaller size. Enhancing the amount of crosslinker also resulted in smaller pores. In fact, the pore size seems to be tunable by varying the chain length and content of the crosslinker. Also, better swelling ability was observed for the nanocomposites containing tetramethylene glycol diglycidyl ether and epichlorohydrin. On the other hand, incorporation of montmorillonite limited swelling ability and improved mechanical features. The preparation procedure is observed in Fig. 7a. The nanocomposite containing 10 wt% of the tetramethylene glycol diglycidyl ether and 5 wt% of montmorillonite was applied in the elimination of crystal violet (Fig. 7b) and the maximum adsorption capacity of 80 mg/g was reported.

Yu et al. (2020) used suction filtration to immobilize Au and TiO_2 nanoparticles onto the surface of the cellulose membrane. They considered multiple roles for the cellulose layer; it could play the role of filter (in the fabrication process), supporter (in the water purification step), and thermal insulator. Incorporation of both Au and TiO_2 nanoparticles at the same time has the advantage of presenting plasma evaporation and photocatalytic degradation simultaneously. In addition to that, the presence of Au nanoparticles within the nanocomposite has some other benefits. It can prohibit electron–hole recombination, which is known as one of the most important restrictions in the photocatalytic processes. Also, due to their photothermal conversion and consequently thermal effect, Au nanoparticles are able to enhance the efficiency of the photocatalyst.

Mallakpour and Nezamzadeh Ezhieh (2017) used the potential of polysaccharides to prepare suitable adsorbents for deletion of polluted water from Cd^{2+}. In this regard, at first, valine and starch were used to modify multi-walled carbon nanotubes in order to bring functional groups on its surface. Then, this nanocomposite was used as a nanofiller to be inserted in a chitosan/PVA blend. The prepared chitosan/PVA-based nanocomposite showed improved thermal stability and adsorption capability compared to the pure chitosan/PVA blend. From Fig. 8a, it is obvious that incorporation of 70 wt% of the prepared nanofiller enhanced Cd^{2+} adsorption capability, dramatically. For example, the removal efficiencies were 98.42% mg/g and 76.80 mg/g in applying 60 mg of the chitosan/PVA-based nanocomposite and bare chitosan/PVA blend as the adsorbent, respectively. They pointed out to the presence of several functional groups within the prepared nanocomposite structure, which promote chelation and coordination with the metal cation, which endow the adsorbent more capability. Figure 8b demonstrates a schematic view from the present functional groups and their doable interactions.

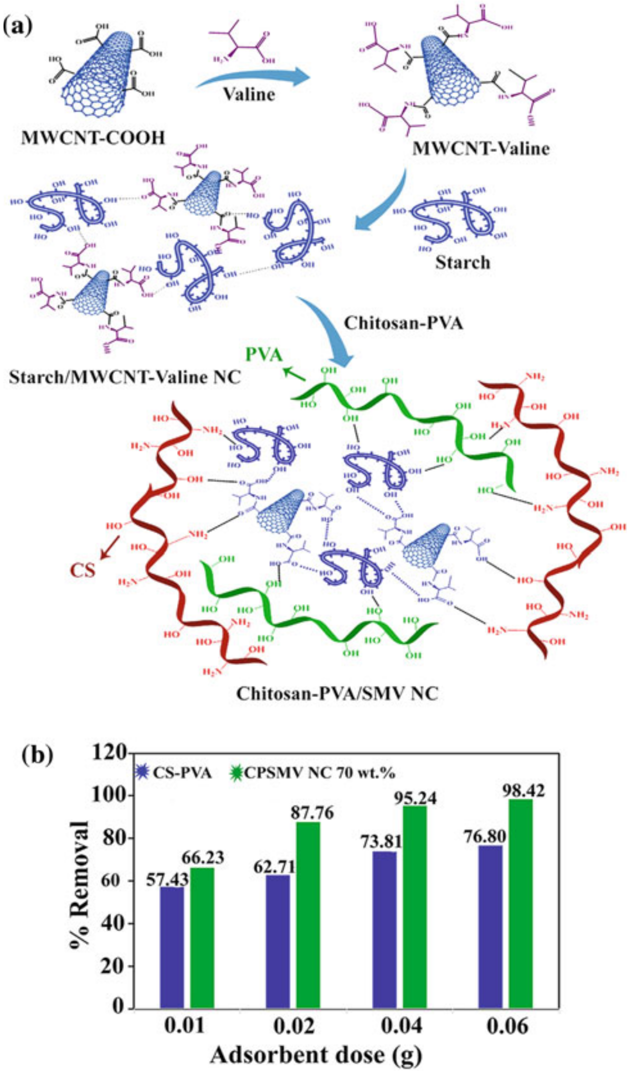

Fig. 8 **a** The images of prepared NC films and a structure of NC with some possible interactions between SMV NC and CS-PVA chains, **b** The percentage of removed Cd(II) ions (R) versus adsorbent dosage for the pure CS-PVA and CPSMV NC 70 wt%. Reprinted from Mallakpour and Nezamzadeh Ezhieh (2017) by permission from Elsevier (NC: Nanocomposite, SMV: Starch/multi-walled carbon nanotubes-Valine, CS: Chitosan, PVA: Poly(vinyl alcohol), CPSMV: Chitosan-poly(vinyl alcohol)/SMV)

5.3 Medical Uses

5.3.1 Drug

Polysaccharide hydrogels are known as one of the favorable drug delivery vehicles and a lot of studies have been dedicated to optimize them for these purposes. Hydrophilicity, non-toxicity, and the ability to degrade by time are some benefits of these types of hydrogels (Singh et al. 2020). They have the ability to entrap specific drugs, and then release it during a convenient manner (Eid et al. 2020). But their poor mechanical strength and solubility are factors which confine their usage to some extent (Singh et al. 2020). Several ways such as blending (Mallakpour and Rashidimoghadam 2020), embedding with different inorganic nanostructures, and grafting with several types of artificial monomers (Singh et al. 2020) are proposed as alternatives to modify polysaccharides. Some of the limitations and shortcomings of the conventional drug therapy methods could be overcome by these drug delivery systems. For example, one of the most important concerns in tumor therapy is side effects of using drugs on healthy cells. Herein, the potential of polysaccharide-derived bionanocomposites as carriers for selective delivery of drugs is of great importance. In fact, owing to the several functionalities, these bionanocomposite can interact with drugs and release the drug in a sustainable and some times during a pH-responsive manner, which all enhance the treatment efficiency (Abbasian et al. 2020).

Mahdavinia et al. (2019) applied different amounts of hydroxyapatite in the chitosan matrix to control the release of ciprofloxacin. κ-carrageenan was used with dual functions: as a natural crosslinker and to interact with the ciprofloxacin. While chitosan/κ-carrageenan released 98% of the ciprofloxacin within 120 min, the bionanocomposite

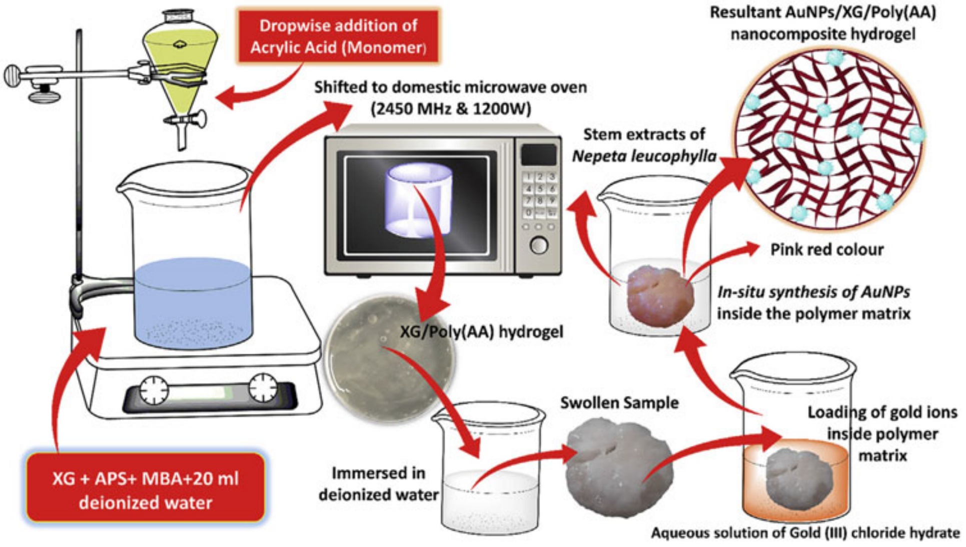

Fig. 9 Schematic representation of synthesis procedure of MW-AuNPs/XG/Poly(AA) nanocomposite. Reprinted from Singh et al. (2020) by permission from Elsevier (MW: Microwave, XG: Xanthan gum, Poly(AA): Polyacrylic acid, APS: Ammonium persulfate, MBA: *N*, *N′* Methylene bisacrylamide)

hydrogel showed a sustained release. Besides, the prepared hydrogels loaded with ciprofloxacin presented antibacterial activity against both *Escherichia coli* and *Staphylococcus aureus*. All the results showed the prepared materials have the potential to be used as drug delivery systems.

Singh et al. (2020) proposed a method for sustained release of amoxicillin rather in basic condition. As presented schematically in Fig. 9, first, xanthan gum was grafted with poly(acrylic acid) by in situ polymerization of acrylic acid under microwave irradiation. Then, Au nanoparticles were prepared in situ in the presence of herbal extract as a natural reducing agent. Compared to the pure xanthan gum, the prepared nanocomposite showed a significant enhancement in Brunauer–Emmett–Teller surface area and this parameter increased from 0.67 m^2/g for the Xanthan gum to 49.58 m^2/g for the prepared nanocomposite. Amoxicillin loading efficiency was 62% for the Xanthan gum grafted with polyacrylic acid and enhanced to 85% in the presence of Au nanoparticles. Thanks to the polymers' functionalities, the prepared nanocomposite had an adjustable drug release, while in the medium with higher pH showed higher release in comparison to the acidic and neutral media. It may be an effective method for colon drug delivery purposes.

A core–shell bionanocomposite composed of β-cyclodextrin as the core and soy soluble polysaccharide as the shell was designed to be used for the controlled release of vitamin E (Eid et al. 2020). Different weight ratios of β-cyclodextrin to soy soluble polysaccharide were used in the preparation process to see the possibility of tuning the properties by changing the composition. The SEM images of the prepared samples (Fig. 10) showed that higher size for pores will be attained in higher amounts of the β-cyclodextrin. On the other side, enhancing the amount of β-cyclodextrin led to enhancement in the mechanical features, which is due to the higher crosslinking degree. However, soy soluble polysaccharide is responsible to create adhesion in the final product. The results also showed that the release of vitamin E was greatly impressed by the β-cyclodextrin amount within the bionanocomposites. As the percentage of β-cyclodextrin was enhanced, more crosslinking between two polymers occurred and this phenomenon suppressed the release of vitamin E. They acclaimed this strategy could be effective to deliver vitamin E to small intestine; however, more studies seem to be needed especially about the in vivo point of view.

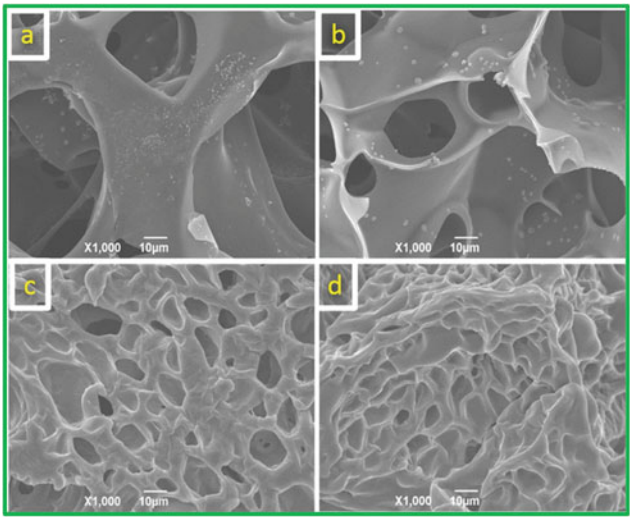

Fig. 10 **a**–**d** SEM images of different lyophilized HGNCs quenched with liquid nitrogen: **a**–**d** HGNCs formed from the weight ratio (10/20), (15/20), (20/20), (25/20) % (β-CD/SSPS), respectively, in aqueous solution. Reprinted from Eid et al. (2020) by permission from Elsevier (SEM: Scanning electron microscopy, HGNC: Hydrogel nanocomposite, β-CD: β-cyclodextrin, SSPS: Soy soluble polysaccharide)

Pectin/Ag nanocomposite films were proposed by Kodoth et al. (2019) to be used for transdermal delivery of Donepezil. Oral therapy of Donepezil has some problems for patients, so its transdermal delivery could be a proper way to overcome the problems. Toxicity of the drug-loaded nanocomposite was studied and results showed compatibility with blood cells. Cumulative drug release within 120 min was reported to be 94%. Totally, taking the antibacterial activity of the nanocomposite film into account, it could be proper for the transdermal delivery of drugs.

Abbasian et al. (2020) developed nanocarriers to enhance the solubility of drugs and consequently enhance its circulation time. For this aim, microcrystalline cellulose was modified using xanthate and then it was coated with dimethyl amino ethyl methacrylate quaternary ammonium alkyl halide as well as polyacrylates-coated nanoparticles. ZnO and Fe_3O_4 nanoparticles were used to inhibit drug afflux and enhance its intracellular cumulation. The prepared nanocomposite was conjugated with methotrexate to be used for targeted therapy of breast cancer cell line. The release behavior of the prepared nanocomposite was studied in vitro and it seemed to be a pH-responsive phenomenon. The releasing rate in simulated physicochemical conditions, i.e., pH = 7.4 and temperature of 37 °C was slow, while in pH = 5.4 and temperature of 40 °C, which is known as the cancerous simulated conditions it showed faster release. They declared this method could be an alternative for conventional chemotherapy.

Encapsulation of 5-fluorouracil in ZnO/carboxymethyl cellulose/chitosan nanocomposites has been proposed for effective delivery of this drug to the colon (Sun et al. 2019). In this methodology, at first, nanocomposite beads based on carboxymethyl cellulose embedded with small quantities of ZnO nanoparticles were prepared. In order to create a protective layer against acidic gastric juice, chitosan was assembled onto the carboxymethyl cellulose using electrostatic interactions between two polysaccharides. The drug-release behavior of the prepared nanocomposite in conditions similar to gastrointestinal was studied and <20% of 5-fluorouracil was released during 2 h at pH = 1.2, which was similar to gastric fluid. However, in higher pHs, the rate of drug release enhanced and 80% of 5-fluorouracil released at pH = 6.8 after 5 h. Finally, it was observed in pH = 7.4 release rate was even higher. The probable mechanism for these observations may be ionization of amino functional groups of the external chitosan layer and presence of ZnO nanoparticles, which provides a pathway allowing the drug to release. However, over the time and exhaustion of the chitosan layer, exposure to higher pHs led to protonation of the carboxymethyl cellulose layer and facilitate the drug release.

In a study by Mallakpour and Khodadadzadeh (2018), the ability of starch/multi-walled carbon nanotubes nanocomposites for delivery of zolpidem was studied. At first, multi-walled carbon nanotubes were modified using D-glucose to make it hydrophilic. Afterward, starch-based nanocomposite films containing different amounts of multi-walled carbon nanotubes were prepared. They were reacted with oleic acid to make them amphiphilic and prepare starch nanoparticles. It is worth to note that nanoparticles were formed only when multi-walled carbon nanotubes were present and without them, i.e., in the presence of just starch, no nanoparticles were formed. Finally based on dynamic light scattering results, nanocomposite embedded with 2 wt% of multi-walled carbon nanotubes loaded with the intended drug had the lowest mean diameter. Based on the transmission electron microscopy [TEM] micrographs showed in Fig. 11, it seems the zolpidem-loaded nanocomposites show different morphology compared to the nanocomposite before treatment with oleic acid and drug loading. The zolpidem-loaded amphiphilic nanocomposites appeared as semi-spherical nanoparticles bearing multi-walled carbon nanotubes as the cores.

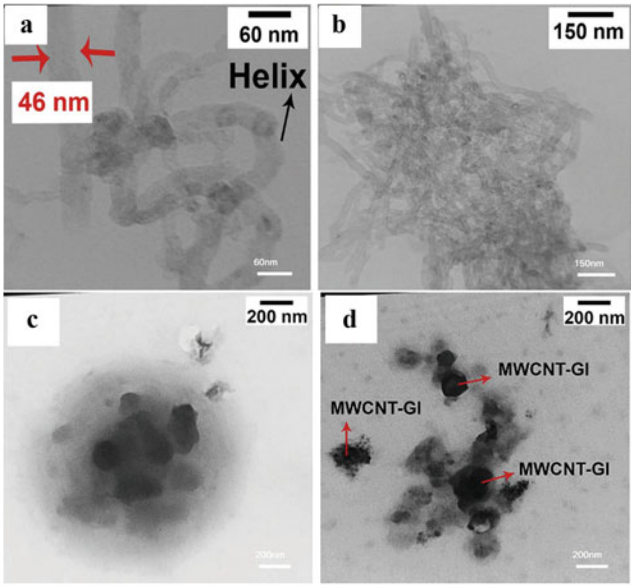

Fig. 11 TEM micrographs of starch/MWCNT-Gl 1 wt% (**a**) and (**b**) and ZM-loaded nanoparticles obtained from Amph (4) (**c** and **d**). Reprinted from Mallakpour and Khodadadzadeh (2018) by permission from Elsevier (TEM: Transmission electronmicroscopy, MWCNT: Multi-walled carbon nanotubes, Gl: Glucose, ZM: Zolpidem, Amph: Amphiphilic)

5.3.2 Tissue Engineering

Bone defects may be caused by trauma, tumors, infections, or other diseases and there is a need for proper materials to be used for bone repair or to be replaced with the damaged bone. Bone tissue engineering is working in this field and hitherto, lots of progress has been gained (Mallakpour and Rashidimoghadam 2020). It has been proved that polysaccharides could be proper candidates to be used for the preparation of scaffolds instead of conventional materials, since they have the benefit of entering the body without creating any cytotoxicity or immunogenicity (Kazimierczak et al. 2019). Another important factor in the polysaccharide-derived implants is their biodegradability, which let the scaffold to degrade during formation of the tissue (Mallakpour and Abbasi 2020).

Govindaraj et al. (2018) used extracted pectin from Jackfruit peel with different weight percentages to prepare pectin/apatite bionanocomposites. The prepared bionanocomposites were evaluated to be used as bone graft materials. The results confirmed both superior mechanical strength and biocompatibility for the bionanocomposite containing 0.1 wt% of the pectin. They acclaimed that –OH and –COOH functional groups of the pectin promote Ca^{2+} binding, and consequently crystal nucleation and growth in the osteogenesis.

Mallakpour and Abbasi (2020) designed a bionanocomposite based on chitosan and tragacanth gum embedded with a hybrid of SiO_2 and Ag nanoparticles with the potential to support formation of the hydroxyapatite during immersion in the simulated body fluid. As demonstrated in FESEM images of the bionanocomposites, after 28 days immersion in the simulated body fluid (Fig. 12), tetragonal pyramidal-shaped hydroxyapatite can be observed for the bionanocomposite with the SiO_2/Ag ratio of 1/1. The antibacterial activity of the bionanocomposites was studied and satisfactory results were observed against both *Staphylococcus aureus* and *Escherichia coli.* They pointed out to the antibacterial feature of both polysaccharides which were used as the polymer matrix.

Incorporation of magnesium fluorohydroxyapatite in the sodium alginate matrix led to bioactive materials with potential to be applied in the tissue engineering (Mallakpour et al. 2020). In this study, the as-mentioned ceramic nanoparticles were used in different weight ratios for the preparation of alginate-based nanocomposites and their bioactivity potency was followed through immersion of the prepared nanocomposites in the simulated body fluid for 28 days. The pictures attained from FESEM confirmed formation of a thick layer of hydroxyapatite on the samples' surface. They suggested to the ability of the sodium alginate to form gel in the presence of Ca^{2+}, which makes it proper for biomedical applications.

Microporous bionanocomposites based on chitosan and agarose were prepared by incorporation of 40 and 70 wt% of nanohydroxyapatite (Kazimierczak et al. 2019). It was observed the amount of incorporated nanohydroxyapatite greatly overshadowed the status of the functional groups. While, in lower amounts of the nanohydroxyapatite, all of the nitrogen atoms were in the form of protonated amide/amine functionality, but for higher amounts nitrogen in the form of = N– bonds were observed. These phenomena affected the surface polarity. As was established by X-ray photoelectron spectroscopy and wettability test, functional groups of the bionanocomposite containing 40 wt% of nanohydroxyapatite were more polar and its surface was more hydrophilic, which all resulted to the lower protein adsorption ability than the other bionanocomposite. However, the bionanocomposite containing a lower amount of nanohydroxyapatite showed better osteoinductive properties, both bionanocomposites had the potential to be used in bone tissue engineering.

Carboxymethyl cellulose and gelatin were linked together through hydrogen bonding and hydroxyapatite was synthesized in situ to strengthen this blend (Sarkar et al. 2018). Different proportions of the carboxymethyl cellulose to gelatin were used and the nanocomposite with equal amounts of both polymers showed the highest compressive strength and elastic modulus. The prepared nanocomposites showed the ability to support proliferation and differentiation of MG-63 cells, which are known as the osteoblast-like cells. Also, biodegradability and ability of the nanocomposites to form bone apatite in the simulated body fluid were studied and it was observed that by enhancing the immersion time of the nanocomposites in the simulated body fluid, more apatite will deposit on its surface.

Mallakpour and Rashidimoghadam (2020) tried several routes to modify chitosan and make it proper for bone tissue engineering. At first, PVA was used to enhance chitosan flexibility. After blending with PVA, different percentages of multi-walled carbon nanotubes were inserted within the blended polymeric matrix and bioactivity of the prepared nanocomposites was evaluated via immersion within simulated body fluid for 30 days. Finally, nanocomposite 3 wt% showed the most capability for the hydroxyapatite formation while in the case of the blended polymeric matrix without multi-walled carbon nanotubes no clear hydroxyapatite crystal was observable.

5.3.3 Antibacterial Materials

Taking a look at recent developments in the antibacterial agents shows that polysaccharides have indubitable role in this area. One of the most popular antibacterial agents is nanosized Ag and polysaccharides could be green replacements for unsafe reducing agents in their preparation route (Ma et al. 2016). In spite of vast applications of these nanoparticles, aggregation diminishes their antibacterial activity. Polysaccharides are known as one of the most favorable capping agents and stabilizers for these nanoparticles (Goel et al. 2019). In some cases, polysaccharides have the potential to act alone as the antibacterial moieties but their application in the form of polysaccharide/metal or metal oxide bionanocomposites led to attaining desirable properties (Prokhorov et al. 2019).

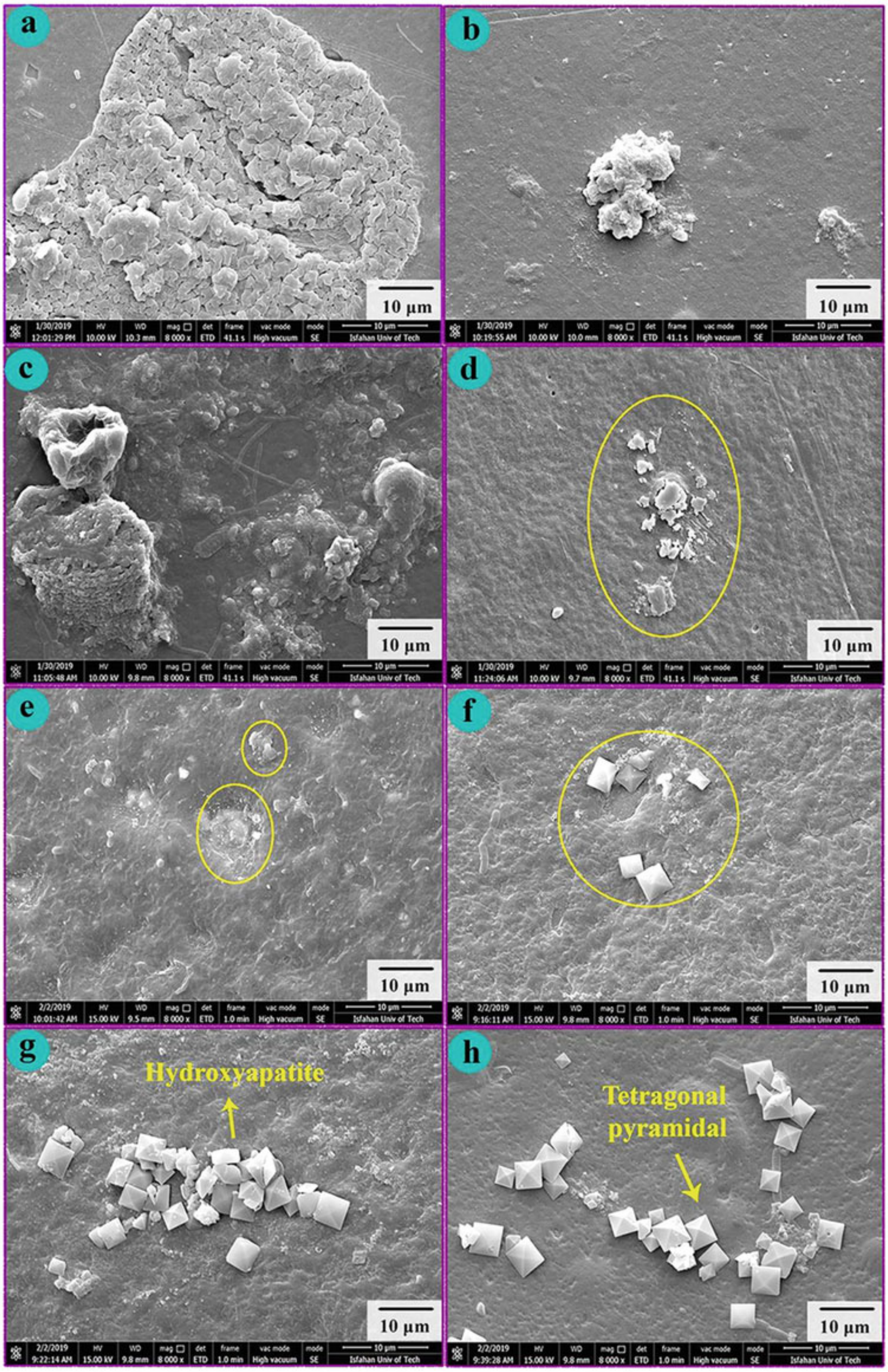

Fig. 12 FESEM photomicrographs after IVB test for **a** pure CT, **b** CT-TG blend, **c** CT-TG/SiO_2 nanocomposite (2 wt%), **d** CT-TG/SiO_2 nanocomposite (5 wt%), **e** CT-TG/SiO_2, nanocomposite (8 wt%), **f** CT-TG/SiO_2@Ag (1/0.3) nanocomposite, **g** CT-TG/SiO_2@Ag (1/0.5) nanocomposite, and **h** CT-TG/SiO_2@Ag (1/1) nanocomposite. Reprinted from Mallakpour and Abbasi (2020) by permission from Elsevier (FESEM: Field emission scanning electron microscopy, IVB: In vitro bioactivity, CT: Chitosan, TG: Tragacanth gum)

Javaid et al. (2018) used the potential of chitosan to add antibacterial feature to polyurethane. For this aim, they prepared bionanocomposite films by applying different mole ratios of chitosan and 1, 4-butane diol during a step-growth polymerization. Antibacterial activity showed an uptrend by enhancing the amount of chitosan. They commentated interaction between chitosan molecules with the positive charge and microbial cell wall with negative charge leads to the hydrolysis of peptidogycans in the bacterial wall, and consequently outflowing the intracellular electrolytes. In addition to that, chitosan is capable to interfere osmotic balance by changing the bacterial wall permeability and as a result prevents growth of the bacteria.

Rabbi et al. (2020) proposed cellulose-based biocompatible nanocomposite with antibacterial performance by incorporation of Ag nanoparticles. In this regard, cellulose was supplied from jute pulp and Ag nanoparticles were synthesized in situ using herbal extract as the reducing agent. Figure 13 suggests that fabricated cellulose/Ag nanocomposite showed efficient antibacterial activity during the disk diffusion test, while it showed a maximum inhibition zone of 18 mm against *Escherchia coli*, which was comparable to Ceftriaxone as the positive control. However, its effectiveness was lower than Ag nanoparticles. But thanks to its less toxicity compared to the Ag nanoparticles, it has been acclaimed as the efficient antibacterial material in different areas such as wound dressing and different textiles. Along with this characteristic, the prepared nanocomposite also showed catalytic performance.

Bouttier-Figueroa and Sotelo-Lerma (2019) proposed galactomannan/ZnO nanocomposites as efficient antibacterial agents against *Escherichia coli* and *Staphylococcus aureus*. The higher the galactomannan amount, the lower the antibacterial activity. But it could not deny the important role of the polysaccharide since the presence of galactomannan along with ZnO nanoparticles is vital to inhibit their precipitation in aqueous media. On the other side, in the synthesis process of ZnO nanoparticles, galactomannan acts as a nanoreactor for the formation and growth of ZnO with a hexagonal wurtzite structure.

One of the most important causes of the bacterial infections is biofilm formation, which is not easily curable with commonly used antibiotics (Goel et al. 2019). Goel et al. (2019) prepared a nanocomposite hydrogel with the ability to exterminate biofilms. They pointed out the role of κ-carrageenan as a reducing and capping agent for the green synthesis of Ag nanoparticles under microwave irradiation. Then, hydrogel nanocomposites were prepared using KCl crosslinking method. Owing to plenty of functional groups within the κ-carrageenan structure, its presence on the surface of Ag nanoparticles leads to outstanding colloidal stability for them without any aggregation even after 6 months. The prepared nanocomposite hydrogel was an effective antibacterial agent against both Gram-positive and Gram-negative bacteria. Also, 500 µg/mL of the κ-carrageenan-capped Ag nanoparticles were capable to inhibit the growth of *Staphylococcus aureus* and *Pseudomonas aeruginosa* biofilms and had potential to be used in packaging and biomedical areas.

Prokhorov et al. (2019) tried to demonstrate that electrical conductivity could affect the antibacterial performance of the chitosan/Cu nanocomposites. Different concentrations of Cu precursor were used for the preparation of nanocomposites with different amounts of Cu nanoparticles. They acclaimed an electron-transferring phenomenon is responsible for the observed antibacterial activity of the prepared nanocomposites. In fact, electron transfer from negatively charged bacteria to positively charged Cu nanoparticles will lead to dissociation of the bacterial membrane. It is worth to note that the maximum inhibitory against bacterial growth is observed under the electrical percolation threshold, which happened at low amounts of Cu nanoparticles.

Pectin has been used as the reducing and capping agent for the in situ synthesis of Ag nanoparticles (Hileuskaya et al. 2020). To ensure whether, type of the applied pectin will affect physicochemical features of the Ag nanoparticles, three different kinds of pectin with different degree of esterification and varied molecular weight were used. Also, the effect of pectin content was considered in this study. Well-dispersed Ag nanoparticles with a size of 8–13 nm were formed in the presence of low-methoxyl and high-methoxyl pectin. However, in the case of amidated low-methoxyl pectin rather aggregated nanoparticles were observed in TEM. These greatly affected the antibacterial

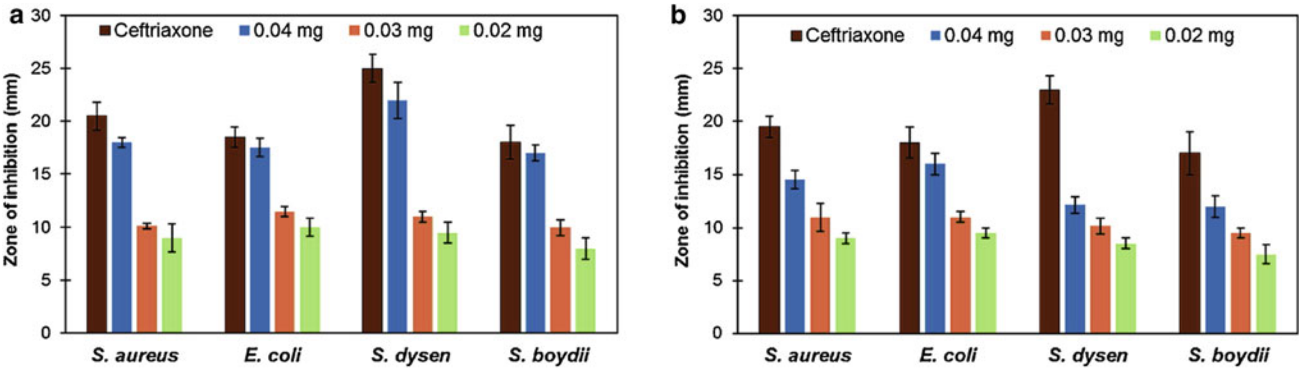

Fig. 13 Inhibition zone (mm) for four different pathogens against different amounts (mg/disk) of **a** AgNPs and **b** SCJC/Ag nanocomposite particles. Reprinted from Rabbi et al. (2020) by permission from Elsevier (SCJC: Sub-micrometercrystalline jute cellulose)

activity of the prepared Ag nanoparticles. Interestingly, no bacterial inactivation was observed in the case of aggregated Ag nanoparticles, while nanoparticle prepared in the presence of low- and high-methoxyl pectin presented inhibition zones against *Escherichia coli*, *Bacillus pumilus*, and *Bacillus subtilis*. Also, enhancing the amount of pectin had a positive effect on the bacterial growth inhibitory. Indeed, when pectin:Ag mass ratio was 10:1, no antibacterial activity was observed, but enhancing this ratio to 25:1, satisfactory results were observed. They illustrated the role of pectin in the reduction of Ag particle size, which directly affects its antibacterial performance. Meanwhile, pectin is capable to adhere to the bacterial membrane and promote antibacterial agent delivery.

5.3.4 Wound Dressing

During daily activities, different injuries may be caused in skin and it needs care by using proper wound dressings until healing. An ideal wound dressing should be able to keep the wound zone humid, gaseous permeable, absorb exudates, and have antibacterial property to prevent infection (Xu et al. 2019). Some polysaccharides meet these requirements and are proper candidates to be used in the fabrication of wound dressing. For example, it has been pointed out to the capability of chitin to promote movement of keratinocytes to wound, and consequently accelerates healing (Mehrabani et al. 2018).

Deng et al. (2020) designed a nanocomposite hydrogel based on agarose containing Fe^{3+} nanoparticles to use for wound infection treatments. The nanocomposite prepared at the optimum conditions showed satisfactory mechanical performance as well as proper wound disinfection and healing of the wound in the animal model. The prepared hydrogel also demonstrated antibacterial behavior and it showed inhibition zone for *Staphylococcus aureus* (diameter = 1.5 cm) during the Oxford cup method. Also in the agar plate assays, 99% reduction in the number of *Staphylococcus aureus* colonies compared to the control sample was observed. Taking into account their biocompatibility and photothermal sterilization capability, the prepared nanocomposite hydrogels could be proper for antibacterial wound dressing applications.

A wound dressing composed of chitosan, PVA, and acacia gum embedded with ZnO nanoparticles was prepared using electrospraying by Güldiken et al. (2020). The effects of concentration of chitosan, acacia gum, and ZnO nanoparticles on the nanocomposite's features were studied. Best cell viability was observed when weight percentages of chitosan and acacia gum were 8 wt% and 2 wt%, respectively. This composition was selected for further studies and maximum cell viability was attained when 0.6 of ZnO nanoparticles were inserted within the blended polymer matrix.

In a study, Mazloom-Jalali et al. (2020) designed a series of nanocomposite films based on chitosan and polyethylene glycol embedded with different amounts of zeolitic imidazolate framework-8 nanoparticles to be used as a wound dressing. The nanocomposites were loaded with cephalexin to evaluate their drug-release efficiency. The tensile strength of the nanocomposites seemed to be improved by incorporation of the nanoparticles. Nanocomposite film containing 2 wt% of zeolitic imidazolate framework-8 showed the best cell viability during cytotoxicity test, which may be due to more controlled release of the loaded drug. However, cell viability decreased by enhancing the nanocomposite film concentration. Figure 14a illustrates this trend well. Antibacterial activity of the prepared nanocomposites was studied using the disk diffusion method and nanocomposites containing 3 and 4 wt% of the nanoparticles showed the strongest antibacterial activity. Figure 14b shows nanocomposite film containing 4 wt% of zeolitic imidazolate

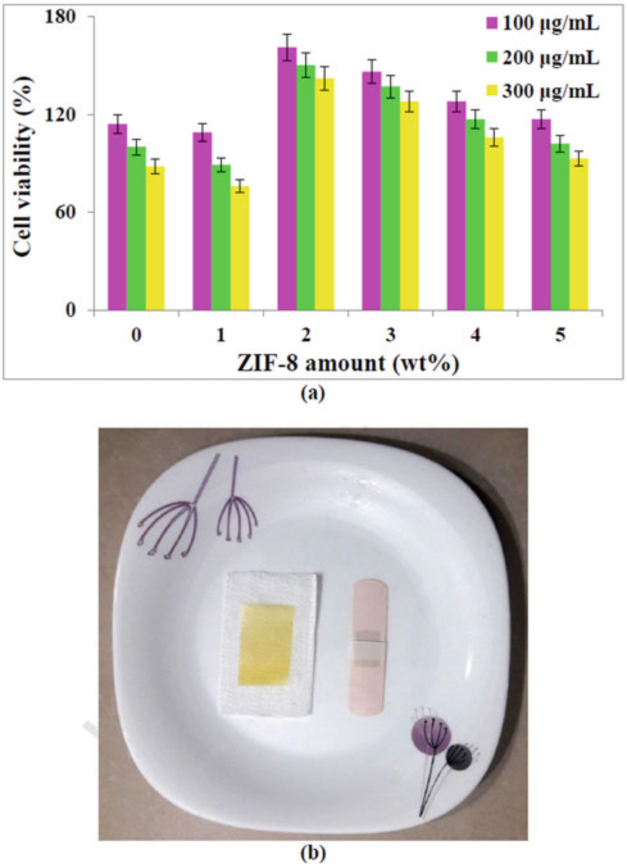

Fig. 14 **a** The cell viabilities of nanocomposite films containing 0–5% of ZIF-8 NPs evaluated by the MTT assay using L929 fibroblast cells and different concentrations of the films (100, 200, and 300 µg/mL). **b** The digital photograph indicating the optimum film containing 4% ZIF-8 NPs (film 5) adhered on the sterile gauze cotton (left) to be used on wounds along with a commercial band aid (right). Reprinted from Mazloom-Jalali et al. (2020) by permission from Elsevier (ZIF-8: Zeolitic imidazolate framework-8)

framework-8 nanoparticles, which has been adhered to a sterile gauze and it may have the capability to be used as wound dressing.

A hydrogel composed of guar gum-grafted-polyacrylamidoglycolic embedding with Ag nanoparticles has been suggested by Palem et al. (2019) as a potential wound dressing. $NaBH_4$ was used as both reducing agent for the in situ fabrication of Ag nanoparticles from its precursor and plays the role of crosslinker for fast fabrication of hydrogel. However, presence of Ag nanoparticles reduced the cell viability of the prepared hydrogel nanocomposite and it endows bacterial inactivity to the hydrogel, which is known as one of the requirements of wound healing materials. As an advantage, the nanocomposite hydrogel was processable to different shapes. Thanks to crosslinking via borate ions, the hydrogel was injectable and stretchable.

Chitosan/dextran nanocomposite loaded with curcumin was designed as an advanced wound dressing (Xu et al. 2019). Apart from inhibitory effects for *Streptococcus mutans* and *Escherichia coli* growth, the prepared curcumin-loaded nanocomposite had the potential to be used for tissue regeneration and deposition of collagen on the abdominal wound tissue.

Pan et al. (2019) pointed out an important issue that restricts antibacterial materials, i.e., leaching the antibacterial agent which causes deactivation of the material and damages to the environment. They propose covalent bonding of guanidine-based polymer onto baggase cellulose using epichlorohydrin as a coupling agent. Satisfactory antibacterial activity without any leaching, high degree of swelling, proper cell viability, and improved mechanical strength confirmed that it could be proper to be used for wound dressing applications.

Mehrabani et al. (2018) suggested the advantage of using chitin in the preparation of chitin/silk fibroin-based bionanocomposites containing different percentages of TiO_2 nanoparticles to be used as a wound dressing. It was observed that participation of chitin within the bionanocomposite helped to improve mechanical features as well as biodegradability. Also, blood clothing was improved in the presence of chitin, which could be due to its cationic characteristic. Meanwhile, presence of TiO_2 nanoparticles endows significant antibacterial and antifungal properties to the bionanocomposites.

5.4 Catalyst Supports

Some excellent features of the polysaccharides prompted scientists to use them as the catalyst supports. Apart from their renewability, they contain a lot of functional groups which enable them to bind with metals. Also, they are not soluble in a wide range of organic solvents (Rincon et al. 2019), which remove obstacles for catalyst recovery (Nguyen 2019; Rincon et al. 2019).

A bionanocomposite based on modified chitosan has been proposed as a catalyst for a series of Hantzsch condensation reactions (Asgharnasl et al. 2020). For this aim, chitosan was first modified with creatine-terephthaloyl chloride ligand and then Fe_3O_4 nanoparticles were prepared in situ in the presence of as-modified chitosan. Figure 15 shows uniform distribution of the Fe_3O_4 nanoparticles with the average particle size of 25–30 nm. Then, the catalytic performance of the prepared bionanocomposite in the synthesis of a series of 1, 8-dioxo-decahydroacridine derivatives was evaluated and high-yield percentages of the products along with green reaction conditions were observed.

Nguyen et al. (2019) used a hybrid of polysaccharides including 2-hydroxypropyl-β-cyclodextrin and sodium alginate as a support for palladium nanoclusters. The resulted bionanocomposite was used as the catalyst in degradation of 4-nitrophenol, methyl orange, and rhodamine B and their complete degradation occurred within 24 min, 20 min, and 16 min, respectively. Also, the catalyst efficiency in Sonogashira coupling reaction of phenylacetylene with a series of aryl halides as model precursors was studied and showed satisfactory yields for those aryl halides having electron-neutral and electron-donating groups. The catalyst was capable to reuse several times and they acclaimed the problem of palladium catalysts recyclability has been solved to high extents in this study.

A nanocomposite based on cellulose was designed by Maleki et al. (2019) to be used as a catalyst for the synthesis of dihydropyridine and polyhydroquinoline derivatives. A bimetallic system composed of Cu and magnetic γ-Fe_2O_3 nanoparticles was used to immobilize on the cellulose surface. The plausible mechanism which illustrates the role of γ-Fe_2O_3/Cu@cellulose in the activation of the reactants as well as some of the intermediates of the reaction is demonstrated in Fig. 16. As the synergism, presence of both Cu and γ-Fe_2O_3 nanoparticles on the cellulose endows to the resulted nanocomposite some important features such as easy separation and reusability. In the presence of the suggested catalyst, the mentioned reactions can be carried out without any need for harsh reaction conditions such as using toxic solvents, reflux, complex workup procedures, and low yields, which are commonly being criticized by green chemistry.

One of the limitations in the usage of $NaBH_4$ is the low rate of hydrolysis at room temperature. In a study, Liao and Huang (2020) used magnetic chitin/Cu hydrogel nanocomposites to overcome this problem. It was observed that the concentration of Cu^{2+} precursor and $NaBH_4$, catalyst amount, and temperature were effective factors on the catalytic performance of the prepared nanocomposites. Owing to the magnetic response, the catalyst had the capability to be

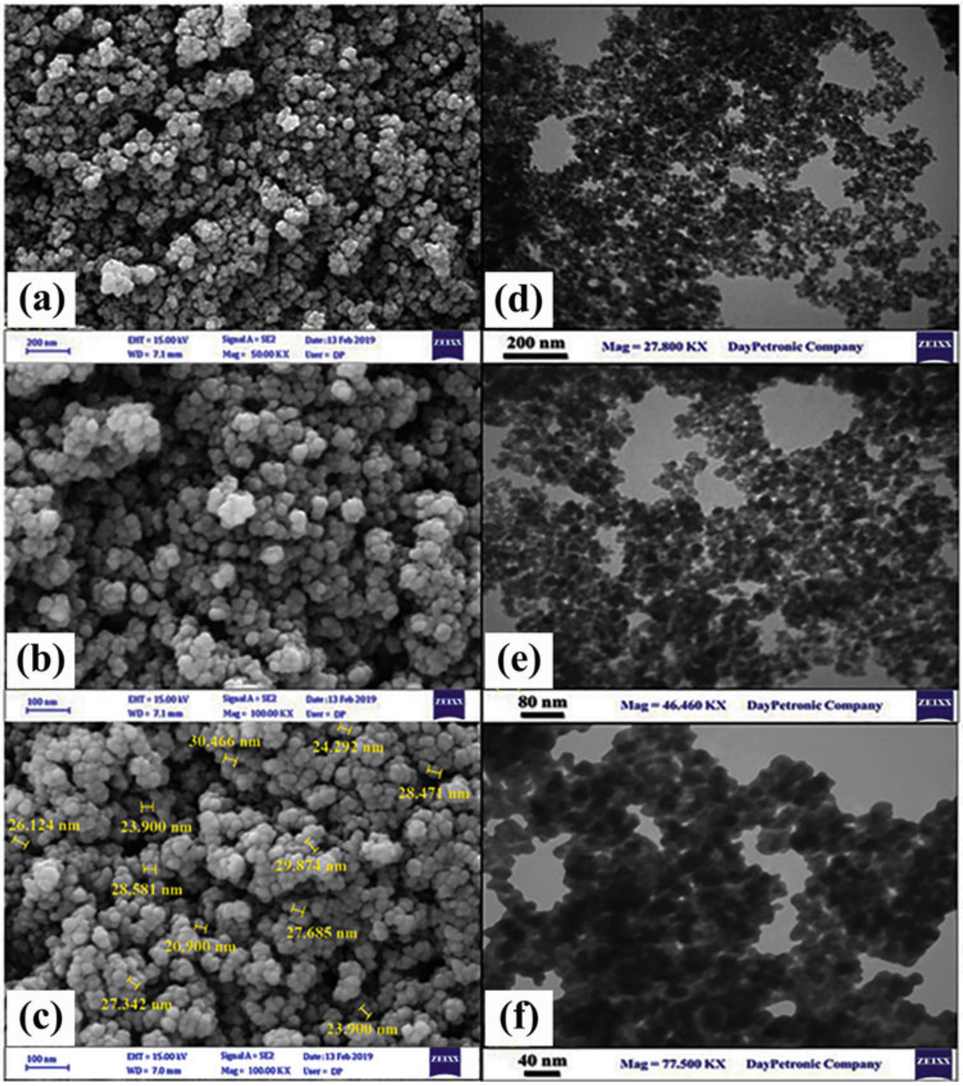

Fig. 15 **a**–**c** FESEM images of the magnetic chitosan-terephthaloyl-creatine bionanocomposite, **d**–**f** TEM images of the magnetic bionanocomposite. Reprinted from Asgharnasl et al. (2020) by permission from Elsevier (FESEM: Field emission scanning electron microscopy, TEM: Transmission electron microscopy)

separated from the reaction mixture using a magnetic field and be used without any loss in the conversion rate.

Veisi et al. (2020) prepared a core–shell bionanocomposite to be used as a support for the production of Pd NPs. For this aim, Fe_3O_4 nanoparticles were prepared, and then they were coated with aminopropyl silica. Finally, the prepared hybrid was functionalized with chitosan to introduce different functional groups including hydroxyl and amine on its surface. These functionalities provide a proper substrate for coordination of metal ion and the prepared Pd nanoparticles will be anchored on the surface of the chitosan-encapsulated Fe_3O_4/SiO_2 system. The fabricated nanocomposite was applied in Suzuki–Miyaura coupling reactions of a series of aryl halides and it showed superior performance over other Pd-based catalysts. Also, its efficiency in catalyzing the reduction of 4-nitrophenol to 4-aminophenol was studied and satisfactory results were obtained.

Abolghassem et al. (2019) used α-chitin as a template for the synthesis of ZnO nanoparticles. In this procedure, ZnO nanoparticles were produced in situ during a hydrothermal process and then the prepared chitin/ZnO nanocomposite was used as a catalyst for the synthesis of benzo[a]pyrano(2, 3-c)phenazine derivatives. This green manner was proposed as an efficient way to produce these pharmaceutically important materials in satisfactory yields.

A blend composed of chitosan and PVA was used with dual function to provide both carbon and nitrogen in the preparation of Ag nanoparticles embedded with nitrogen-doped carbon nanocomposite (Alhokbany et al. 2019). Figure 17 shows the related procedure, schematically. The prepared nitrogen-doped graphite carbon matrix affords a bed for not only proper dispersion of Ag nanoparticles, but also enhances its recyclability and consequently its life time. The catalytic efficiency of the prepared nanocomposites with relatively supreme surface area

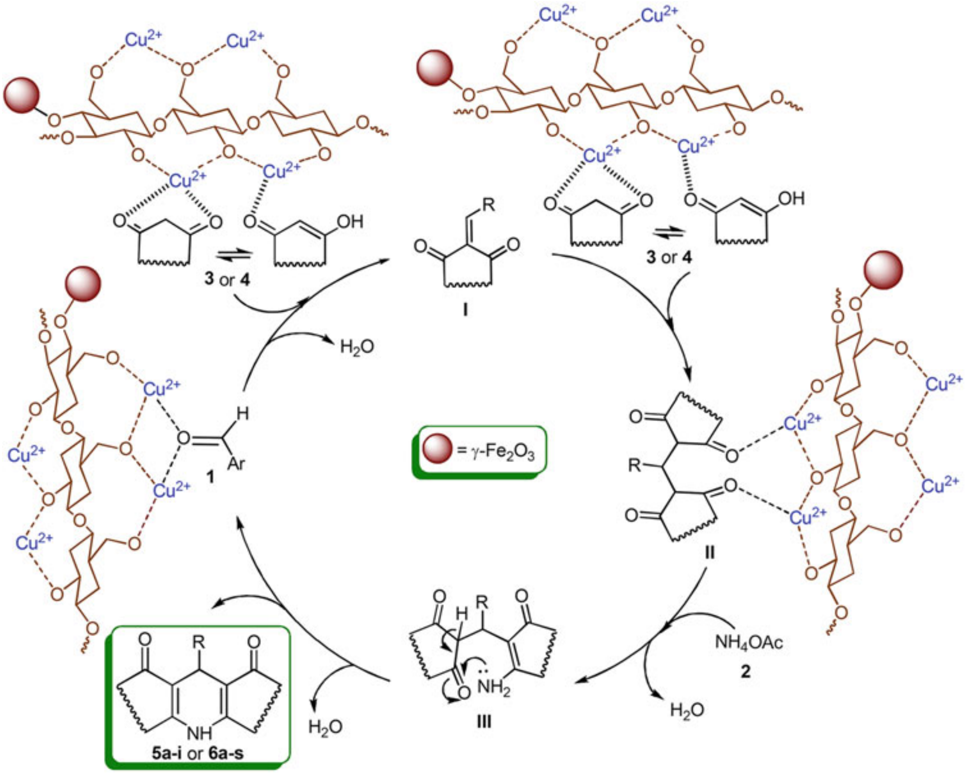

Fig. 16 Proposed mechanism for the synthesis of 1, 4-dihydropyridine and polyhydroquinoline derivatives using γ-Fe_2O_3/Cu@cellulose. Reprinted from Maleki et al. (2019) by permission from Elsevier

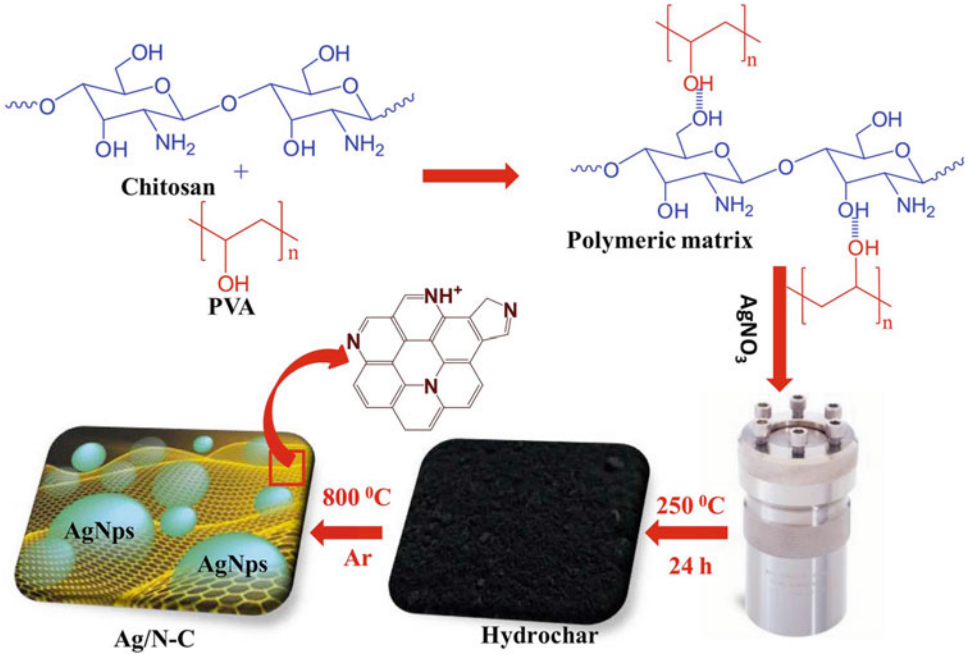

Fig. 17 The synthesis routes for hydrochar and Ag/N–C nanocomposite. Reprinted from Alhokbany et al. (2019) by permission from Elsevier (N–C: Nitrogen-doped carbon)

in the reduction of 4-nitrophenol to 4-aminophenol in the presence of $NaBH_4$ was evaluated and 98% of the reduction occurred within 40 min.

Agar was used as a support to obviate the recycling problem of CuO nanoparticles in the catalytic reactions (Kamal 2019). For this aim, CuO was prepared ex situ during a microwave heating route and then its nanocomposite with agar/CuO weight ratio of 9/1 was fabricated. The catalytic efficiency of the nanocomposite in reducing a series of nitroarenes including 4-nitrophenol, 2, 6-dinitrophenol and 2-nitrophenol was investigated and acceptable results were observed. However, it showed lower activity compared to some other catalysts, but the main advantage of this catalyst was its capability to be reused several times by maintaining the efficiency.

Bonardd et al. (2019) prepared a series of bionanocomposites containing different amounts of Au nanoparticles with a catalytic performance for the conversion of *p*-nitrophenol to *p*-aminophenol. Taking into account the interaction between $AuCl_4^-$ complexes with amino functional groups of the chitosan, it was used as both reducing and stabilizing agents for the in situ preparation of the Au nanoparticles. The photocatalytic activity of the prepared bionanocomposites depends on the amount of Au nanoparticles, whereas by enhancing the content of Au nanoparticles from 10 to 40 wt%, the rate constant of the reduction reaction enhanced from 48 to 75 1/s.

6 Concluding Remarks

Daily life is encompassed by a wide variety of polymer-based composites and those derived from natural resources are of great importance. Over time, population growth and depletion of petroleum resources have forced humans to turn to renewable resources. One of the most accessible and affordable natural materials is polysaccharides, which may be the best replacement for the petroleum-based polymers. The Earth is plenteous of polysaccharides and they could be exploited from animals, microorganisms, plants, or any other natural source and they have the potential to be used instead of petrochemicals in different sectors. They may appear in either natural or modified forms. As was discussed in detail, their combination with organic/inorganic nanomaterials leads to high-demand bionanocomposites with a wide range of applications, e.g., medical, water treatment, catalysis, packaging, etc. Some examples of recent works were brought in this regard, in which satisfactory performance was observed for the related application. In addition to their cost-effectiveness, they proposed the opportunity to pay more attention to green chemistry. Indeed, this would be a road to convert cheap and in some cases wastes to value-added products. However, the declared examples have been carried out in the laboratory and it seems more studies and trials need to be done to industrialize them for the practical applications.

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Multi-utilisation of Cow Dung as Biomass

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Abstract

Cow dung or cow manure is a heterogeneous substance excreted by bovine animal species as waste. It also contains water, microbiota, feed scraps and dead skin. The demand for livestock and dairy products has led to the exponential growth in cow dung generation in the past decades. Cow dung is primarily disposed in the environment, used as organic fertiliser or used as solid fuel in rural areas. However, severe environmental and ecological damage has been caused by indiscriminate disposal and improper elimination of cow dung into the surrounding. This alarming problem can be addressed by converting cow dung into biofuel via thermochemical process or be used as organic fertiliser after vermicompost treatment. Moreover, cow dung can be used for electricity production, heat, biochar and friction composites. A cow dung to biofuel conversion systems should be efficient and well controlled to offer economically feasible energy generation and limit environmental pollution. Hence, the objective of this chapter is to analyse the physio-chemical properties of cow dung and evaluate its potential for multi-utilisation as biofuel and organic fertiliser. Moreover, the chapter discusses advanced processes of thermochemical energetic conversion of cow dung to assess its potential as a sustainable renewable source.

Keywords

Cow dung • Generation • Composting • Physio-chemical properties • Fertiliser • Combustion • Anaerobic co-digestion • Vermicompost • Biochar • Advance techniques

1 Introduction

Dairy farming is one of the largest and fastest-growing industries in the world. In 2020 the global cattle population count reached 987.51 million head (Statista 2012). Moreover, the estimated dairy market value worldwide is 673.8 billion USD which is expected to pass 1 trillion USD by 2024 (Shahbandeh 2019). Hence, it is evident that the growth of cattle production will not decline in the near future. As the cattle population increases, livestock manure generation increases proportionally—with that comes unavoidable waste disposal problems. Livestock waste is a serious concern for public health and the environment as it releases harmful pathogens, noxious gas, and odour (Masud et al. 2019). According to the United Nations report, livestock contributes globally 14.5% of all greenhouse gas pollution (carbon dioxide, methane, nitrous oxide, etc.), half of which comes from cows (DeMartini 2017). Cattle generate more methane by volume than humans as a cow produces approximately 200 litres of methane per day (DeMartini 2017). Moreover, improper and indiscriminate cow dung dumping or using it for landfilling poses further challenges. If cow manure is not treated properly before applying it to soil the phosphorus and nitrogen in the cow dung can contaminate nearby water bodies during rainfall. Therefore, it is essential to use modern waste treatment technologies to properly manage cow dung and avoid global scale environmental pollution. The exorbitant cost of running a cow waste treatment system is prohibitive for most developing and least developed countries. Hence, this

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chapter discusses multi-utilisation of cow dung as biomass, which will add economic value to waste product and make the management process sustainable and affordable.

A report by the Food and Agricultural Organization (FAO) indicates that in 2017 the world cattle population (of 141 countries) including dairy cattle, non-dairy cattle and buffaloes produced 66.74 billion kg of manure (Livestock manure storage 2020). Research has shown that 1 kg of fresh cow dung can produce an estimated 0.03 m^3 of biogas per day (Oluremi et al. 2018). Therefore, the world can collectively produce approximately 2 billion m^{3-} of biogas each year which is equivalent to 1.14 billion litres of petroleum or ten Giga watt-hour of energy. Moreover, 20–25 m^3 of cow dung have a total energy value of 100–125 kWh, which can be converted into 35–40 kWh of electricity and 55–75 kWh of heat energy (Sorathiya et al. 2014). Therefore, theoretically, the biomass potential of cow dung is 3.5 Giga watt-hour of electricity and 5.5 Giga watt-hour of heat energy. Hence, significant economic and energy asset can be generated from cow manure waste. Thus, research and development work must be continued to invent multi-utilisation of cow dung waste as biomass. An adequate cow dung management system can produce enough energy to support its own farming operation as well as reduce global greenhouse gas pollution. Through policy and regulations, sustainable waste management system can be adopted (Masud 2014, 2017, 2019).

Various waste management applications of cow dung are discussed in this chapter that could potentially ensure higher profit to livestock owners while mitigating the environmental pollution. Additionally, the work aims to establish the intrinsic and physio-chemical characteristics of cow dung and evaluate its potential for multi-utilisation. Section 2 highlights the generation of cow dung around the world. In Sect. 3, the physio-chemical properties of cow dung are discussed. Section 4 discusses the conventional application of cow dung, such as organic fertiliser and solid fuel. Finally, Sect. 5 focuses on advance methods of cow dung utilisation as organic fertiliser, biogas, biochar and reinforcement of friction composites.

2 Cow Dung Generation Around the World

Cow dung consists of digested grain and grass. It is rich in nutrients and organic materials, as nitrogen, Phosphorus, and Potassium are present in cattle manure.

The production of cattle manure in different countries depends upon various factors such as the number of cattle, Gross Domestic Product (GDP), geography, farming system and manure processing system.

2.1 Cow Dung Generation in Developed Countries

Cow dung generation scenario of 35 developed countries of the world is discussed in the following section to understand the biomass potential of cow dung and to propose appropriate waste treatment technologies (see Fig. 1). The discussion is based on geographical and economical point of view, to hopefully encourage policymakers to promote the use of cow dung for energy and organic fertiliser applications.

This graph (Fig. 1) shows the number of cattle and the amount of manure produced in developed countries (Livestock manure storage 2020). The horizontal axis indicates the number of dairy animals and the vertical axis shows the amount of manure in kilogram, the size of the bubble shows the GDP of the respective country, and different colour shows different continents. The United States of America produces the maximum amount of cow dung, which is about 4619.66 million kg per annum, where the number of cattle and buffaloes is 93.70 million head (Livestock manure storage 2020). The minimum amount of manure production among developed countries is in Malta, which is about 1.05 million kg per annum, where the number of cattle and buffaloes are 14.18 thousand head (Livestock manure storage 2020). Average production of these 35 developed countries is about 385.78 million kg, and different continents have various contributions in this regard. The highest average production is seen in the North America continent, estimating almost 2588.19 million kg per annum, other continents are far away from this production rate. In Australia continent, average production is around 1159.62 million kg per annum, nearly 1000 million less than the amount produced by America (Livestock manure storage 2020). Though almost all countries in Europe are developed country, the manure production in Europe is again 1000 million less than Australia. Although the continent of Europe has the highest number of developed countries, the average amount of manure is about 194.60 million kg per annum, which is the second-lowest among all other continents. However, only one country of Asia, Japan is placed in this graph, and the average amount of manure is 168.73 million kg per annum (Livestock manure storage 2020). Generally, all the countries follow the same trait; the amount of manure increases with the increasing number of animals; therefore, all the countries are aligned in a straight line. Figure 1 indicates the respective GDP of each country to analyse the purchasing power of its citizens. Countries with higher GDP can potentially adopt advanced and expensive technologies. The cow dung generation varies drastically among the developed nations due to land availability and the number of human

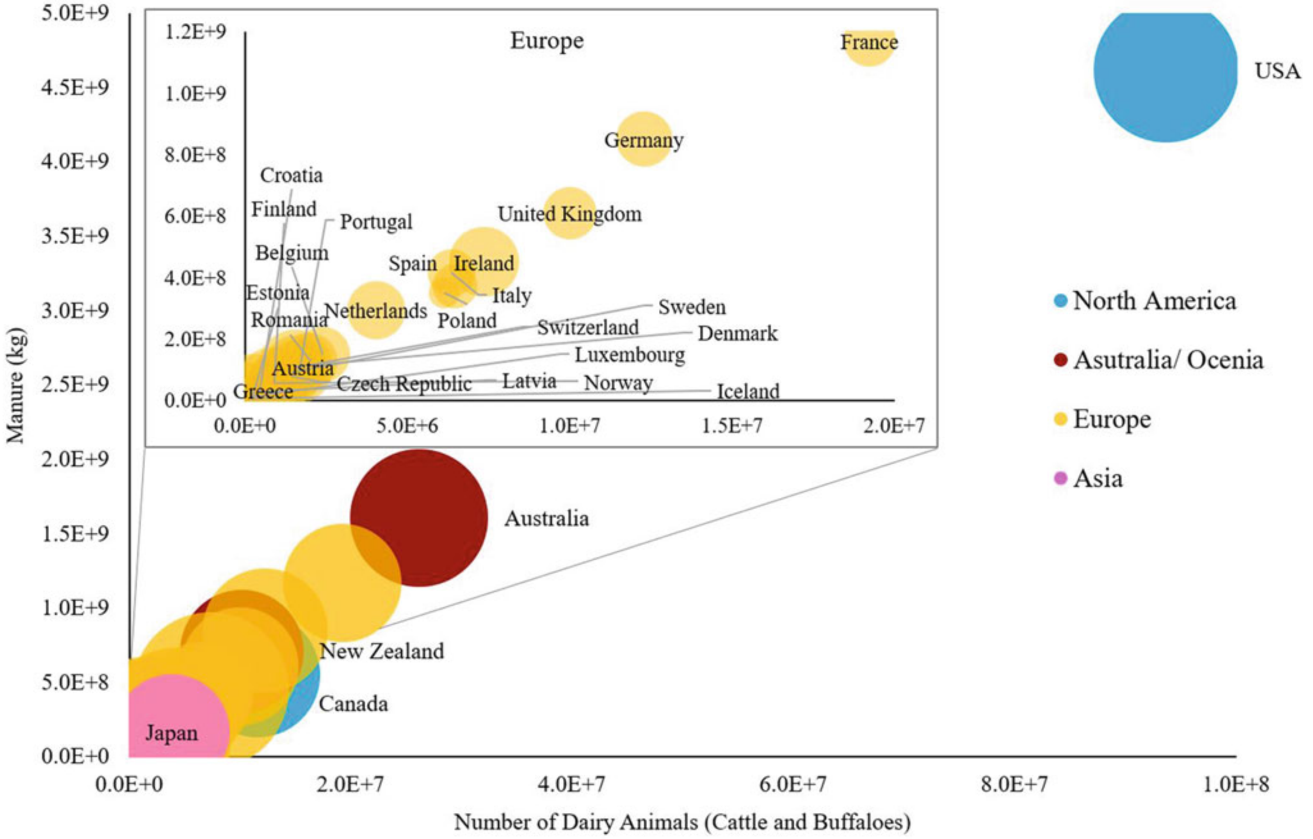


Fig. 1 Manure generation scenario (per annum) of developed countries in 2017

populations. Since all of the developed countries have higher GDP, they can adopt any advanced technologies irrespective of cost and maintenance challenges. There is no identifiable relationship between GDP and manure production. So, while suggesting treatment methods on cow dung-based energy production for developed countries, efficiency, and environment impact should be considered rather than the overall cost.

2.2 Cow Dung Generation in Developing Countries

According to the United Nations World Economic Situation, more than 70 countries are enlisted as developing countries. Major part of Asia, Africa, North and South America is in this list as developing countries represent almost half of the world’s population (see Fig. 2).

Figure 2 illustrates the number of dairy animals and amount of manure production in developing countries (Livestock manure storage 2020). The smaller square in the right of the graph shows the countries whose production rate is less than 50 million kg. The colour of the bubbles reveals the continents and size of the bubble indicates the GDP of the particular country.

In case of developing countries, the effect of GDP on adoption challenges becomes critical. In the developing country spectrum, the highest GDP is in Qatar (61264 USD), and the lowest GDP is in Cameroon (1422 USD). Therefore, despite Cameroon generating a significant amount of cow dung (236.63 million kg per annum), due to low purchasing power of its citizens, they can not adopt expensive manure waste management technologies. In contrast, Qatar, due to its strong economic power, can easily integrate expensive and efficient advanced waste conversion techniques. The highest amount of manure is produced by Brazil, estimating 9185.71 million kg per annum, and the lowest amount of manure is produced by Singapore, which is only 7133 kg per annum (Livestock manure storage 2020). In this case, since both Brazil and Singapore have high GDP, they can also adopt any biomass conversion technologies. However, the same can not be said for developing countries with least GDP. So efficient plan for using manure as a source of energy should be based on the purchasing power of countries with least GDP. However, there are some countries in this graph which are not placed in the straight line like other

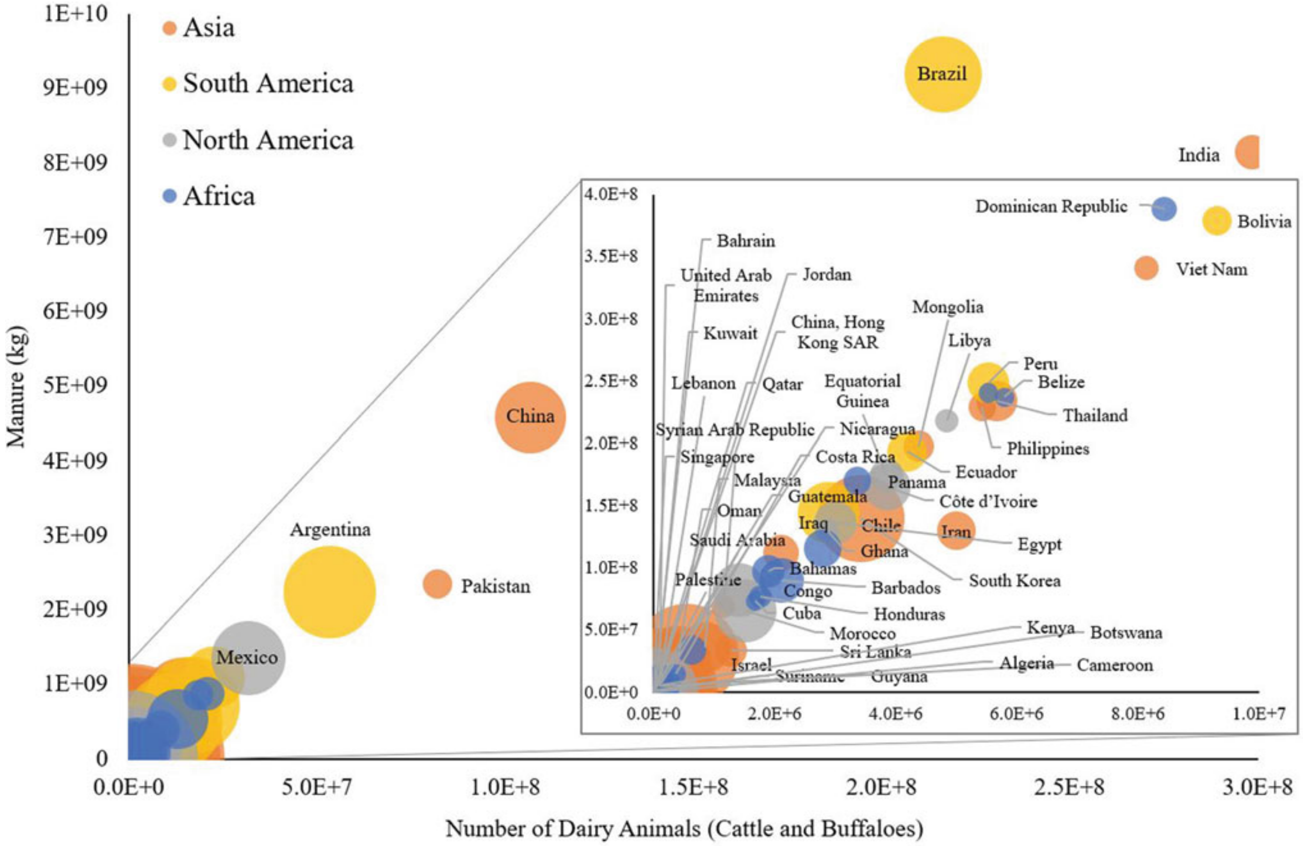


Fig. 2 Manure generation scenario (per annum) of developing countries in 2017

countries. For example, Pakistan, India and Iran have deviated from the slope of the graph, as they have more cattle numbers but less amount of manure production. The proportional relation does not apply for these countries, and the proposal regarding the conversion of cow dung should be different for these particular countries who showed anomalies. Further study is required to analyse the cost feasibility of multi-utilisation cow dung management system.

The total amount of manure produced by these 67 developing countries is about 591.57 million kg per annum (Livestock manure storage 2020). Unlike the graph of developed countries, the continent of Asia has the highest number of countries in this graph, and the highest average amount of manure production is estimated at 675.59 million kg per annum (Livestock manure storage 2020). The second-highest average amount of manure production continent is Africa, which produces almost 237.64 million kg per annum cow dung. The average production of manure of South and North America is 29.68 million kg per annum and 4.45 million kg per annum, respectively. The developing nations show more production of cattle manure than the developed nations; therefore, the proposal should be more feasible for these developing nations.

2.3 Cow Dung Generation in the Least Developed Countries

The cow dung generation data of 39 least developed countries are represented in Fig. 3 (Livestock manure storage 2020). This graph is prepared to aid the budgeting process and help to estimate treatment costs. These countries have a large number of cattle that produces a considerable amount of manure. However, because of the low GDP per capita, adopting expensive technology is not feasible for these nations. If cow dung can be used as sustainable biomass resource, it can deliver economic improvement in these countries.

Figure 3 follows the same format as the previous figures, and in the least developed region, most of the countries are on a straight line. That means most of the countries prove the proportionate relationship between the number of cattle and the amount of manure. However, some countries show incongruities and do not follow the proportionate relationship. Bangladesh and Nepal are such countries that deviate from the general trend. These countries have more dairy animals, but the amount of manure produced is less compared to other countries in the same region of the graph. Due

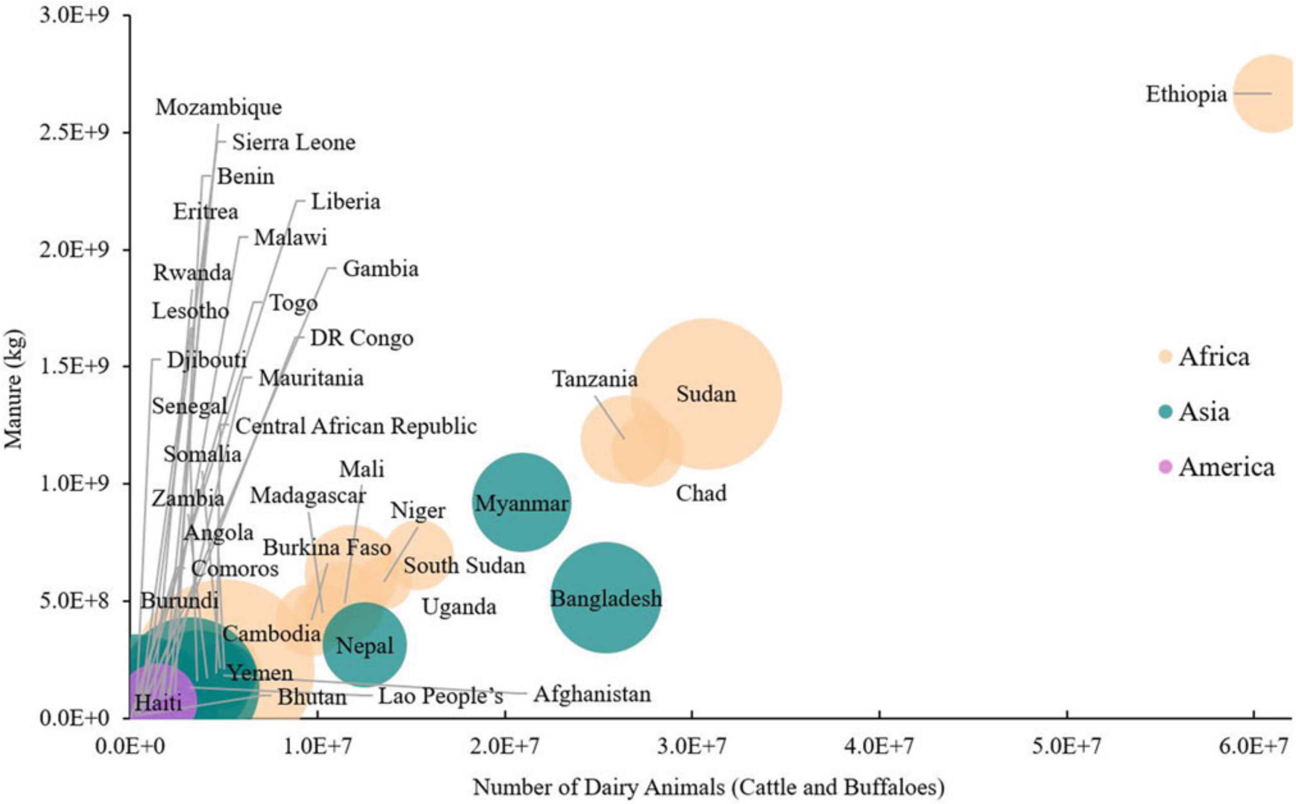


Fig. 3 Manure generation (per annum) (2017) scenario in least developed countries

to some issues like lack of proper technical and farming facilities, these countries show this discrepancy.

The average production of manure by the 39 least developed countries is about 348.79 million kg per annum. Maximum amount of manure is produced by Ethiopia valuing 2667.03 million kg per annum, and minimum amount is produced by Liberia estimating 1.895 million kg per annum (Livestock manure storage 2020). Africa and Asia continent produce an average of 374.19 and 288.895 million kg per annum, respectively (Livestock manure storage 2020). The maximum GDP among the least developed countries is of Angola, which is 4096 US dollar, and the amount of manure generation is 207.29 million kg per annum. This is marginally less than the maximum production of manure by Ethiopia though the difference of GDP between Angola (4096 USD) and Ethiopia (757 USD) is almost 3339 US dollar. Based on GDP evaluation, it is evident that the farmers and local businesses of the least developed countries have limited purchasing power. Hence, only inexpensive waste conversion technologies are feasible for these countries. However, exclusive cost-benefit analysis should be done before recommending waste management techniques for countries with a struggling economy and least GDP. All three graphs discussed above reveal the cow dung generation throughout the world. Considering the vast amount of cow dung generation across the globe, proper measures should be taken to ensure its adequate utilisation for sustainable green energy production.

3 Physio-Chemical Properties of Cow Dung

Understanding the physio-chemical properties of cow dung is imperative to optimise its storage and handling conditions, enhance the treatment process, reduce wastage, and improve its industrial application.

3.1 Composition Analysis

The residues of food consumed by herbivorous bovine animals are generally known as Cow dung. It is a mixture of urine and faeces in the 3:1 ratio. As the foods of cattle are generally plants, leaves and grasses, the manure consists of cellulose, hemicellulose and lignin (the main component of skeletons of plants). Cow dung also contains around 24 various minerals including macro elements like nitrogen, potassium and trace elements like iron, sulphur, magnesium, cobalt, manganese and copper. Just like other manure, cow dung is also rich in microbial diversity, including bacteria such as Bacillus spp., Lactobacillus spp. and Corynebacterium spp., yeast-like Candida, Saccharomyces and Protozoa (Nene 1999; Randhawa and Kullar 2011). However, different bacterial genes that include Escherichia coli, Enterobacter aerogenes, Klebsiella pneumoniae, Klebsiellaoxytoca, Kluyvera spp., Citrobacter koseri, Morgarella morganii, Providencia stuartii, Pasteurella spp., Pseudomonas spp., Providencia alcaligenes are also present in cow dung (Sawant et al. 2007).

3.2 Physical Properties

Physical properties such as fixed carbon, volatiles, heating value, ash and moisture are prerequisites for assessing the feasibility of using cow dung as a sustainable source of biomass. Good understanding of the physical properties helps improve the methods of conversion and handling the process of storage. This reduces the treatment cost and makes the process of cow dung waste treatment more efficient, sustainable and environment friendly.

Figure 4 shows the physical properties of cow dung, which includes percentage content of fixed carbon, volatiles, ash and moisture. Additionally, it also represents the heating value, which is significant for energy analysis. About 83.91% of volatiles are present in cow manure that makes them the perfect feed material for the gasification process. The moisture content of cow dung generally remains 39.24 wt% and varies slightly in different sources (Font-Palma 2019). The higher value of moisture content has an essential consequence in the conversion of the thermochemical process as in order to dry the manure, with low moisture content the cow dung can be dried quickly. The ash content generally varies from 10.8 to 45.2 wt% on a dry basis; 27.72% is a constant quoted in some sources (Font-Palma 2019). The ash content of cow dung (4.7–10.3 wt% dry basis) is higher than in wheat straw (Carlin et al. 2011). Hence, the high-ash content in cattle manure can create certain problems including agglomeration, sintering, erosion, corrosion and deposition. These phenomena occur due to the low melting point of the ash. However, the composition and content of ash usually depend on the bedding type used in different countries. According to Carlin et al., the difference between the properties of low and high-ash mass depends on the management practices of manure (Carlin et al. 2009). Generally, the manure with low-ash contents is collected from cement-paved lots. Manure with higher ash content is collected from unpaved yards. The last two properties of the figure are heating values and fixed carbons with a value of maximum 20.08 MJ/kg and 16.09 wt%, respectively. However, the heating value of cow dung is slightly lower than the heating value of coal (16–24 MJ/kg for sub-bituminous) (Font-Palma 2019).

Figure 5 shows the elements of cow dung in the dry and ash-free sample. The highest percentage is carbon, 49% of the total (Carlin et al. 2009). The high amount of carbon gives the cow dung more heating value and makes it efficient to use as fuel. The second-highest is oxygen which is almost 41%, which ensures efficient combustion. Apart from carbon and oxygen, there is a number of other elements as well, including hydrogen, which is almost 7%. There is a minimal amount of nitrogen and sulphur, 2% and 1%, respectively. Generally, a high amount of sulphur content in organic form is harmful because it emits SOx during thermochemical conversion. Emission of SOx in the air can be a cause of acid rain (Carlin et al. 2009). Even though the Sulphur content in cow dung is only 1.36%, it is higher compared to other organic products. The elemental analysis shows that cow dung has much economic value to use as fuel (because of carbon and oxygen) and as fertiliser (because of Hydrogen and Nitrogen). However, the harmful effect of SOx emissions cannot be neglected.

3.3 Chemical Properties

As mentioned earlier, cow dung is a mixture of organic materials as well as macro and micronutrients. There is also a certain pH, ash and other minor components. In Fig. 6, the minerals and nutrients are arranged in the periodic table as their original position, and the metals are red, transition metals are green, and non-metals are shown in blue. The other properties, including pH, ash content, organic carbon, organic nitrogen and C/N ratio, are represented in Fig. 6.

Soil should be treated with manures having rich nutrients as they are pre-requisite of good fertiliser. The mineral composition includes 14 different macro and micronutrients. The average quantity of macronutrients in the plant, such as carbon, nitrogen, phosphorus, potassium, sulphur, calcium and magnesium are higher than the micronutrients (Iron, zinc, copper, manganese, boron and sodium). As stated earlier in physical properties, carbon is higher than all nutrients, which is about 75 mg/g. Surprisingly calcium is the second-highest amount of nutrient, 19 mg/g, and it even exceeds the concentration of nitrogen (Kirchmann and Witter 1992). Phosphorus has the third place among all minerals having a concentration of about 9 mg/g followed by potassium having 7.3 mg/g. Magnesium and nitrogen almost have the same concentration of 6 mg/g and 6.1 mg/g, respectively. The concentration of sulphur is about 3.6 mg/g, which risks the formation of SOx, and aluminium is about 1.4 mg/g. Among the micronutrients, iron (Fe) has the highest amount of concentration, which is about 2.03 mg/g. manganese and zinc have a concentration of 154 μg/g and 127 μg/g, respectively. Boron and sodium have minimal presence 15 μg/g, and 10 μg/g, respectively.

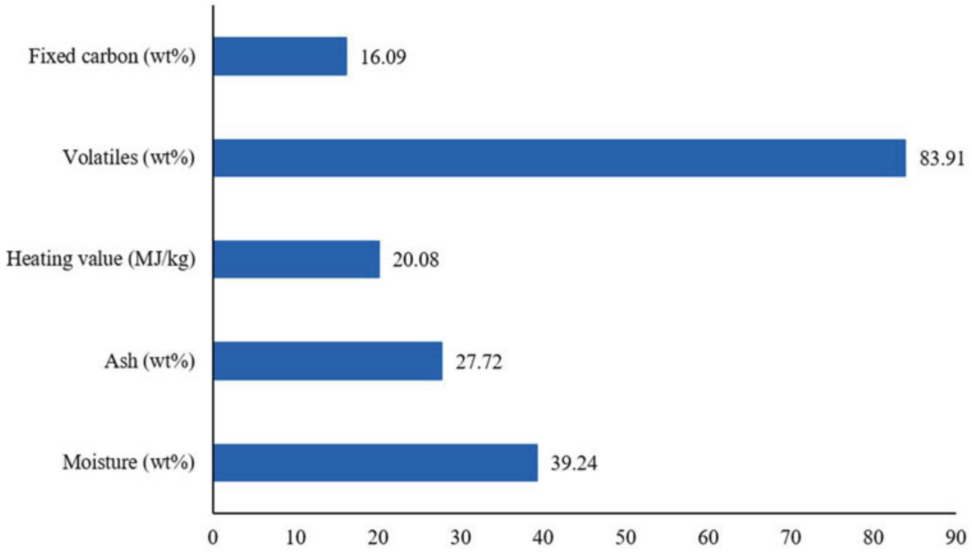


Fig. 4 Physical properties of cow dung

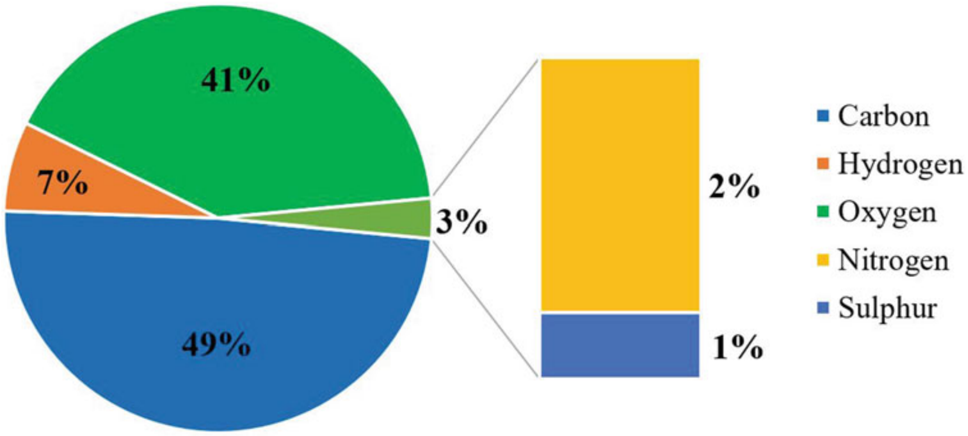
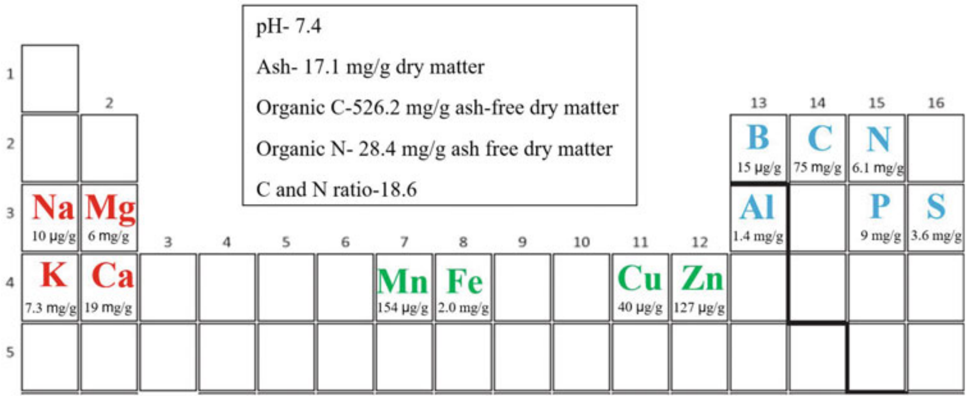


Fig. 5 Elemental analysis (%, dry and ash-free basis)


pH- 7.4

Ash- 17.1 mg/g dry matter

Organic C-526.2 mg/g ash-free dry matter

Organic N- 28.4 mg/g ash free dry matter

C and N ratio-18.6

Fig. 6 Chemical properties and mineral composition

Initially, in fresh cattle faeces, the pH value is 7.4; if it is decomposed aerobically or anaerobically, the pH value increases to a maximum of 8.5. This increase is caused by the formation of ash content and calcium carbonate (which is an alkali) throughout the aerobic decomposition. Similarly, during anaerobic decomposition formation of ammonium carbonate causes the increase (Levi-Minzi et al. 1986; Georgacakis et al. 1982). Unlike pH, organic carbon concentrations do not change much during anaerobic or aerobic decomposition remaining around 526.2 mg/g in ash-free dry matter. The concentration of organic nitrogen is about 28.4 mg/g in the ash-free dry matter, which declines when cow dung is anaerobically treated (Kirchmann and Witter 1989). For this reason, the organic C/N ratio shows different value in aerobic and anaerobic decomposition. In anaerobically treated cow dung, C/N ratio is 19.6, which is higher than the fresh dung (C/N ratio 18.6). However, organic materials with C/N ratio more than 18 can cause immobilisation of nitrogen (Kirchmann and Witter 1992).

In the process of treatment of cow dung, due to gaseous loss, mass is reduced from the total material. In aerobic condition, organic matter, as well as carbon losses increase significantly that is 27.9% of total carbon during this process, whereas in the anaerobic condition, the loss is comparatively less (Kirchmann 1985). Regarding the loss of nitrogen, studies show that during the anaerobic condition, little or no nitrogen loss occurs, but during the aerobic condition, nitrogen loss is higher (Russell and Richards 1917). Therefore, anaerobic storage condition is recommended over aerobic in case of efficient conservation of nitrogen.

4 Conventional Use of Cow Dung

Energy can be harnessed from cow dung in various ways, as discussed below. However, the most common use of cow dung is either as solid fuel or as fertiliser. Generally, composting of cow dung converts it into useful, inexpensive—yet effective fertiliser. Hence, this is one of the most common applications of cow dung throughout the world. Moreover, cow dung as solid fuel is another conventional application—commonly practised in rural areas. Figure 7 shows the typical application of cow dung and highlights their economic and environmental impact.

4.1 Cow Dung as Fertiliser

Cow dung is one of the most effective alternatives to chemical fertilisers; generally known as a bio-fertiliser; it can significantly increase the productivity of the soil. Due to the expeditious nutrient loss, growing costs and noxious environmental effects from inorganic fertilisers, organic manure such as composted cow dung has received considerable attention, and it is acting as a source of plant nutrients for the cultivation of field crops (Place et al. 2003; Duncan 2005). Numerous green organisations advocate the use of cow dung as organic fertiliser in order to promote environmental sustainability.

Cow dung compost can substantially improve the physicochemical properties of soil. However, the application of raw cow dung as fertiliser should ensure that it does not release any pathogens in clean water sources. Composting is considered as a safe method for providing nutrients to the soil as it prevents environmental contamination by expelling harmful pathogens from organic fertilisers. Compost is considered as a good fertiliser consisting of minerals, humus, and most importantly, it is pathogen-free.

Utilisation of composted cow dung as a fertiliser has numerous advantages such as improving the water holding capacity, enhancing the water infiltration, improving the cation exchange capacity of the soil and aeration (break up compacted soils). Production of agroforestry crops requires highly fertile soil, and composted cow dung can maintain the production capacity of the land at its highest level (Ajayi 2007).

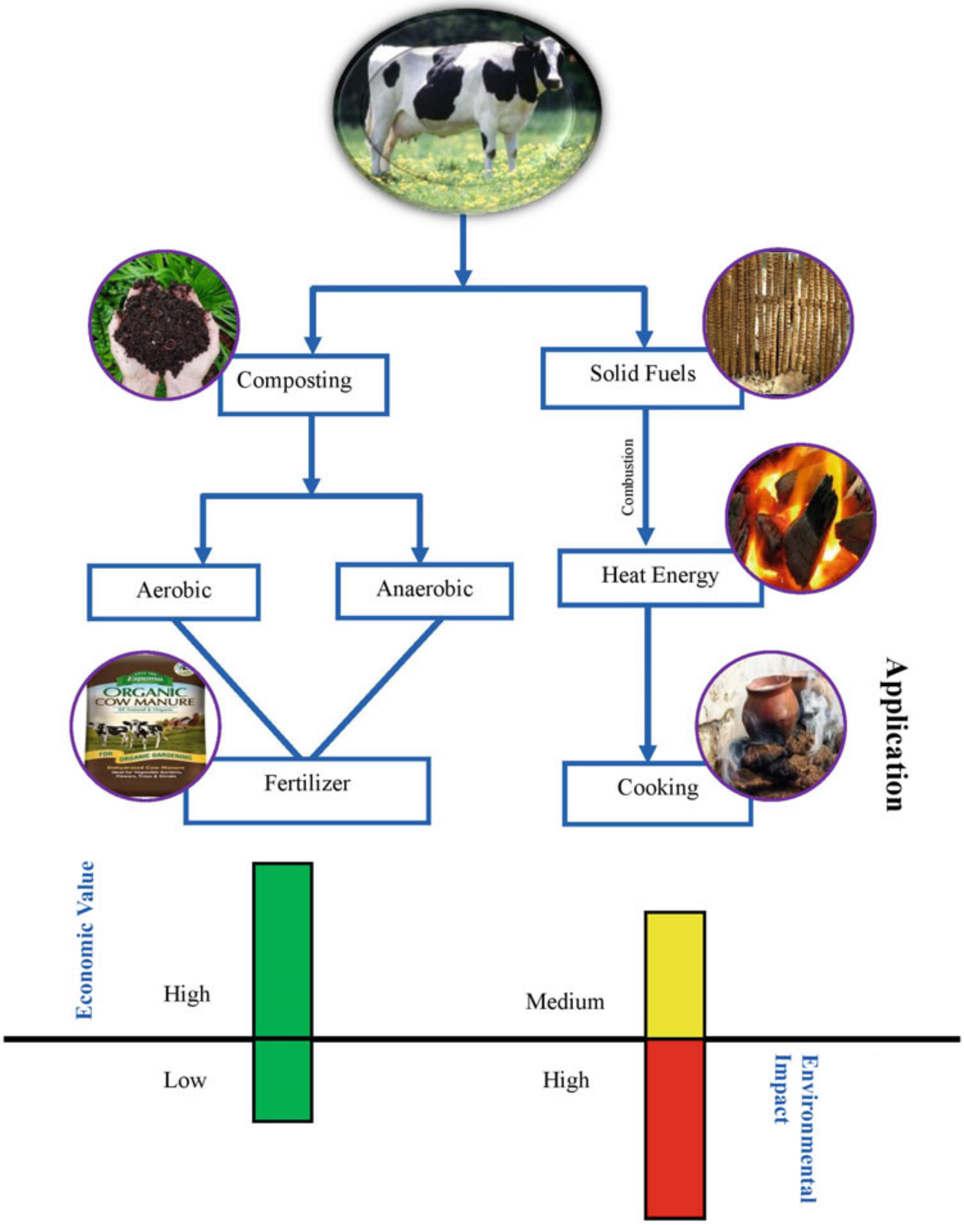
Although chemical fertiliser disturbs the soil physio-chemical properties (e.g., water holding capacity, soil texture and porosity), owing to the rapid growth of population, the requirement of food resources is increasing simultaneously that leads to using the chemical fertiliser (Jhariya and Raj 2014). However, the physio-chemical soil properties can be retained at its maximum level by using the appropriate expanse of composted cow dung as fertiliser (Raj et al. 2014). Nitrogen, phosphorus and potassium (NPK) are the three fundamental plant nutrients that can be sufficiently provided if manure is used properly because cow dung has a significant amount of NPK in a ratio of 3:2:1 (Fulhage 2000).

However, it is generally suggested to use cow manure after composting as it also contains potentially unsafe pathogens and substantial amount of ammonia that can burn the plants. Besides providing the required plant nutrients, manure also aids the growth of beneficial soil organisms. Mandal et al. suggested that 50–92% more yield in Aonla can be produced if bio-fertilisers, organic and inorganics fertiliser can be used in appropriate proportion (Mandal et al. 2013). According to Williams et al. if manure is combined with inorganic fertiliser (nitrogen), then it can lessen the soil acidification and significantly increase the soil productivity by releasing sufficient amount of nutrients (Williams et al. 1995). It can be concluded that composted cow dung assimilates substantial quantities of organic material to the soil, which may eventually improve the overall health of the soil and produce healthy, vigorous plants.

4.2 Cow Dung as Solid Fuel

In order to use cow dung as a fuel, it is dried in any shape (natural, round, flat dung cakes or moulded around a stick) prior to combustion. In order to improve the burning performance of dung, it is sometimes mixed with coal dust or agricultural residues which helps to increase the energy density (Masud et al. 2019).

Fig. 7 Conventional application of cow dung with its comparative economic and environmental impact



The heating value of cow dung is much lower (10000 kJ/kg to 18000 kJ/kg) than wood because of its high moisture content (Witt et al. 2006). While comparing the carbon content, coal and wood have a proportion of (70%–90%) and 50%, respectively. In contrast, dried cow dung has roughly 25% carbon content, because of which large amount of ash remains in the burner as an end product of dung-fire. Although burning cow dung for cooking purposes is one of the renewable and sustainable sources for many poverty prone people throughout the world, the practice must be prohibited as Masud et al. (2020)

- Dung has a significantly higher value as a bio-fertiliser; therefore, if it is used as fuel, then there will not be a sufficient amount to be used as fertiliser that will consequently affect the soil fertility.
- Compared to the combustion of wood; burning dung releases more dioxins and chlorophenols that may substantially affect human health (Masud et al. 2020).
- Although, using dried cow dung as a source of solid fuel is an example of reusing excreta, but one of the major drawbacks is the increased air pollution (Mudway et al. 2005). However, the methanization of dung in a biogas digester is a better alternative from the energy perspective (Masud et al. 2020).

Therefore, considering the economic value and environmental impact that the cow dung have, it is not recommended to use as solid fuel (Masud et al. 2020). There are plenty of advanced techniques that can utilise cow dung as a source of sustainable green energy which is proposed in the next section.

5 Advanced Utilisation of Cow Dung as Biomass

Cow dung is one of the most promising biomass resources due to its abundance irrespective of geological position (discussed in Sect. 2). In response to the global warming crisis, the world is shifting towards sustainable energy technologies, which has encouraged numerous biomass innovations (Masud et al. 2019). Not only these technologies are environmental friendly, but they are also inexpensive to operate since the biomass feed material is comparatively cheap. Through rigorous experimentation of different physio-chemical properties of cow dung, researchers have developed numerous advance applications of cow dung. Such advance applications and their potential are explained below (see Fig. 8).

5.1 Vermicompost Production

Vermicompost is a process through which mineral-rich cow dung can be converted into stabilised humus to improve cultivation (Garg and Kaushik 2005). Vermicompost is an inexpensive and eco-biological technology that usages earthworm aerates, grind and shrade to convert organic waste into soil conditioner and organic fertiliser (Elvira et al. 1998). Modern research in vermicompost has noted remarkable success in managing industrial organic residues (Benitez et al. 2002; Maboeta and Van Rensburg 2003).

Suthar et al. have developed a vermicomposting process using cow dung, guar gum industrial waste and *Perinyxexcavatus* earthworm under laboratory condition (Suthar 2006). Three different combinations of cow dung, guar gum and sawdust were tested for efficient vermicomposting. The compositions contain the following ratio of cow dung: guar gum: sawdust; T_1 (30:40:30), T_2 (20:60:20) and T_3 (15:75:10). Vermicomposting period for all combinations was 150 days. According to their findings, T_2 mixture had a 25.5% nitrogen, 72.8% phosphorus and 20.9% potassium increase than the other mixtures after the same

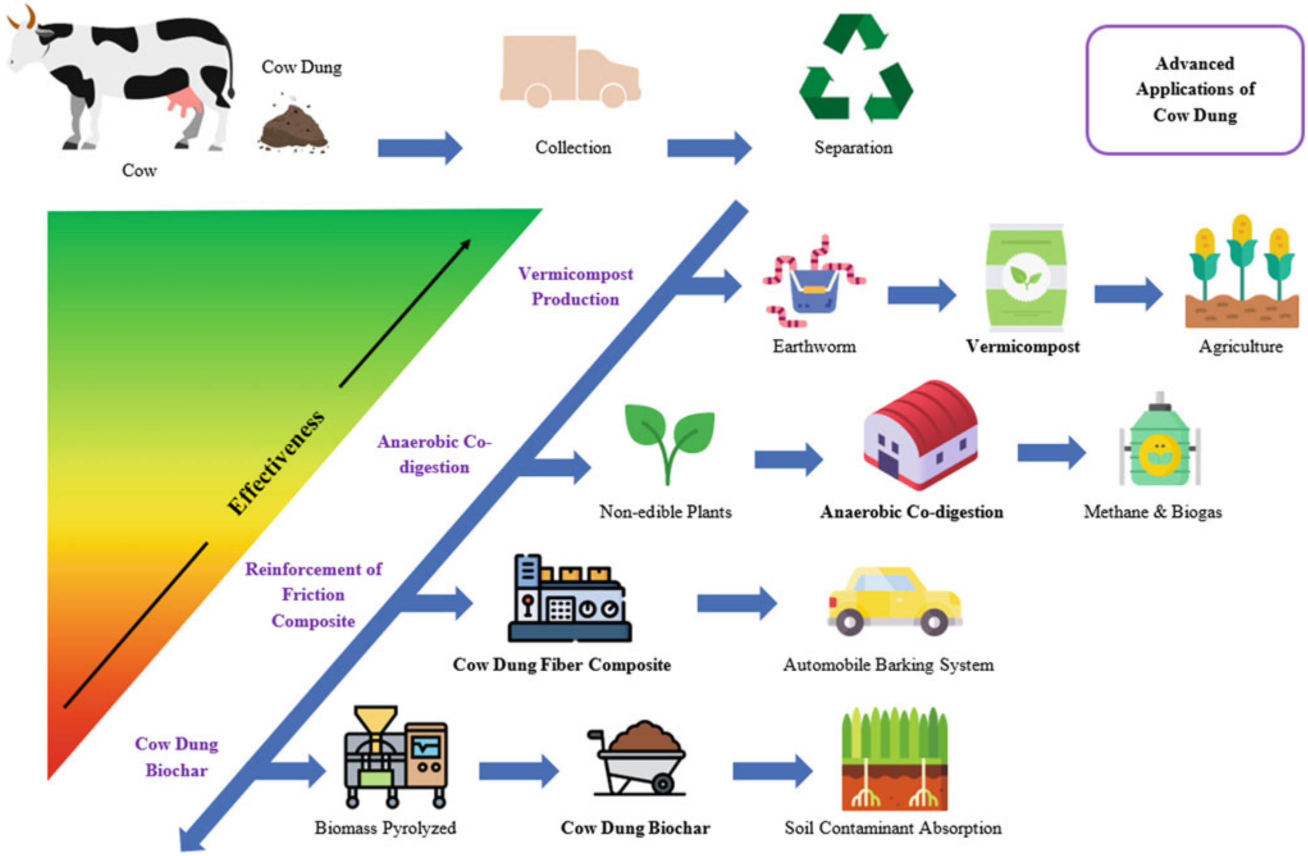


Fig. 8 Advance utilisation of cow dung as biomass

vermicomposting period (Suthar 2006). Moreover, T_2 produces 21.9 and 645.5% more cocoon than T_1 and T_2 mixtures, respectively. Therefore, the research concluded that T_2 mixture is ideal for enhancing vermicomposting coefficient and producing higher mean biomass.

Jjagwe et al. have studied the potential of vermicomposting for effective cattle manure management in Uganda (Jjagwe et al. 2019). During the experiment, 1 kg earthworms were added to 10 kg of cattle manure, and the batch had undergone an 84 days period of vermicompost. Using the sprinkling water system, the moisture content inside the vermicomposting unit was maintained between 60 and 70%. After the harvesting period, based on dry basis, 46% of the mass was successfully converted into vermicompost, 2% was consumed by earthworms, and 52% dissipated to the environment. According to substance flow, 30% of the total carbon content was part of vermicompost, 2% was used by earthworms and rest was released to the environment.

Similarly, 75% of nitrogen was converted into vermicompost, 7% was used by earthworms, and 18% entered the atmosphere. Their research also revealed that vermicompost significantly reduces the greenhouse gas emission from cattle manure. Data show that cumulative emission from vermicompost was only 102 g CO_2, 7.6 g CH_4 and 3.94×10^{-5} g N_2O from per kg of manure. Therefore, vermicompost can be considered as an effective advanced application of cow dung waste. Since this technology is inexpensive and easy to maintain, it can be recommended for low-income developing and least developed countries.

5.2 Anaerobic Co-digestion of Cow Dung

Anaerobic digestion is a type of biodegradation process of organic materials using microorganisms in a sealed, air-tight, and oxygen-free chamber (Masud et al. 2019). This is a promising method of converting organic industrial and domestic waste into biofuels. Anaerobic digestion has environmental benefits as it actively reduces groundwater and soil pollution as the volume of disposable materials is reduced (Ananno et al. 2021). The produced biogas also maintains the balance among the greenhouse gases in the atmosphere (Masud et al. 2020). From an economic perspective, the system delivers a low-cost and rather simplistic approach to provide the rural areas of under-developed and developing countries with suitable energy generating methods. Inexpensive biogas generated from cow dung can be used for food drying and residential heating purposes (Ananno et al. 2020; Masud et al. 2019a, b, 2020).

Singh et al. have investigated the potential of anaerobic co-digestion of cow dung with different types of non-edible oil cakes such as safflower, karanja and jatropha (Singh and Mandal 2011). By using a one litter batch reactor and mixed inoculum technology, the production of methane-enriched biogas was observed. Different mixture ratio of cow dung and non-edible oil cakes was tested to identify optimum methane production condition. The digestion period for all experiments was 41 days at 35 °C temperature. The average yield of methane was recorded as 0.23 to 0.36 Lg-1VS (Litre per gram Volatile Solid Content); biogas 0.49 to 0.52 Lg-1VS and CO_2 generation 0.13 to 0.18 Lg-1VS. The study found that a 1:1 feed material mixture produced maximum methane yield. Anaerobic co-digestion of cow dung and karanja was most effective; yielding an average of 0.36 Lg-1VS methane and 0.52 Lg-1VS biogas. Whereas the combination of cow dung and jatropha was least effective, producing an average of 0.32 Lg-1VS methane and 0.51 Lg-1VS biogas. Moreover, the experiments also showed a 14.8% increase in methane production from 1:1 combination cow dung and karanja compared to cow dung alone (0.31 Lg-1VS). Therefore, it can be concluded in terms of methane-enriched biogas production; anaerobic co-digestion is significantly more effective than anaerobic digestion of only cow dung.

5.3 Reinforcement of Friction Composites

In order to produce an automotive braking system, friction composites containing reinforcing fibres, binders and friction modifiers are widely used (Yun et al. 2010). The traditional materials used for automotive braking system have long-term adverse effect on the environment due to the use of toxic materials. Hence, the modern automotive industry is testing organic lignocellulosic fibres such as bamboo, jute, coir and betelnut for the production of reinforcing fibres (Ma et al. 2012; Nahar et al. 2011; Tran et al. 2011; Yousif et al. 2010). Since these fibres are biodegradable, they are not detrimental to the environment. Moreover, renewability, mass availability and inexpensive production cost have made organic fibres a popular choice for friction composite production. Primarily composed of hemicellulose, cellulose and lignin—these organic fibres have acceptable, friction coefficient, noiseless, low fade and satisfactory resistance to corrosion (Singh et al. 2017).

Ma et al. have studied the possibility of cow dung fibre reinforced friction composite (Ma et al. 2019). Using detailed study and exhaustive experimentation, they have concluded that cow dung positively affects the wear properties of friction composites. Additionally, they have concluded that friction composites reinforced with cow dung have pronounced wear resistance and stable friction coefficient. The experimental analysis shows that friction composite containing 6 wt% cow dung fibre produced the most satisfactory results. Considering the overall performance cow dung fibre reinforced friction composite displayed a recover ratio of 107.7%, fade ratio of 6.9% and 1.61×10^{-1} $cm^3N^{-1}m^{-1}$ sum wear rate. Additionally, scanning electron microscope (SEM) and confocal laser scanning microscope (CLSM) analysis suggest that cow dung-based composite fibre has superior fibre-matrix interfacial adhesion and stable contact plateaus. Therefore, production of cow dung reinforced composite fibre for automotive braking system can be an environment friendly advanced application. Due to the expensive cost of infrastructure development and maintenance, this waste conversion technology is only suitable for developed and high-income developing nations.

5.4 Cow Dung Biochar

Biochar is a mechanical process through which biomass is pyrolysed in a closed container in the absence of air to produce a carbon-rich material (Nabi et al. 2014; Joardder 2017). Primary advantage of producing biochar from livestock is that it reduces waste and eliminates pathogen (Wan et al. 2018). Additionally, numerous studies have reported that manure-derived biochar can be used as adsorbent for soil remediation (Kiran et al. 2017). These types of biochar also have higher ash content and cation exchange capacity compared to plant-derived biochar.

Qin et al. have investigated the properties of cow dung biochar, and the factors influencing its performance (Qin et al. 2019). According to their findings, cow dung biochar (CDB) can be used as an inexpensive absorbent for soil contaminants and as an alternative for landfilling. However, without proper management of used biochar, it may desorb the contaminants, which may cause secondary pollution. Wan et al. have evaluated the potential of CDB for absorbing low concentration of perchlorate from aqueous solution. Their experiments show that based on Langmuir model, maximum recorded absorption capacity was 1787 μg/g for ferric chloride-modified cow dung biochar and 304 μg/g for normal CDB. Considering the production cost, time and pollution footprint, application of cow dung as biochar can be recommended for developing and least developed countries.

6 Conclusion

Dairy animals, especially cows, are the most populous livestock on earth, at any given time there almost 987.51 million of them. Sustaining such an enormous population would be challenging in the near future due to limited energy and water resources available to mankind. Additionally, each year the combined cattle population generates a significant amount of excrement, whose proper handling is a financial and environmental challenge. Therefore, the continued profitability, sustainability, and productivity of the livestock industry depend to a considerable extent on the optimum management practices of cow dung disposal. Adequate management of cow dung should mediate the environmental consequences of improper waste disposal as well as protect the water and air quality of the eco-system through effective waste treatment. Moreover, cost-effective cow dung-based energy generation technologies have the potential to pave the way for sustainable livestock production industry with the potential meet its total energy requirement through its cow dung waste.

Multi-utilisation of cow dung can generate economic profit from excrement that is otherwise dumped on land. Due to its compelling physio-chemical properties, cow dung has considerable potential to be used as an excellent source of biomass energy (see Sect. 3). However, in the current industry, major portion of the produced cow dung is being dumped or used as unprocessed fertiliser. This chapter thus highlights the financial and technical challenges associated with improper cow dung management and discusses the opportunity for multi-utilisation of cow dung as a biomass energy source and composite organic fertiliser. Further research is required to integrate advance cow dung utilisation techniques with the current industry infrastructure. Improved biomass utilisation techniques such as vermicompost, anaerobic co-digestion, production of reinforced friction composites and biochar are recommended to expand the multi-utilisation capacity of cow dung. While some of the advanced utilisation techniques may prove to be expensive, they are highly efficient and environmentally sound. Therefore, based on the energy need and economic conditions, advanced technologies should be chosen only after exhaustive feasibility analysis.

Finally, energy conversion systems that use cow dung as its primary feed should be precisely controlled to prevent environmental pollution. Emission from these plants can contaminate air and water with an adverse effect on human health. Furthermore, cow dung-based biomass energy plants will be economically feasible in regions with an abundance of cow dung. Transportation cost, moisture content control is the focal point of cost optimisation; therefore, the multi-utilisation of cow dung should consider these parameters. New studies must be done to better assess the energetic potential, optimise the operation parameters to gain better overall system efficiency and verify the long-term sustainability for multi-utilisation of cow dung.

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Revalorisation of Agro-Industrial Wastes into High Value-Added Products

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Abstract

Agro-industrial waste represents large economic and environmental problems and is related to a greenhouse gas emissions. However, most of these residues have shown to be a valuable source of bioactive compounds or ingredients that could be used for pharmaceutical, food, cosmetic, and bioenergy industries. The reduction of this waste and the revalorisation of agro-industrial by-products contribute to minimise the ecological impact through bioeconomy or circular economy models. In order to carry out these approaches, extraction techniques play a fundamental role in these processes since they are capable of isolating the compounds of interest but they may apply in a sustainable way. This chapter presents the potential applications of reusing agro-industrial by-products to develop high added value products and the role of these applications in strategies against climate change or in the revaluation of companies. In addition, the main agro-industrial waste from vegetables, fruits, or cereals are described, as well as the main bioactive ingredients detected in these and the main extraction techniques used.

Keywords

Agro-industrial waste • By-products • Green technology • Bioeconomy • Revalorisation • Nutraceuticals • Cosmeceuticals • Functional food

1 Introduction

The population growth and the changes in eating habits have produced during the last decades an increase of the agri-food industries which make or process food products from fruits, vegetables, and cereals (Sagar et al. 2018). This fact has led to an increase in the production of millions of tonnes of agro-industrial wastes which are sometimes unexploited producing a significant environmental impact in addition to an economic impact on the agri-food companies for their management (Tonini et al. 2018). The agro-industrial residues are generally made up of peels, skins, leaves, seeds, pulps, rinds, among other parts of the food species, as well as the entire part of the food product for not meeting different quality criteria such as the state of ripeness or size, among others. In 2011, the Food and Agriculture Organisation of the United Nations (FAO) estimated that about a third of food products were lost or wasted (Gustavsson et al. 2011).

In order to minimise the environmental and economic impacts, different alternatives have been proposed. For

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example, agro-industrial wastes can be reused for bioenergy generation, for composting, or in specific cases, for animal feed. However, these agro-industrial wastes have been characterised by containing nutrients (vitamins, minerals, trace elements), dietary fibres, enzymes, oils, and bioactive compounds (phenolic compounds, carotenoids, glucosinolates, and flavonoids) (Sagar et al. 2018; Saini et al. 2019). The interest in bioactive compounds has increased in recent decades due to their great abundance in the plant kingdom as well as their multiple beneficial properties to prevent and be beneficial against a large number of pathologies such as cancer, cardiovascular, neurodegenerative diseases, and inflammation (Altemimi et al. 2017; Fernández-Ochoa et al. 2020).

Since large amounts of agri-food are considered non-edible food or waste because they do not complete the established standards for their commercialisation, large quantities of food by-products are generated throughout the supply chain from the initial steps to the final consumption stages (Torres-Valenzuela et al. 2020). In this scenario, the presence of bioactive compounds makes it possible to use them for the development of high added value products such as functional foods, nutraceuticals, cosmeceuticals, or applications in the textile or pharmaceutical industries. To isolate these phytochemical compounds, a sophisticated step of extraction has to be carried out to use them later in the potential applications related to high added value products (Kumar et al. 2017). For this objective, different extraction strategies have been optimised to do this process more sustainable, such as ultrasound-assisted extraction (UAE), subcritical water extraction (SWE), microwave-assisted extraction (MAE), supercritical fluid extraction (SFE), or enzyme-assisted extraction (EAE) (Marić et al. 2018).

The possibility of reusing agro-industrial wastes for the elaboration of high added value products reduces the environmental impact but also represents an attractive proposal for companies that can generate new alternative ways of business opportunities. These types of strategies, defined as a circular economy, have been related to the sustainable development goals and are increasingly being implemented by companies in recent years (Sauvé et al. 2016; Rodriguez-Anton et al. 2019).

In this chapter, the potential applications of high added value products obtaining from the reuse of agro-industrial waste and the role that these applications can have in the bioeconomy of companies and in strategies against climate change are presented. In addition, the main agro-industrial wastes from vegetables, fruits, or cereals are described, as well as the main phytochemical compounds present in them and the green extraction techniques to isolate these phytochemicals.

2 The Role of Agro-Industrial Wastes in Bioeconomy

Globally, large amounts of agro-industrial wastes and by-products, which can be ‘on/off farm’ contribute to environmental stress. However, sustainable development has to do with a movement of building on ‘circular economy’ or ‘bioeconomy’ by high value-added products based on agro-industrial waste recycling. Moreover, it could align with the achievement of carbon neutrality and the obtainment of the UN Sustainable Development Goals (El-Chichakli et al. 2016).

Regarding the terms, there are different concerns about Green, Circular, and Bio-economy, but despite the differences, they have common economic, environmental, and social aims (D’Amato et al. 2017). As a definition of bioeconomy (Fig. 1), Carus and Dammer 2018reported that bioeconomy compiles the production of renewable biological resources and the revalorisation of these sources for developing high value-added products, such as food, feed, bio-based products, and bioenergy (Carus and Dammer 2018).

This concept can be applied to countless industries, but particularly in food and cosmetic sectors, there is a high interest in green and sustainable approaches that could totally or partially replace current synthetic compounds for active ingredients obtained from natural sources. In this sense, agro-industrial wastes are a source of bioactive compounds, which can cause such wastes to be reused and revalued by means of the following applications (Gordobil et al. 2020).

2.1 Bioenergy

Bioenergy includes biofuels and biomass which are considered a solution to address future shortages and rising fossil fuel prices. In this field, in order to avoid the competition between energy and food production, a second-generation of bioenergy from agro-industrial residues is gaining global recognition for their potential of providing sustainable bioenergy (Tonini et al. 2016). As it is well known, agro-industrial by-products contain important amounts of carbon, macro- and micronutrients that could be used for bioenergy production. In literature, there are many examples of the use of these agro-industrial residues in this field. For example, in Ghana, tropical fruit (pineapple and mango), and cocoa residues are used as a substrate in biogas production, reducing dependence on grid electricity and synthetic fertilisers and maintaining soil carbon levels (Kamp and

Fig. 1 Role of agro-industrial by-products in bioeconomy

Østergård 2016). Other examples are the use of olive mill wastewater and wine-grape by-products for methane production. To this end, an anaerobic co-digestion of these residues was carried out obtaining efficient results (Fountoulakis et al. 2008).

2.2 Animal Feeding

The use of agri-food by-products for animal feeding is an ancient use. For this reason and because of the great availability of produced agro-industrial residues, the incorporation of these industrial by-products in the animal feeding is a potential strategy to decrease the ecological and water footprint associated with crop cultivation (Correddu et al. 2020). In addition, the presence of bioactive phytochemicals in these residues provides an added value in animal health. For example, the positive effect of polyphenols from agro-industrial residues on oxidative status in wethers has been demonstrated (Ishida et al. 2015). Furthermore, in case of ruminants, these have the unique capacity to use fibre due to their rumen microbes. Hence, cereals can be replaced for these residues (Mirzaei-aghsaghali and Maheri-sis 2013). However, some aspects should be considered since it has been demonstrated that agro-industrial residues rich in phenolic compounds, usually deprive nutrient digestibility *versus* traditional feedstuffs. This fact is related to a high content of lignin and tannin (Correddu et al. 2020).

2.3 Functional Food

Agro-industrial by-products from fruit and vegetable processing provide an important source of bioactive compounds such as fibre, antioxidants, and prebiotics. This fact makes that these co-products could be incorporated for the development of functional food (Hernández-Alcántara et al. 2016). For example, olive mill wastewater is a by-product with high phenolic content from the virgin olive oil production. When this agro-industrial residue is added into vegetable oils, milk beverages, or meat products, it reduces the lipid oxidation, improves the oxidative status of the products, and provides antimicrobial effects (Caporaso et al. 2018). In other studies, the fruit and vegetable solid residue generated from the manufacture of an isotonic beverage was used for functional biscuits and cereal bars, with high fibre and mineral content (Ferreira et al. 2013). A similar process has been also applied in the case of cactus pear flour and pineapple peel flour when they were incorporated in cooked sausages inoculated with lactic acid bacteria, which improved the thermostability lactic acid bacteria in this food during storage (Díaz-Vela et al. 2015).

2.4 Nutraceuticals

Unlike functional foods, nutraceuticals are healthy products elaborated from foods that are formulated and consumed in defined dosages and in a drug format (El Sohaimy 2012). Therefore, the rich composition of wastes from the food industry makes them suitable for the development of nutraceuticals as an alternative to synthetic substances (Rudra et al. 2015). To this end, many conventional and emerging technologies are used to extract bioactive compounds from agro-industrial residues for nutraceutical development (Galanakis 2013). This allows many food industry residues have been selected for the development of nutraceuticals. Examples of this can be found in pomegranate seed waste using an enzymatic green extraction process to obtain high quality oil, food-grade proteins, and fibre; in peel of citrus plant for flavonoid extraction by supercritical CO_2; or in coffee waste residues for obtainment of phenolic compounds using subcritical water under semi-continuous flow conditions (Talekar et al. 2018; Giannuzzo et al. 2003; Mayanga-Torres et al. 2017).

2.5 Cosmeceuticals

Increasing attention has also recently been devoted to a marked trend in the cosmetic industry toward the development and manufacture of high value products from natural sources. Likewise, ethical consumerism has reached the cosmetic industry, raising the question of sustainable development. In addition to that, it is known that the excessive consumption of ingredients for solar UV damage, like organic UV filters, is related to the environmental impact by exhibiting hormonal activity that affects negatively to the reproduction cycle of organisms (Gordobil et al. 2020). In fact, consumers are currently aware of circular economy and sustainability concepts, looking for "green" products. In this sense, bioactive compounds extracted from food by-products, such as phytonutrients, microbial metabolites, dairy-derived actives, minerals, vitamins, or animal proteins, may have skin benefits resulting in new high value-added products as cosmeceuticals (Prakash, L. and Majeed, M. Natural ingredients for anti-ageing skin care. Househ. Pers. Care Today 2009). The most widely reported are bioactive phenolic compounds because of their photoprotective and antioxidant properties (Panzella 2020).

3 Green Technologies for Obtaining Bioactive Ingredients from Agro-Industrial by-Products

The revalorisation of agro-industrial wastes to obtain functional ingredients have had an interest growing by the industries to achieve a circular economy decreasing the environmental impact as well as increase the use of their own resources. To this end, different advanced extraction technologies that allow to use green and Generally Recognised as Safe (GRAS) solvents (water, ethanol, deep eutectic solvents) have been developed and applied to attain a great variety of functional ingredients, minimising the solvent, and energy consumption and increase the effectiveness of the extraction processes (Ameer et al. 2017). The uses of some of these advanced extraction techniques to attain functional ingredients from different agri-food by-products are detailed in Table 1.

Food by-products (e.g., leaves, peels, barks, or pomaces) are an important source of bioactive compounds. However, the concentrations of these bioactive compounds are sometimes reduced being necessary an extraction procedure to concentrates them. In this sense, pressurised liquid extraction (PLE) has been used to attain different phytocomplexes which are enriched mainly in phenolic compounds from food by-products (Herrero et al. 2015). For example, this technique has been used to discern the effect of grape pomace fermentation to obtain enriched extracts in anthocyanins and tannins with high antioxidant capacities (Vergara-Salinas et al. 2013).

Additionally, PLE was compared with conventional extraction in order to attain phenolic enriched extracts from olive pomace. PLE revealed a high capacity to extract a wide variety of phenolic compounds and obtain more concentrated extracts than conventional extraction (Cea Pavez et al. 2019). Despite the fact that PLE is a versatile extraction method since it can work with a wide variety of solvents and provide high yield, some thermolabile compounds, such as anthocyanins, can be slightly degraded because of the extraction conditions (Machado et al. 2015). Although PLE has been used mainly to recover phenolic compounds, it has demonstrated to be an useful technique to retrieve carbohydrates such as inulin and pectin, which are compounds that belong to soluble fibre (Ruiz-Aceituno et al. 2016; Guo et al. 2012) and, in a minor proportion, oils (Eller et al. 2010) from agri-food by-products. In summary, PLE is a versatile

Table 1 Green technologies for obtainment of bioactive ingredients from agro-industrial by-products

Extraction technique	By-product	Solvents	Optimum conditions	Target	References
PLE	Grape pomace	Water	For anthocyanins: 100 °C for 5 min For tannins: 150 °C for 5 min	Anthocyanins and tannins	Vergara-Salinas et al. (2013)
	Olive pomace	Ethanol and water	137 °C and 52% ethanol and 20 min	Phenolic compounds	Cea Pavez et al. (2019)
	Olive filter cake	Ethanol and water	120 °C and 50:50 ethanol water for 20 min	Phenolic compounds	Lozano-Sánchez et al. (2014)
	Dried basil wastewaters	Water, ethanol and ethyl lactate	For rosmarinic acid: 50 °C 75:25 ethanol: water for 20 min For caffeic acid: 50 °C 100% ethanol for 20 min	Rosmarinic and caffeic acids	Pagano et al. (2018)
	Pomegranate peels	Water	40 °C for 5 min	Phenolic compounds	Çam and Hışıl (2010)
	Orange peels	Water	500 MPa, 55 °C for 10 min	Pectins	Guo et al. (2012)
	Artichoke	Water	75 °C for 27 min	Inulin	Ruiz-Aceituno et al. (2016)
	Tomato seeds	Ethanol	100 °C for 7 min	Oils	Eller et al. (2010)
MAE	Artichoke external bracts	Water	120 °C for 3 min	Inulin	Ruiz-Aceituno et al. (2016)
	Dragon fruit peel	Water	35 °C for 8 min	Betalain	Thirugnanasambandham and Sivakumar (2017)
		Water	45 °C, solid-liquid ratio 24 g/L for 20 min	Pectins	Thirugnanasambandham et al. (2014)
	Fig peel	Water and ethanol	63 °C, 100% ethanol for 5 min	Anthocyanins	Backes et al. (2018)
	Black carrot pomace	Water ethanol	348 W, 19 mL/g, 20% of ethanol for 10 min	Phenolic compounds	Kumar et al. (2019)
	Olive leaves	–	250 W, 5 g of sample for 2 min	Phenolic compounds	Sahin et al. (2017)
		Deep eutectic solvents and water	80 °C, 43% of water for 17 min	Phenolic compounds	Alañón et al. (2020)
	Grape pomace	Water and ethanol	408 W, 24% of ethanol and 76% of water, 24/1 mL/g for 5 min	Phenolic compounds	Tsali and Goula (2018)
	Sage	Water and ethanol	600 W, 46% ethanol and 54% water, 40 mL/g for 19 min	Phenolic compounds and flavonoids	Zeković et al. (2017)
SFE	Peach leaves	CO_2 and ethanol	150 bar, 60 °C and 6% of co-solvent	Phenolic compounds	Kazan et al. (2014)
	Pomelo peel	CO_2 and mix of water:ethanol	390 bar, 80 °C, 85% of ethanol for 49 min	Flavonoids	He et al. (2012)
	Grape marc	CO_2 and water or ethanol	100 bar, 40 °C 15% of water for 300 min	Phenolics and proanthocyanins	Da Porto et al. (2014)
	Grape seed	CO_2 and ethanol	80 bar, CO_2 flow rate 6 kg/h and 20% of co-solvent	Phenolics and proanthocyanins	Da Porto and Natolino (2017)
	Cacao pod husk	CO_2 and ethanol	299 bar, 60 °C and 14% of ethanol for 144 min	Phenolic compounds	Valadez-Carmona et al. (2018)
	Spinach by-product	CO_2 and ethanol	390 bar, 56 °C and 10% of ethanol for 216 min	Lutein and chlorophyll	Derrien et al. (2018)
	Tomato by-product	CO_2	550 bar, 52 °C for 180 min	Lycopene	Urbonaviciene and Viskelis (2017)
	Mentha spicata leaves	CO_2	120 bar, 43 °C for 110 min	Essential oils	Shahsavarpour et al. (2017)

(continued)

Table 1 (continued)

Extraction technique	By-product	Solvents	Optimum conditions	Target	References
UAE	Winery by-products	Water and ethanol	20 kHz, 500 W, 44% ethanol, 15 on −5 off, for 3 min	Phenolic compounds	Poveda et al. (2018)
	Hippophae rhamnoides L. by-products	Water and ethanol	250 W, 68% ethanol, 22 mL/g for 12 min	Flavonoids	Cui et al. (2017)
	Bamboo shoots by-products	Water	40 kHz, 240 W and 20 mL/g for 40 min	Polysaccharides	Chen et al. (2019)
	Grape seeds	Water and ethanol	28 kHz, 250 W 50 °C, 62% ethanol, 30 mL/g for 20 min	Phenolic compounds	Vural et al. (2018)
	Pomelo peel	Water	40 kHz, 25 °C 40 mL/g, for 60 min	Naringin and hesperidin	Van Hung et al. (2020)
	Mango Peel	Acidified water (pH 2.5)	20 kHz, 500 W, 5 on −5 off, 40 mL/g, 80 °C for 15 min	Pectin	Wang et al. (2016)
	Mulberry leaves	Water	60 W, 60 °C, 15 mL/g for 20 min	Polysaccharides	Ying et al. (2011)
	Blueberry wine pomace	Water and ethanol acidified	400 W, 61 °C, 22 mL/g for 24 min	Anthocyanins	He et al. (2016)
	Olive leaves	Water and ethanol	50 W/cm^2, 63% ethanol, 59 °C, 28 mL/g for 71 min	Oleuropein	Vural et al. (2020)

advanced extraction method to recover a wide variety of bioactive compounds from different by-products with higher yields as well as greater variety of compounds than conventional extractions methods.

MAE has been described as a fast, efficient (in terms of solvent consumption) and relative high-performance technology which offers the possibility of attaining "green" products with high qualities and low costs (Sahin et al. 2017). In contrast to PLE, MAE allows the extraction of thermosensitive compounds such as essential oils or anthocyanins (Thakker et al. 2016; Backes et al. 2018). Moreover, this extraction technique facilitates the use of GRAS solvents such as ethanol and water (Kumar et al. 2019), deep eutectic solvents (Alañón et al. 2020), or the possibility of working without solvent (solvent free) (Sahin et al. 2017) to obtain extracts from different by-products. For instance, MAE has been applied to obtain phenolics from grape or sage by-products using water:ethanol mixtures improving the extraction of some specific compounds compared with conventional extractions (Tsali and Goula 2018; Zeković et al. 2017). In addition, different natural deep eutectic solvents (NADES) have been used in combination with MAE, revealing that it is a promising sustainable alternative to attain high quality extracts from food by-products. NADES have been used to attain enriched extracts from *Lippia* leaves (Ivanović et al. 2018), olive pomace (Chanioti and Tzia 2018), or soy by-products (Bajkacz and Adamek 2017), proving to be safe solvents and an alternative to traditional solvents.

Supercritical fluids extraction has been broadly applied to recover compounds which have low polarity such as essential oils, fatty acids or terpenoids. Overall, the main solvent used is CO_2 due to its supercritical points (31 °C and 74 bars) (Azmir et al. 2013). Nevertheless, to obtain some polar compounds, the use of different co-solvent such as ethanol or water is necessary (Pimentel-Moral et al. 2018; He et al. 2012). Furthermore, SFE is a technology which can be used from lab scale to industrial scale (Herrero et al. 2015) being an interesting technology to recover specific phytochemicals from food waste and by-products. The high selectivity of this technique has allowed obtaining extracts enriched in specific compounds, such as lutein (Derrien et al. 2018), essential oils (Shahsavarpour et al. 2017), or lycopene (Urbonaviciene and Viskelis 2017) from spinach, *Mentha* species or tomato by-products, respectively. Moreover, the use of different co-solvents together with the different extraction conditions may significantly affect the diffusivity, density, and polarity of solvents enabling the recovery of more polar compounds. For instance, extracts enriched with proanthocyanins and flavonoids from grape or *Castanea sativa* by-products have been obtained by SFE technique (Da Porto et al. 2014; Da Porto and Natolino 2017; Pinto et al. 2020).

UAE has been described as an economical, versatile, simple, safe, effective, and advanced extraction method to obtain bioactive compounds from different sources (Varo et al. 2019). UAE has generally obtained better results in terms of time and energy consumption than conventional extraction. For instance, the extraction of pectin from mango peels or tomato wastes was faster than conventional extraction (Grassino et al. 2016; Wang et al. 2016; He et al. 2016). One of the most important advantages of this extraction technique is that can be combined with other advanced extraction methods, such as PLE or MAE, to improve the recovery of bioactive compounds (Machado et al. 2017; Sun et al. 2019). Moreover, UAE has been previously used with a high variety of green solvents such as water and ethanol, but also with NADES to obtain phenolic enriched extracts (Espino et al. 2018; Bosiljkov et al. 2017). UAE has been widely implemented to revalorise several food wastes such as olive leaves (Vural et al. 2020), fruits peels (Wang et al. 2016; Van Hung et al. 2020), or winery by-products (He et al. 2016; Poveda et al. 2018). The great versatility together with short extraction times provided by this technology have demonstrated that UAE is an interesting alternative to revalorise food by-products.

In summary, the application of advanced extraction technologies to obtain functional ingredients from different agri-food wastes and by-products is a current common practice which allows isolate bioactive compounds from agro-industrial wastes to develop added high value products.

4 Agro-Industrial by-Products for Industry Applications

New opportunities for earning additional income are related with the sustainable utilisation of agri-food wastes and by-products. This effective valorisation can efficiently produce high added value products reducing environmental stress by decreasing unwarranted pollution. In this sense, by-products of different sources as vegetables, fruits, or cereals and their main applications are described in Table 2.

4.1 Vegetables

The increase in the use of vegetables in the food industry to produce processed products (e.g., juices, purees, canning, salads, etc.) implies a high generation of waste derived from the vegetables used. This type of waste includes peels, stems, leaves, stalks, florets, pulps, or the discarding of vegetables by different criteria such as size, ripeness, and poor condition, (Sagar et al. 2018; Ben-Othman et al. 2020).

In 2009, Laufenberg et al. estimated the global production and wasted quantities of vegetables in 865.8 and 70.2 million metric tons, respectively (Laufenberg and Schulze 2009). These horticultural wastes have been used for bioenergy generation (electricity, biogas, biodiesel) as well as bio-fertiliser production in order to reduce its environmental impact (Suthar 2009; Singh et al. 2012).

Vegetable peels represent one of the most important wastes in the processing industry (Akyol et al. 2016). For example, tomato peels contain a high concentration of lycopene, which is responsible for the red colour but has also been attributed beneficial properties for the prevention of certain pathologies such as chronic diseases (cardiovascular disorders) or cancer (Jr et al. 2010). Besides these compounds, tomato by-products also contain high amounts of phenolic compounds, such as caffeic and chlorogenic acids; fatty acids, pectin, vitamins, and minerals (Mehta et al. 2018; Ninčević Grassino et al. 2019). On the other hand, potato and onion peels are also characterised by their high content of phenolic compounds. In fact, it has been described that the 50% of potato phenolics are located in the peel (Akyol et al. 2016). In this sense, potato and onion peels have been identified for their dietary fibre content as well as bioactive compounds such as carotenoids and phenolic compounds, highlighting their high concentration of catechin, quercetin, and gallic acid (Hallabo et al. 2018). Besides onion peel, other different onion by-products are generated like roots which are rich in flavonoids and organo-sulphur compounds (Lanzotti 2006).

Broccoli is another vegetable that presents different by-products (i.e., leaves florets, stalk, seed, mix.), which have been characterised showing the high presence of glucosinolates. Glucoraphanin has been the glucosinolate detected in highest concentration, which is involved in the formation of sulforaphane that has been related to beneficial health properties. In addition, phenolic compounds (i.e., chlorogenic and neochlorogenic acids) and flavonoids (i.e., kaempferol or quercetin) have been also detected in broccoli by-products (Thomas et al. 2018). The phytochemical composition of cauliflower wastes, such as leaves and stems, has also been explored highlighting the presence of phenolic acids and flavonoids (Gonzales et al. 2014).

4.2 Fruits

Fruit health benefits are well acknowledged due to the presence of multitude bioactive compounds (Slavin and Lloyd 2012). Despite being consumed mainly fresh, fruits processing entails the production of massive quantities of by-products such as seeds, stones, stem, peel, skin, pomace, bagasse, or pulp. Merely the beverages processing industries produce about 20–60% of fruit by-products (Kowalska et al. 2017). However, precisely in the non-edible fraction is where major quantities of value health promoting compounds can be found (Ayala-Zavala et al. 2011; Trigo et al. 2020).

As much as 40% of grapes usually end up as by-products after winemaking and juice processing (Friedman 2014). In grape pomace (skins and seeds) large amounts of a wide

Table 2 Agro-industrial by-products as source of bioactive ingredients for different approaches

Type	Species	By-products	Items of interest obtained	Beneficial properties	Uses	References
Vegetables	Jalapeño (*Capsicum annuum*)	Seed Placenta	Phenolic compounds	Antioxidant capacity	Functional food and nutraceuticals	Trigo et al. (2020)
	Beetroot (*Beta vulgaris*)	Pomace	Phenolic compounds and pigments (betaxanthins and betacyanins)	Antioxidant capacity	Functional food and nutraceuticals	Sandoval-Castro et al. (2017)
	Carrot (*Daucus carota* subsp. *sativus*)	Green tops (leaves and stems)	Essential oils	Antimicrobial activity	Nutraceutical and cosmeceutical formulations	Kushwaha et al. (2018)
	Garlic (*Allium sativum*)	Husk	Phenolic compounds	Antioxidant and anti-bacterial activities	Food and pharmaceuticals industries	Chiboub et al. (2019)
	Onion (*Allium cepa*)	Brown skin Top-bottom	Dietary fibre and phenolic compounds	Good source of dietary fibre and antioxidant capacity	Functional food	Chhouk et al. (2017)
	Potato (*Solanum tuberosum L.)*	Peels	Dietary fibre and phenolic compounds	Antioxidant activity,	Functional foods (e.g. biscuits)	Ninčević Grassino et al. (2019)
	Tomato (*Solanum lycopersicum*)	Tomato paste	Substrate for the cultivation of Enterobacter A47 bacteria and the production of a microbial polymer	Source of nutrients	A microbial polymer, FucoPol, a value-added fucose-rich extracellular polysaccharide	Benítez et al. (2011)
	Tomato (*Solanum lycopersicum*)	Pomace (skin, seed and pulp)	Dietary fibre, vitamin C, phenolic compounds and minerals	Source of antioxidants, minerals, and dietary fibre. Enhance shelf-life in bakery products	Food ingredients in bread and muffins	Jr et al. (2010)
	Tomato (*Solanum lycopersicum*)	Peel	Phenolic compounds, fatty acids and pectin	Tin corrosion inhibitor (pectin)	Functional ingredients	Mehta et al. (2018)
	Broccoli (*Brassica oleracea* var. italica)	Florets, stalk and mixture	Glucosinolates, polyphenols and flavonoids	Source of sulforaphane and other bioactive compounds	Functional food ingredients	Lanzotti (2006)
	Cauliflower (*Brassica oleracea* var. *botrytis*)	Outer leaves	Phenolic compounds and flavonoids	Antioxidant activity	Functional ingredients	Thomas et al. (2018)
	Cauliflower (*Brassica oleracea* var. *botrytis*)	Leaf residues	Phenolic compounds	Antimicrobial capacity	Animal feed, functional food and nutraceuticals	Antunes et al. (2017)

(continued)

Table 2 (continued)

Type	Species	By-products	Items of interest obtained	Beneficial properties	Uses	References
Fruits	Mango (*Mangifera indica*)	Peel Seed coat Seed kernel	Phenolic compounds	Antioxidant and antiproliferative activities	Pharmaceutical products	Sanz-Puig et al. (2015)
	Pineapple (*Ananas comosus* var. *Comosus*)	Pomace	Polyphenols, anthocyanins and carotenoids	Antioxidant activity. Good source of dietary fibre, protein, calcium, and ascorbic acid	Products with high nutritional value	Castro-Vargas et al. (2019)
	Avocado (*Persea americana*)	Peel Seed	Phenolic compounds	Antioxidant capacity	Pharmaceuticals products and products with high nutritional value	Nagarajaiah and Prakash (2016)
	Banana (*Musa paradisiaca*)	Peel	Full extract	Antimicrobial activity	Pharmaceuticals products	Rosero et al. (2019)
	Banana (*Musa paradisiaca*)	Peel	Phenolic compounds, anthocyanins and catecholamines	Antioxidant capacity, lipid peroxidation inhibitor	Functional ingredients	Kapadia et al. (2015)
	Apple (*Malus domestica*)	Seed	Phenolic compounds especially phloridzin	Antioxidant capacity	Chewing gum enriched with phloridzin	González-Montelongo et al. (2010)
	Apple (*Malus domestica* var. Lobo)	Peel	Dietary fibre, phenolic compounds and minerals	Antioxidant capacity	Industrial processing	Gunes et al. (2019)
	Sweet lemon (*Citrus medica* var. *limetta*)	Pomace	Polyphenols, anthocyanins and carotenoids	Antioxidant activity. Good source of dietary fibre, protein, calcium, and ascorbic acid	Products with high nutritional value	Castro-Vargas et al. (2019)
	Orange (*Citrus sinensis* L.)	Pomace	Polyphenols, anthocyanins and carotenoids	Antioxidant activity. Good source of dietary fibre, protein, calcium, and ascorbic acid	Products with high nutritional value	Castro-Vargas et al. (2019)
	Orange, Lemon and Clementine (*Citrus L.*)	Peel	Phenolic compounds and flavonoids	Antioxidant activity	Nutraceutical and cosmeceutical formulations	Gorinstein et al. (2001)
	Olive (*Olea europaea*)	Olive mill wastewaters	Polyphenols	Reduce oxidative stress. Promote dermal regenerative bio-processes	Nutraceutical and cosmeceutical formulations	Gómez-Mejía et al. (2019)
	Olive (*Olea europaea*)	Olive leaves	Phenolic compounds	Antioxidant capacity and	Animal feeding	Alfano et al. (2018)

(continued)

Table 2 (continued)

Type	Species	By-products	Items of interest obtained	Beneficial properties	Uses	References
				decreased DNA damage in leukocytes		
	Blue grapes (*Myrciaria vexatorMcVaugh*)	Pomace	Polyphenols, anthocyanins and carotenoids	Antioxidant activity and good source of protein, dietary fibre, calcium, and ascorbic acid	Products with high nutritional value	Castro-Vargas et al. (2019)
	Cacao (*Theobroma cacao*)	Seed	Phenols, flavonoids, tannins, alkaloids, steroid, cardiac glycoside, terpenoids, anthraquinones and saponins	Antioxidant activities and potential anticancer property	Pharmaceutical products	Mattioli et al. (2020)
	Hazelnut (*Coryllus avellana*)	Peel	Phenolic compounds, fibre and fatty acids	Nutritional and antioxidant value	Animal feeding	Ebuehi et al. (2019, Campione et al. (2020)
	Hazelnut (*Coryllus avellana*)	Shell	Lignins	Antioxidant capacity and UV blocker agent	Cosmeceutical formulations	Carus and Dammer (2018)
	Chestnut (*Castanea sativa*)	Inner and outer shells, burs and leaves	Phenolic compounds and tannins	Antioxidant and antimicrobial capacity	Nutraceuticals and antioxidant additives	Caccamo et al. (2019)
	Pomegranate (*Punica granatum L.*)	Peels, marc	Phenolic compounds, anthocyanins	Antioxidant activity, Inhibition of human platelet aggregation	Potential novel ingredients (i.e. polyphenol enriched apples)	Silva et al. (2020)
	Berries (*VacciniumL.*)	Berry press residues	Phenolic compounds, anthocyanins	Antioxidant activity	Functional ingredients	Turrini et al. (2020)
	Walnut (*Juglans regia*)	Shell	Lignins	Antioxidant capacity and UV blocker agent	Cosmeceutical formulations	Carus and Dammer (2018)
Cereals	Barley (*Hordeum vulgare*)	Milled husks	Fibre	Gut microbiota modulator	Animal feeding	Klavins et al. (2018)
	Oat (*Avena sativa*)	Fibre residue	Fibre	Gut microbiota modulator	Animal feeding	Klavins et al. (2018)
	Rye (*Secale cereal*)	Bran	Fibre	Gut microbiota modulator	Animal feeding	Klavins et al. (2018)
	Wheat (*Triticum* spp.)	Brann Germ Shorts	Tannins, carotenoids, total phenolic and total flavonoids contents	Antioxidant capacity	Functional food	Berger et al. (2014)
	Wheat (*Triticum* spp.)	Bran Middling Aleurone	Phenolic acids, betaine and choline	Presence of bioactive compounds	Animal feeding and functional food	Smuda et al. (2018)
	Maize (*Zea mays*)	Bran Germ	Tannins, carotenoids, total	Antioxidant capacity	Functional food	Berger et al. (2014)

(continued)

Table 2 (continued)

Type	Species	By-products	Items of interest obtained	Beneficial properties	Uses	References
		Germ meal	phenolic and total flavonoids contents			
	Maize (*Zea mays*)	Germ Bran	Fibre and proteins	Improvement of the nutritional, sensory and textural properties of wheat bread	Human feeding (bread)	Spaggiari et al. (2020)
	Rice (*Oryza sativa*)	Bran Germ Husk	Tannins, carotenoids, total phenolic and total flavonoids contents	Antioxidant capacity	Functional food	Berger et al. (2014)
	Rice (*Oryza sativa*)	Husk	Momilactones A and B	Antioxidant and anti-skin-ageing capacity	Cosmeceutical formulations	Pontonio et al. (2019)

spectrum of phenolic acids, flavonols, proanthocyanidins, flavonols, tannins, stilbenes, and anthocyanins still remain (Averilla et al. 2019). In similar way, other berry press residues (blueberries, cranberries, bilberries, pomegranate…) are also excellent source of anthocyanins and other phenolic compounds (Turrini et al. 2020; Klavins et al. 2018). In apple by-products such as pomace or peels resulting of cider and juice production, bioactive compounds are more concentrated than in the whole fruit (Barreira et al. 2019). These apple by-products are characterised by the high content of dietary fibre, pectins as well as phenolic compounds such as hydroxycinnamic acids, catechin, quercetin, epicatechin, or dihydrochalcones, mainly presenting in peel (Gorinstein et al. 2001; Barreira et al. 2019). Citrus waste is a rich source of value-added phytochemicals such as phenolic acids, flavones, limonoids, and flavanones, primarily naringin, hesperidin and narirutin, and neohesperidin (Gómez-Mejía et al. 2019). Citrus peel is also a good source of essential oils which are composed of terpenes such as limonene but also comprise other volatile compounds as phenylpropanoids, aldehydes, or alcohols (Mahato et al. 2019). The valuable components of tropical fruits by-products have also been recently revealed.

Mango peel and kernel (24–40%) are characterised by the high content of dietary fibre, carotenoids, tocopherols, phenolic compounds as phenolic acids, and flavonoids, among others, benzophenones and xanthanoids as mangiferin. Mango seed is also used for the recovery of starch and oil with excellent qualitative properties (Jahurul et al. 2015; Asif et al. 2016). Pineapple by-products represent almost 60% including crown, peel, bottom, stem, and trimmings. Some of these by-products are used for the extraction of bromelain, a proteolytic enzyme for peptides release (Mazorra-Manzano et al. 2018). Meanwhile, dietary fibre, starch, essential amino acids, and polyphenols like prodelphinidins, and procyanidins and catecholamines can be isolated from banana peel which represents around 35–40% of the fresh fruit (González-Montelongo et al. 2010; Rebello et al. 2014).

4.3 Cereals

Cereals (*Graminea* family), which are the most important world food crop, possess nine kinds of species that are available (wheat, rice, oat, rye, barley, millet, corn, sorghum, and triticale) (Galanakis 2018). During cereals manufacturing, huge amounts of by-products with interesting nutritional and bioactive potential compounds are obtained. These include minerals, vitamins, phenolic compounds, fatty acids, carotenoids, or proteins, among others (Saini et al. 2019) with high potential to combat several disorders (Fu et al. 2020). For example, the milling industry covers huge amounts of bran, the brewing industry provides brewer's spent grain and the ethanol industry contributes with distiller's grain (Roth et al. 2019).

In this scenario, *Avena sativa*, commonly known as oat, is one of the major cereal grains produced worldwide (annual production of 22 million tonnes) (Ralla et al. 2018). During oat processes, a common by-product is oat bran, that is rich in *ß*-glucan (10.4%), in addition to considerable amounts of minerals (magnesium, iron, copper, and potassium) (Butt et al. 2008). Due to its composition, bran oat has soothing, moisturising, anti-irritating, anti-ageing effects, and is also a safe skin protectant against UV damage (Aburjai and Natsheh 2003). Regarding oat germ oil, it represents approximately 7% of the total kernel weight and is rich in triacylglycerols, phospholipids, and oleosins. It also presents high levels of antioxidants, such as vitamin E, flavonoids, sterols, and avenanthramides, that provide important moisturising properties (Robards et al. 2009). Another principal crop is rice with an annual production around 760 million tonnes (Khir and Pan 2019). During rice milling, by-products such as husks, bran, and germ are produced (Senthil Kumar et al. 2010) and these are rich in minerals, vitamins, cellulose, carbohydrates, fatty acids, proteins, and phytochemicals (Aparecida et al. 2012) responsible for the cosmetic properties (antiwrinkle, protection against UV damage and preventing melanin hyperpigmentation) (Wang 2019). In addition to that, rice bran contains oryzanol, a phytochemical with an effect similar to vitamin E in growth promotion, hormonal secretions, and blood circulation (Sohail et al. 2017). For wheat, bran has been used as feed, however, it can be used for numerous biorefinery approaches due to its carbohydrate fraction (Roth et al. 2019). Moreover, corn by-products are rich in amino acids, minerals, and antioxidants that are normally associated with the skin effects reported, namely, the capacity to restructure and strength the skin barrier, maintaining the levels of epidermis hydration (Barrera-Arellano et al. 2019).

5 Concluding Remarks

Giving a glimpse on the available literature recently, agri-food residues are postulated as excellent sources of valuable bioactive ingredients with further applications in different industries as food, pharma, bioenergy, or cosmeceutical. However, there are still many gaps and goals that need to be achieved in order to establish successful revalorisation processes.

First of all, terms such as waste, residue, or by-products should be substituted by others for a better consumers' acceptability. Strategies should be aimed at the revalorisation of co-products or side streams of food production recovering value-added substances that will be incorporated in different items. Industries require the implementation of new approaches to exploit the revalorisation of side streams enabling their reuse and put back into the supply chain. In this sense, management of industries is challenged to move from a linear economy to a circular economy, since it endorses the optimisation of natural resources by manufacturing improvement and reducing the amount of residues through promotion of closed-loop processing system. Undoubtedly, this novel conceptualisation would entail an extra profitable economic activity for industries.

Within this framework, the development of sustainable green technologies, which are emerging in the last years, plays a key role. In many cases, the isolation of target compounds is not an easily accomplished task. Most of the co-products generated are perishable and highly fermentable due to high moisture (80–90%) and large amount of nutrients. Therefore, a stabilisation process is required to preserve the desired compounds and their functionalities. On the other hand, small quantities of target compounds usually coexist with a multitude of other components, so the extraction process must be, as much as possible, efficient to achieve higher retrieval rates of bioactive compounds and sustainable for not leading to an even bigger problem.

However, despite the promising evidences of the revalorisation processes, its implementation is still at micro-level. Despite the many researches pointing out the feasibility of the revalorisation of agro-industrial co-products, other industrial issues such as scale up, operational costs, or viability of industrial application should be addressed deeply in the future. Furthermore, the implementation of revalorisation strategies in this sector requires adaptation procedures inside the industry and the cooperation of all supply chains. Only the industrial symbiosis enables the possibility of taking full advanced of by-products utilisation reducing residual or treating them effectively while novel and safe value-added products will be generated.

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Biomass to Xylose

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Abstract

Lignocellulosic (LC) feedstock is the most economical and renewable natural feedstock of chemicals and energy. It is primarily composed of lignin, cellulose, and hemicellulose which are woven together and render the biomass recalcitrant to degradation. Hemicellulose is the second largest component of this biomass that is degraded to obtain large quantities of xylose. The effective utilization of the xylose is one of the most significant pre-requirement for economical bioconversion of LC biomass into biochemicals and biofuels. However, there are still some bottlenecks in the bioconversion of xylose, due to limitations to exploit xylose metabolism pathways. To overcome these issues, various research works have been carried out to engineer the transporters and enzymes involved in xylose utilization. Successful progress in this regard will boost xylose yield and titer, leading to the economical bioprocessing of the LC biomass. In order to understand biomass transformation strategies, firstly structural composition of LC biomass is introduced that is followed by the discussion on the chemical and enzymatic hydrolysis of biomass. Moreover, the importance of pretreatment as a prerequisite operation to biomass saccharification has also been highlighted along with an overview on various pretreatment methods. Finally, the significance of xylose as a raw material, its efficient utilization and the challenges concerning co-fermentation of sugars for the production of biofuels and other value-added chemicals by yeasts have been discussed.

Keywords

Biomass • Chemical degradation • Enzymatic degradation • Hemicellulose • Xylose

1 Introduction

The reliance of modern world on fossil fuels as chemical and energy feedstock is at stake due to high cost, volatile geopolitical scenarios, limited reserves, irregular prices, and harmful consequences on the environment (Vennestrøm et al. 2011). Extensive research on coal and biomass was started in Germany and in few other countries during world wars I and II for the production of chemicals and fuels (Faith 1945). Since, plant biomass is natural, abundant, and renewable source and has less impact on environment, it has become a choice for today's world to use it for the synthesis of fuels and chemicals (Vennestrøm et al. 2011; Perlack 2005).

2 Plant Biomass

The plant biomass as defined by Roberts et al. (1985) is the mass of plant present above or below ground and is produced (just by terrestrial plants) at the annual rate of 2.3×10^{11} metric tons of wood that can replace 66% of world's energy or 7×10^{11} metric tons of coal (Lynd et al. 2002). Plant biomass has been proven to be a great renewable feedstock for the synthesis of chemicals, fuels, heat, and power generation and has potential to displace petroleum products (Brown et al. 2015) mainly because of its cost competitiveness and for being environmentally friendly.

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2.1 Structure of Plant Cell Wall

The structure of plant cell wall varies from different tissues within a plant and also from species to species. It exists in two forms, primary and secondary. During the plant cell division, primary cell wall is formed which is responsible for the protection and cell to cell interaction and to support the basic structure. However, secondary cell wall is formed after the cell division (Houston et al. 2016).

2.2 Composition of Lignocellulosic Feedstock

Lignocellulosic (LC) feedstock is mainly consists of an aromatic polymer lignin, and polymeric carbohydrates, i.e., hemicellulose and cellulose (Ejaz et al. 2019). The proportion of these components significantly varies (Table 1) depending on the hardwood or softwood from which it is derived, i.e., species, variety, growth conditions, and maturity (Abdel-Hamid et al. 2013; Singh and Olsen 2011; Kim et al. 2010).

3 Hemicellulose

Hemicellulose is abundantly present in nature and consists of different heteropolymers of short and branched-chain sugar molecules. It is low molecular weight component and is associated with lignin and cellulose through covalent and non-covalent interactions (Shariq and Sohail 2019). The content of hemicellulose is 28% in softwood and 35% in hardwood (Balat et al. 2008). The amounts of different hemicellulosic components in softwood and hardwood are listed in Table 2. D-glucuronic acids, D-galacturonic acids, and 4-O-methylglucuronic are typical sugar acids in hemicelluloses (Saha 2003). Hemicelluloses present in hard or softwood or in grasses also differ in their composition and linkages (Table 3). All monosaccharides in hemicelluloses are classified into hexoses and pentoses and are linked through different interactions (Cardona and Sánchez 2007; Battaglia et al. 2011). The common commercial sources of hemicelluloses are the bran, or seed coats, and other agricultural sources including wheat straw, corn cob, and corn stalks (Ochoa-Villarreal et al. 2012).

3.1 Xylan

Xylan is the largest hemicellulose component (Balat et al. 2008) that is linked with lignin and cellulose by hydrogen and covalent bonds (Patel and Savanth 2015). Commonly, xylan is present with galacturonic acid, β-1,4-D-xylopyranose, and rhamnose, with modifications in the acetyl side group and glucuronic acid (Wierzbicki et al. 2019). Therefore, xylan can be categorized into glucuronoxylan, arabinoxylan, glucuronoarabinoxylan, and homoxylan (Dhiman and Mukherjee 2018). To this backbone, α-1, 2-4-O-methyl D-glucopyranosyl residues are attached in case of hardwood, while in case of softwood the α-1, 3-L-arabinofuranosyl units are present (Sedlmeyer 2011).

4 Conversion of Lignocellulosic Biomass

The chemical and biological conversion of LC feedstocks are aimed to obtain sugars (Hahn-Hägerdal et al. 2006), however, complex chemical composition of the feedstock caused hindrance to access sugars by the enzymes (Himmel et al. 2007). Hemicellulose, cellulose, and lignin are differently amenable because of differences in their structure and chemical composition. Structurally, lignin is a cross-linked biopolymer of phenylpropane units. On the other hand, anhydrous glucose units are present in cellulose while different monomers of C5 sugars are present in hemicellulose. The compositional ratio of carbon, oxygen, and hydrogen and the inert chemical structures caused restriction in chemo-catalytic conversion of LC biomass to chemicals and fuels (Pandey and Kim 2011; Sun et al. 2011). Therefore, proper combination of chemical and/or enzymatic pretreatment is required to get greater yields

Table 1 Composition of plant biomass in few waste materials

Feedstock	Lignin (%)	Cellulose (%)	Hemicellulose (%)	References
Corncob	20.3	31.7	34.7	Rivas et al. (2002)
Rice straw	14	37	24	Lachke (2002)
Switch grass	17.6	31	20.4	Singla et al. (2012)
Bamboo	20	40	20	Lachke (2002)
Birch	21	40	39	Rydholm (1965)
Wheat straw	23.4	38.2	21.2	Singla et al. (2012)
Newspaper	21	61	16	Ackerson et al. (1991)
Sugarcane bagasse	23.5	43.8	28.6	Pereira et al. (2011)

Table 2 Distribution of different hemicellulosic components in wood (Belgacem and Gandini 2008; Lundqvist et al. 2002; Willför et al. 2005a, b, 2008)

Hemicellulose	Softwood (%)	Hardwood (%)
Arabinogalactans	1–15	0.1–1
Arabinomethylglucuronoxylans	15–30	0.1–1
Galactoglucomannans	60–70	0.1–1
Glucomannans	1–5	1–5
Methylglucuronoxylans	5–15	80–90
Other galactans	0.1–1	0.1–1
Pectins	1–5	1–5

Table 3 Linkages present in various types of hemicelluloses (Bhaumik and Dhepe 2016)

Type	Components	Linkages
Galactoglucomannan	Mannose, galactose, glucose, acetyl substitution	1, 4-, 1, 6-
Softwood hemicellulose Arabinogalactan	Glucuronic acid, galactose, arabinose	1, 3-, 1, 6-, 1, 4-, 1, 5-
Hardwood hemicellulose Glucomannan	Mannose, glucose	1, 4-
Arabino-4-Omethylglucuronoxylan	Xylose, glucuronic acid, arabinose, methyl substitution	1, 4-, 1, 2-, 1, 3-
O-Acetyl-4-O-methylglucuronoxylan	Glucuronic acid, xylose, other substitution (acetyl, methyl)	1, 4-, 1, 2-
Arabinoglucuronoxylan/Arabinoxylan	Arabinose, xylose, glucuronic acid, other substitution (acetyl, coumaroyl, feruloyl, methyl)	1, 4-, 1, 3-, 1, 2-, 1, 2/3-

of sugars from both cellulose and hemicellulosic components (Lau and Dale 2009; Wyman et al. 2005). The glycosidic bonds between the sugar monomers are broken during the LC hydrolysis using chemicals or enzymes or a combination of both. Since the costs of combined chemical and enzymatic pretreatment is the potential drawback to enzymatic hydrolysis (Binder and Raines 2010) so, the development of highly active catalysts for the selective catalytic conversion of plant biomass to desired products remains a formidable challenge (Nosrati-Ghods et al. 2018). After hydrolysis, the most abundant sugars present in the LC hydrolysates are glucose (C6 sugar) and xylose (C5 sugar) (Singla et al. 2012; Lachke 2002).

5 Pretreatment of Lignocellulosic Feedstock

The use of pretreatment methods depends on the fraction of lignin, hemicellulose, and cellulose in feedstock. Delignification is necessary prior to hydrolysis of hemicellulosic and cellulosic component (Kumar et al. 2009). Acid mediated hydrolysis of hemicellulosic fraction under controlled conditions results in the production of sugars, which are highly value-added compounds for biorefinery. Since hemicelluloses are amorphous and branched as compare to cellulose, therefore, organic acids with lower acid strength can more efficiently hydrolyze hemicellulose than mineral acids (Bhaumik and Dhepe 2016; Fanta et al. 1984). The activation energy of hydrolysis of hemicellulose to sugars varies from 50 to 199 kJ mol^{-1} that depends on the linkages present in hemicellulose and its source (Mäki-Arvela et al. 2011). Table 4 describes the yield of xylose from biomass through different pretreatment processes.

5.1 Use of Hydrogen Peroxide (H_2O_2)

One strategy to remove lignin in LC biomass is to use H_2O_2 as an oxidizing agent (Mosier et al. 2005). The use of H_2O_2 generates carboxylic acids which cause problems in later stages of biomass processing, hence they need to be neutralized or removed (Azzam 1989). H_2O_2 pretreatment also results in the loss of significant amount of hemicelluloses (Bhaumik and Dhepe 2016).

Table 4 Xylose yield after pretreatment of biomass

Solvent	Biomass	Xylose yield (%)	References
H_2SO_4	Sugarcane bagasse	83.3	Pessoa et al. (1997)
$FeCl_3$ and hydrogen peroxide in a mixed solvent (DMSO/water)	Corn cob	92	Yu et al. (2018)
H_2SO_4	Sugarcane bagasse	7–13	Jacobsen and Wyman (2002)
H_2SO_4	Wheat straw	97	Mäki-Arvela et al. (2011)
HCl	Wheat straw	73	
H_2SO_4	Aspen wood	76.4	
Trifluoroacetic acid	Wheat straw	80	
H_2SO_4	Brewer's spent grain	94.2	
H_2SO_4	Corn stover	82	
H_2SO_4	Oak hardwood	83	
H_2SO_4	Rice straw	77	
HCland l-ethyl-3-methylimidazolium chloride ([EMIM]C1)	Corn stover	79	Binder and Raines (2010)

5.2 Use of Alkali

Pretreatment of feedstock at higher pH is carried out by using concentrated or dilute alkali at low pressure and temperature (Qadir et al. 2018). Along with lignin removal, removal of uronic acid and acetyl substitution in the hemicellulose is also possible by using potassium hydroxide, sodium hydroxide, calcium hydroxide, and ammonium hydroxide (Chang and Holtzapple 2000; Soto et al. 1994). Intermolecular ester bonds between polysaccharides and lignin are hydrolyzed by alkaline pretreatment (Sun and Cheng 2002). However, polysaccharides undergo oxidation reaction or these are hydrolyzed due to alkaline conditions (Bhaumik and Dhepe 2016).

5.3 Use of Concentrated Acids

Concentrated acids not only decrystallize cellulose but also cleave the hemicellulose and cellulose into sugars and catalyze the hydrolysis of glycosidic bonds (Smeets et al. 2007). In the United States, 80–90% conversion of hemicellulose and cellulose into sugars is carried out by sulfuric acid (Dunning and Lathrop 1945; Farone WA 1998). However, hazards are associated with the use of concentrated acids and also recycling is difficult which limits the adoption of this technology.

5.4 Use of Dilute Acids

Acids such as HCl, HNO_3, H_2SO_4, or H_3PO_4 are used in industries for catalytic hydrolysis of hemicellulose. Carvalheiro et al. (2008) reported the hydrolysis of hemicellulose by 0.5–1.5% sulfuric acid at 120–160 °C. Some advantages of using dilute acid pretreatment were reported by Esteghlalian et al. (1997) as

a. higher reaction rate,
b. low acid consumption,
c. cost-effective than alkaline pretreatment,
d. recycling is not required.

It is worthy to consider that pretreatment temperature and catalyst concentration affect the formation of chemical inhibitors (Mussatto and Roberto 2004). Processes at high-temperature result in the formation of inhibitory compounds in the hydrolysate (Téllez-Luis et al. 2002). According to Carrasco and Roy (1992), acid-catalyzed hydrolysis of hemicellulose at higher temperature favors the depolymerization. Nonetheless, inhibitory compounds are essentially generated and considered as the major drawback of dilute acid catalyzed hydrolysis (Jeffries 1983).

5.5 Use of Ionic Liquid

Less hazardous solvents such as ionic liquids (ILs) can facilitate hydrolysis of LC biomass. ILs are salts with low melting points and show promising ability as a catalyst for chemical derivatization (Zhu et al. 2006; El Seoud et al. 2007) and nonwoven fiber production (Hermanutz et al. 2006). ILs act on the non-covalent interactions in the LC without any significant degradation. ILs cleave the linkages of hemicellulose and lignin (Bhaumik and Dhepe 2016). Hemicelluloses recovered by IL pretreatment showed enhanced enzymatic digestibility (Binder and Raines 2010). The sugars released from ILs treated hemicelluloses are easily recovered and act as efficient feedstock for ethanol production and microbial growth (Binder and Raines 2010). However, high cost of ILs renders them less competitive for large-scale production (Yang and Wyman 2008).

6 Limitations of Chemical Pretreatment

Chemicals hydrolyze LC biomass by cleaving cellulose and hemicellulose into individual sugar molecules. As discussed earlier, strong acids act by disrupting intra and inter-chain hydrogen bond network and decrystallize cellulose to make it more accessible to the reagents. However, the adoption of this technology also has some drawbacks due to the hazardous nature of concentrated acids (Binder and Raines 2010), high cost of materials required for construction of corrosion resistant reactors (Jönsson and Martín 2016), and flammability and explosiveness. The formation of furfural, levulinic acid (LA), and formic acid from LC degradation is another impediment as these compounds act as inhibitory by-products and affect the enzymatic hydrolysis or fermentation (Ussiri and Lal 2014).

7 Enzymatic Hydrolysis of Biomass

Enzymatic hydrolysis is a process in which biochemical conversion of LC biomass (lignin, cellulose, and hemicelluloses) takes place followed by the release of monomeric sugars. The effectiveness of enzymatic hydrolysis is significant for the proficient transformation of biomass to the ideal products (Kucharska et al. 2018). Recent reports suggest that enzymatic hydrolysis has become more suitable because it offers many advantages over chemical hydrolysis. Enzymatic hydrolysis is environment friendly process as there is no problem with the handling of enzymes as compared to acids. It is also not necessary to use costly corrosive resistant materials. Enzymes are highly selective and exhibit high specificity to form a single product from their substrates. Enzymatic processes require normal temperature and pressure to perform, hence, are considered as lower energy-intensive process. Formation of fewer undesirable by-products is yet another advantageous factor over acidic or alkaline hydrolysis (Brummer et al. 2014; Chen 2015). However, in order for it to work properly, several factors affecting enzymatic hydrolysis need to be considered and optimized (Azmi et al. 2017).

7.1 Enzymes Involved in Biomass Hydrolysis

Cellulose and hemicelluloses are the carbohydrate polymers which are enzymatically hydrolyzed through multistep process by the synergistic action of cellulases and hemicellulases. Table 5 illustrates the major enzymes involved in the LC biomass degradation. There are four cellulase enzymes (Endoglucanase, β-glucosidase, cellobiohydrolases, and exoglucohydrolases) that work together for complete degradation of cellulose (Wahlström and Suurnäkki 2015).

It is imperative to note that hemicellulose is easily hydrolyzed than cellulose (Maitan-Alfenas et al. 2015) yet a more complex group of enzymes called hemicellulases is involved in its degradation. These include endoxylanases or Endo-β-1,4-xylanase (Enzyme Commission [EC] number 3.2.1.8), α-glucuronidase (EC 3.2.1.139), β-xylosidase (EC 3.2.1.37), α-glactosidase (EC 3.2.1.22), α-L-arabinofuranosidase (EC 3.2.1.55), ferulic acid esterase (EC 3.1.1.73), acetyl xylan esterase (EC 3.1.1.72), and endo-1,4-β-D-mannanase (EC 3.2.1.78) (Kumar and Murthy 2013; Van Dyk and Pletschke 2012). The accessory enzymes are supplemented during biomass saccharification to enhance the sugar yield (Robl et al. 2013).

7.1.1 Endo-β-1, 4-Xylanase

Endo-β-1, 4-xylanase, (EC 3.2.1.8), is one of the noteworthy hydrolytic enzymes among various xylanases that de-polymerize the xylan to xylobiose and xylooligomers. β-1, 4-glycosidic internal bonds in the polymer of xylan are cleaved by these endo-β-1, 4-xylanase (Cha et al. 2014). Xylanases, in general, were classified into different categories or families of glycosyl hydrolase (GH) number (3, 5, 7, 8, 10, 11, 30, 39, 43, 52, and 54) based on the protein's primary structure; whereas, endo-β-1,4-xylanases are included in the GH family 10 and 11 (Bhardwaj et al. 2019). Several reviews have documented many bacterial and fungal isolates for endo-β-1, 4-xylanase production (Dhiman and Mukherjee 2018; Maheshwari et al. 2000; Subramaniyan and Prema 2002; de Vries and Visser 2001; Manju and Singh Chadha 2011) among which thermophilic strains are of biotechnological significance (Manju and Singh Chadha 2011).

Table 5 Main enzymes required to degrade lignocellulose to monomers

Component	Enzymes	References
Lignin	Lignin peroxidase, manganese peroxidase, and laccase	Van Dyk and Pletschke (2012), Chauhan (2019), Xu et al. (2017)
Pectin	Pectate lyase and pectin methyl esterase, polygalacturonase and rhamnogalacturonan lyase	Van Dyk and Pletschke (2012), Tayi et al. (2016)
Hemicellulose	β-mannosidase, α-glucuronidase, acid esterase,α-galactosidase,ferulic acid esterase, p-coumaric, α-L-arabinofuranosidase,β-xylosidase, endomannanase, acetyl xylan esterase and Endo-xylanase	Kumar and Murthy (2013), Van Dyk and Pletschke (2012), Manju and Singh Chadha (2011)
Cellulose	Endoglucanase, β-glucosidase and Cellobiohydrolase	Wahlström and Suurnäkki (2015), Van Dyk and Pletschke (2012)

7.1.2 β-Xylosidase

β-xylosidase (EC 3.2.1.37) is the main enzyme responsible for hydrolysis from non-reducing ends of xylooligosaccharides and xylobiose to liberate monosaccharides (Kumar and Murthy 2013; Van Dyk and Pletschke 2012). Purified β-xylosidase usually prefers xylobiose as substrate than xylan. β-xylosidases attribute to a significant role after xylan has undergone a sequential hydrolysis by accumulating short oligomers of β-D-xylopyranosyl that may act as inhibitor for endo-β-1, 4-xylanase. β-xylosidases then remove the cause of inhibition leading to efficient hydrolysis of xylan (Zanoelo et al. 2004). These enzymes are placed into five GH families; 3, 39, 43, 52, and 54 among which GH3 and GH43 are the well-characterized β-xylosidases so far (Dodd and Cann 2009).

7.1.3 α-L-Arabinofuranosidase

The side chain groups of arabinans, arabinoxylans, and arabinogalactans are liberated by the supplementary enzymes, α-arabinofuranosidases. These enzymes act synergistically with other arabinohydrolases, such as endo-(1, 5)-α-L-arabinanases (EC 3.2.1.99) for the complete hydrolysis of hemicelluloses. First α-L-arabinofuranosidases (EC 3.2.1.55) catalyze the non-reducing end of L-arabinofuranosyl residues from arabinan then endo-(1,5)-α-L-arabinanases produce a variety of arabino-oligosaccharides by efficient hydrolysis of the resulting debranched backbone (Dimarogona and Topakas 2016). These arabinohydrolases produced by several fungi and bacteria belong to the GH family 43, 51, 54, 62, and 93 (Manju and Singh Chadha 2011; Wefers et al. 2017).

7.1.4 Acetyl Xylan Esterases

Acetyl xylan esterases (3.1.1.72) play a vital role to degrade xylan. It breaks the ester bonds between xylose and acetyl residues which facilitates degradation of xylopyranosyl residues by endo-β-1, 4-xylanases (Kim et al. 2020; Hettiarachchi et al. 2019). The action of these enzymes on polysaccharide substrate leads to exposure of new sites on xylan chain and subsequently improves binding with depolymerizing endoxylanases (Manju and Singh Chadha 2011).

Biely et al. (1985) described acetyl xylan esterases produced from many fungi and bacteria. *Aspergillus niger*, *Schizophyllum commune*, *Trichoderma reesei,* and *Aureobasidium pullulans* have been widely reported for their esterases production. More precise activities are exhibited towards acetylated glucuronoxylan by these fungal esterases than plant and animal esterase, and hence are termed as acetyl xylan esterases (Bajpai 2014).

Feruloyl esterases (EC 3.1.1.73) degrade the ester linkages between the ferulic acid and arabinose substitutions which also affects cross linking of xylan with lignin. These feruloyl esterases act by cleaving xylan or oligosaccharides derived from xylan and release ferulic acid. Feruloyl esterases are members of carbohydrate esterase (CE) family 1, while acetyl xylan esterase is reported as a members of EC family 1–7, 12, and 16 (Manju and Singh Chadha 2011).

7.1.5 α-D-Glucuronidases

α-D-Glucuronidases (EC 3.2.1.131) degrade α-1,2 bonds between xylose residues and glucuronic acid present in glucuronoxylan. Nevertheless, the action of enzymes on a specific substrate varies depending on microbial source. It has been observed that to some extent α-glucuronidase activity is obstructed by the acetyl groups close to the glucuronosyl substituents (Bajpai 2014). So far, all the α-glucuronidases have been classified as members of family 67.

7.1.6 Endo-1, 4-β-D-Mannanase

Endo-1, 4-β-D-mannanases (EC 3.2.1.78) are the enzymes that degrade the linkages of β-D-1,4 mannopyranosyl present within the major chain of galactomannan, glucomannan, galactoglucomannan, and mannan to release short chains of β-D-1, 4-manno-oligomers. β-mannosidases (EC 3.2.1.25) further hydrolyze β-D-1, 4-manno-oligomers to mannose. The manno-oligosaccharides, the foremost hydrolysis product of mannan are also considered as potential prebiotics. The β-mannanases are classified in 5, 26, and 113 GH families (Xia et al. 2016).

8 Microorganisms Involved in Hemicellulase Production

Microorganisms play a vital role in the production of enzymes necessary for biomass saccharification. Substantial research has been conducted on the isolation of numerous microorganisms belonging to molds, yeasts, bacteria, and actinomycetes involved in cellulase and hemicellulase production (Ravindran and Jaiswal 2016). For that reason, different strategies like bioprospecting of microorganisms are used to explore more efficient microbes to hydrolyze crude substrates, followed by screening of the best candidates that produce novel enzymes (Maitan-Alfenas et al. 2015). Table 6 shows various microorganisms that have been documented for the hemicellulase production utilizing different substrates.

9 Xylose Fermentation

During the pretreatment and hydrolysis of biomass, several inhibitory compounds such as furaldehydes, acetic acid, formate, phenolic derivatives are also formed (Moysés et al. 2016). The concentration of these compounds relies upon the biomass type and pretreatment methods and hydrolysis conditions. Nonetheless, the presence of these compounds even at lower concentration may hinder fermentation thus reducing the yield and productivity. Hence a number of strategies have been employed to minimize the influence of inhibitory compounds by using recombinant strains to improve xylose fermentation. The upshot of the development of recombinant strains is that bacteria and yeasts can co-ferment pentoses and hexoses into ethanol and other value-added products and yield more than that of mono-cultures (Kwak and Jin 2017). Few of the recombinant strains are listed in Table 7 that could utilize xylose for the production of some value-added products. There are many naturally occurring microorganisms that can readily ferment hexoses (glucose, mannose, and glactose) to ethanol and other value-added chemicals however, only a few native strains are capable of fermenting pentoses (particularly

Table 6 Some of hemicellulase producing microorganisms using different substrates

Strains	Substrate used	Type of hemicellulase	References
Penicillium sp. CFR303	Coffee by-products	Xylanase	Murthy and Naidu (2012)
P. digitatum, Aspergillus niger	Pectin, glucose Wheat bran	α-l-arabinofuranosidase	Patel and Savanth (2015), Meena et al. (2017)
T. lanuginosus	Corn cobs	β-xylosidase and xylanase	Manju and Singh Chadha (2011)
Malbrancheaflava	Sorghum straw	Feruloyl esterase, acetyl esterase, β-xylosidase, xylanase and arabinofuranosidase	Sharma et al. (2016)
Bacillus aestuarii	Commercial xylan	Xylanase	Chauhan et al. (2015)
B. borstelensis	Rice husk	Endoxylanase	Budhathoki et al. (2011)
Thermobacillusxylanilyticus	wheat straw and wheat bran	Xylanases, arabinosidase and esterase	Rakotoarivonina et al. (2014)
Pseudozymahubeinsis	Beechwoodxylan	β-xylosidase	Mhetras et al. (2016)
Bacillus sp. 3A	locust bean gum,	β-mannosidase	Regmi et al. (2016)
Lysinibacillus sp.	sugar cane bagasse, corn cob, corn straw and wheat bran	Xylanase	Alves-prado et al. (2010)
Paenibacillus species	Sugarcane bagasse	Xylanase	Di Marco et al. (2017)
Aspergillus niger FTCC 5003	Palm kernel cake	β-Mannosidase	Abdeshahian et al. (2010)
Aspergillus oryzae	Copra	β-Mannosidase	Regalado et al. (2000)
Aspergillus niger I-1472	Sugar beet pulp	Feruloyl/pcoumaroyl esterase	Dilokpimol et al. (2017), Bonnin et al. (2002)
Aspergillus niger ADH-11	Wheat bran	α-LArabinofuranosidase	Patel and Savanth (2015)

(continued)

Table 6 (continued)

Strains	Substrate used	Type of hemicellulase	References
Aspergillus foetidus MTCC 4898	Wheat bran	Xylanase	Chapla et al. (2010)
Penicillium sp. CFR303	Coffee by-products	Xylanase	Murthy and Naidu (2012)
P. digitatum, Aspergillus niger	Pectin, glucose Wheat bran	α-l-arabinofuranosidase	Patel and Savanth (2015), Meena et al. (2017)
T. lanuginosus	Corn cobs	Xylanase and β-xylosidase	Manju and Singh Chadha (2011)
Malbranchea flava	Sorghum straw	Xylanase, β-xylosidase, arabinofuranosidase, acetyl esterase, and feruloyl esterase	Sharma et al. (2016)
Bacillus aestuarii	Commercial xylan	Xylanase	Chauhan et al. (2015)
B. borstelensis	Rice husk	Endoxylanase	Budhathoki et al. (2011)
Thermobacillus xylanilyticus	Wheat straw and wheat bran	Xylanases, arabinosidase, and esterase	Rakotoarivonina et al. (2014)
Pseudozyma hubeinsis	Beechwood xylan	β-xylosidase	(Mhetras et al. 2016)
Bacillus sp. 3A	Locust bean gum	β-mannosidase	Regmi et al. (2016)
Lysinibacillus sp.	Wheat bran, corn straw, corncob, and sugar cane bagasse	Xylanase	Alves-prado et al. (2010)
Paenibacillus species	Sugarcane bagasse	Xylanase	Di Marco et al. (2017)
Aspergillus niger FTCC 5003	Palm kernel cake	β-Mannosidase	Abdeshahian et al. (2010)
Aspergillus oryzae	Copra	β-Mannosidase	Regalado et al. (2000)
Aspergillus niger I-1472	Sugar beet pulp	Feruloyl/pcoumaroyl esterase	Dilokpimol et al. (2017), Bonnin et al. (2002)
Aspergillus niger ADH-11	Wheat bran	α-LArabinofuranosidase	Patel and Savanth (2015)
Aspergillus foetidus MTCC 4898	Wheat bran	Xylanase	Chapla et al. (2010)

xylose) usually with lower efficiency (Maitan-Alfenas et al. 2015) (Table 8).

Utilization of xylose-fermenting microorganisms at commercial scale is often restricted because of slow fermentation rates. *S. cerevisiae,* a "GRAS" (Generally Regarded as Safe) (Ostergaard et al. 2000) organism is preferred over the native xylose utilizing microorganisms for ethanol production regarding sturdiness against various industrial environments such as high osmotic pressure, low pH, phage contamination, and high alcohol concentration. However, this yeast is incapable to efficiently consume xylose as a sole carbon source (Kwak and Jin 2017; Eliasson et al. 2001). Though some bacteria, like *Zymomonas mobilis* and genetically modified *Escherichia coli*, have the ability to ferment sugars, *S. cerevisiae* because of its elevated ethanol tolerance and wide public acceptance is still the organism of choice and has been a main focus to improve its xylose fermentation for industrial production of ethanol (Moysés et al. 2016; Chu and Lee 2007).

9.1 Limitations of Xylose Metabolism in *S. cerevisiae*

Ideally microorganisms foreseen for biomass conversion should have the abilities to (1) assimilate a wide range of substrates, (2) readily ferment concentrated substrates, and (3) tolerate the inhibitory by-products and ethanol.

The lack of ability of *S. cerevisiae* to utilize xylose for growth has been credited to many reasons including incompetent uptake of xylose (Kötter and Ciriacy 1993), a redox imbalance caused by xylitol dehydrogenase (XDH) and xylose reductase (XR) (Bruinenberg 1986), scant activity of xylulose kinase (XK), and an ineffective pentose phosphate pathway (PPP) (Walfridsson et al. 1995). Xylose uptake in *S. cerevisiae* takes place by facilitated diffusion via hexose transporters (Hxt) gene family, but with much lesser affinities than glucose. In a study by Hamacher et al. (2002), individual Hxt genes were introduced and constitutively expressed in *S. cerevisiae* TMB3201 and it was revealed that

Table 7 Xylose utilization in various recombinant microorganisms for value-added chemicals and biofuel production

Recombinant strains	Method used	Product obtained	References
Saccharomyces cerevisiae	Homologous recombination	Ethanol	Ma et al. (2012)
Zymomonas mobilis	Site specific	Ethanol	Agrawal et al. (2011)
Escherichia coli	Cloning from plasmid	1, 2, 4-butanetriol	Zhang et al. (2016)
Klebsiella oxytoca	Plasmid DNA isolation	1, 4-Butanediol	Wang et al. (2017)
Escherichia coli	Plasmid DNA isolation	Ethylene glycol	Chae et al. (2018)
Escherichia coli	Cloning from plasmid	1, 2, 4-butanetriol	Cao et al. (2015)
Trichoderma reesei	Site-directed	Ethanol	Xu et al. (2015)

Table 8 Xylose utilization in native strains for value-added chemicals and biofuel production

Strain	Xylose concentration g L^{-1}	Product obtained	References
Aspergillus flavipes	52	Ethanol	Hauli et al. (2013)
Saccharomyces cerevisiae(ATCC 26497)	1.6	Xylitol	Patiño et al. (2019)
Saccharomyces cerevisiae BY4741	2	Xylitol	Johansson and Hahn-Hägerdal (2002)
Spathaspora passalidarum	30	Ethanol	Hou (2012)
Trichoderma longibrachiatum	20	Xylooligosaccharides	Saleh et al. (2016)
Geotrichum sp.	1.27	Xylitol	Matos et al. (2016)
Candida pseudorhagii	47.6	Ethanol	Ali et al. (2017)
Hamamotoa lignophila	45.3	Ethanol	Ali et al. (2017)
Meyerozyma guilliermondii	38.8	Ethanol	Ali et al. (2017)
Sugiyamaella sp.	40.65	Ethanol	Ali et al. (2017)
Pichia kudriavzevii	30	Ethanol	Nweze et al. (2019)

at a concentration of 2% xylose, glucose transporters with high affinity (galactose transporter [Gal2] and Hxt7) and intermediate affinity (Hxt4 and Hxt5) are required for xylose uptake. Hxt5 and Hxt7 are expressed by native *S. cerevisiae* when xylose is given as sole carbon source and hence considered to be predominantly important for xylose metabolism (Chu and Lee 2007).

The specificity of XR for Nicotinamide adenine dinucleotide phosphate (NADPH) and strong preference of XDH for Nicotinamide adenine dinucleotide (NAD) causes a redox imbalance leading to excessive xylitol accumulation consequently ethanol yield is decreased (Zhang et al. 2012); the phenomenon has been broadly studied in native xylose-fermenting yeasts. Therefore, availability of oxygen is also attributed to regulate xylose metabolism in yeasts. Lesser amount of oxygen (1.5–5 mmol L^{-1} h^{-1}) is required for conversion of xylose to ethanol at higher yield (Agbogbo et al. 2007). Therefore careful regulation of oxygen is required. Under anaerobic conditions, cell growth and ethanol production are rigorously limited (Maitan-Alfenas et al. 2015).

Xylulose, a product of XR and XDH is metabolized to ethanol by *S. cerevisiae* but at a low rate. Metabolism of xylulose is limited by the expression level of XK in *S. cerevisiae*. Hence, a slower rate of xylulose consumption is linked with the slower XK activity leading to limiting xylose metabolism. Yu et al. (Yu et al. 1995) reported lower yield of ethanol when xylulose (50 g L^{-1}) was supplied as a sole carbon source while significantly higher ethanol yield was observed in the presence of glucose (50 g L^{-1}) by the strain ATCC 24860 of *S. cerevisiae* (Chu and Lee 2007).

The rate of xylulose fermentation is partly controlled by non-oxidative PPP (Johansson and Hahn-Hägerdal 2002). The activity of important enzymes transaldolase (TAL) and transketolase (TKL) in the non-oxidative PPP has been associated with rate-limiting steps for xylose and xylulose utilization in recombinant *S. cerevisiae*. Xylulose-5-phosphate (X5P) and ribose-5-phosphate (R5P) is converted to sedoheptulose 7-phosphate (S7P) and glyceraldehydes-3-phosphate (GA3P) by the action of TKL. While TAL converts S7P and GA3P to fructose-6-phosphate (F6P) and erythrose-4-phosphate (E4P). Depletion of either of the intermediary GA3P or F6P results in ineffective xylulose fermentation in *S. cerevisiae* (Chu and Lee 2007).

To overcome the challenges related to limitations of xylose fermentation, a number of strategies using recombinant technology have been developed such as discovering new pathways for xylose utilization, reducing the influence of undesired by-products, and solving redox imbalances (Moysés et al. 2016).

9.2 Engineering of *S. cerevisiae* Strains for Improved Xylose Fermentation

Recently, advanced techniques have been employed for the improvement of xylose fermentation by engineering the most widely used *S. cerevisiae.* Three separate approaches have been applied to habituate *S. cerevisiae* strains for the efficient metabolism of xylose. The first approach is to grow the recombinant *S. cerevisiae* aerobically and then familiarizing the strain to anaerobic conditions. Two distinct phenotypes with smaller (class I) and larger (class II) populations were generated during this approach. Class I could ferment xylose/glucose to ethanol with increased xylose uptake rates, while class II was capable of growing on xylose under anaerobic conditions. The second approach involves the cultivation of a recombinant strain utilizing only xylose first, then shifting to a xylose-glucose mixture and again shifting to merely xylose, generating a strain that could ferment 4.5% xylose to ethanol (yielding 0.14 $g\ g^{-1}$) anaerobically. The third approach relies on using native strains through natural selection which spontaneously give rise to mutant strains of *S. cerevisiae.* Attfield and Bell (2006) demonstrated that a non-genetically modified strain of *S. cerevisiae* (MBG2303) was evolved in 1463 days of natural selection and more than 23 mating cycles of breeding. This strain could utilize 5% xylose producing a little xylitol, glycerol, and ethanol (0.58 $g\ L^{-1}$) under aerobic growth (Chu and Lee 2007).

Genetically engineered strains of *S. cerevisiae* (with xylose-metabolizing genes from other xylose-fermenting yeasts) have bestowed the capability of xylose utilization as a only carbon source and reported to generate ethanol at theoretical yield of 0.51 $g\ g^{-1}$ from xylose (Ostergaard et al. 2000). Cunha et al. (2019) studied xylose-fermenting capabilities of industrial strain of *S. cerevisiae* with individual and combined XR/XDH and xylose isomerase (XI) pathways that resulted in a decrease in xylitol accretion and improved xylose utilization and ethanol production. Kuyper et al. (2003) also described the xylose fermentation by recombinant *S. cerevisiae* (RWB202) expressing a cloned XI. The strain under anaerobic conditions could utilize 2% xylose when AraA gene from *Piromyces* species (anaerobic fungus) was expressed in *S. cerevisiae.*

10 Xylose Metabolism Pathways

There are several microorganisms reported to ferment xylose directly to ethanol in significant quantities, namely the yeasts *Pachysolen tannophilus* (Cha et al. 2014), *Kluyverornyces marxianus* (Sharma et al. 2017), *Candida* spp. (Kaewwichian et al. 2019; Zhao et al. 2020), *Zymomonas mobilis* (Zhang et al. 2012) as well as molds (Panagiotou and Christakopoulos 2004). Many other yeasts have been documented for the ower yield of ethanol (Maleszka and Schneider 1982; Maleszka et al. 1982).

To facilitate complete utilization of xylose, microorganisms have evolved different xylose utilization pathways. In bacteria, xylose is directly converted to 5-xylulose and then phosphorylated to 5P-xylulose by a XI pathway. *E. coli* has a native xylose utilizing pathway which employs major facilitator superfamily (MFS) protein XylE and XylFGH, while in some special situations AraE (the arabinose symporter) can act as a xylose transporter (Zhao et al. 2020; Hasona et al. 2004). The native xylose transporters of Clostridia (*xylT*, *xylFGH*) and *E. coli* are much alike. However, molds and yeast use two-step oxidation-reduction pathway in which a XR first reduces xylose to xylitol, and then XDH oxidizes xylitol to 5-xylulose. In Archaea, the xylose transporters belong to the ABC class that exhibits similarity to bacteria. This pathway involves oxidation of xylose to the tricarboxylic acid cycle by the action of many genes (encoding 2-keto-3-deoxyxylonate dehydratase, xylonate dehydratase, XDH, and α-ketoglutarate semialdehyde dehydrogenase) (Zhao et al. 2020; Wagner et al. 2018).

11 Production of Advanced Biofuels and Value-Added Chemicals from Xylose

In recent years, many wild or engineered strains have attracted great attention for the sustainable manufacture of advanced biofuels via metabolic pattern of xylose fermentation and chemicals by utilizing xylose via synthetic pathway (Kim and Woo 2018). Usually xylose constitutes a significant portion of LC biomass, therefore, it can economically be utilized for conversion to bioethanol and other chemicals (Nweze et al. 2019). Figure 1 shows schematic diagram for bioconversion of LC biomass to numerous value-added chemicals.

11.1 Production of Lactic Acid

Lactic acid (2-hydroxypropanoic acid) is an organic acid of important commercial interest. It is produced either

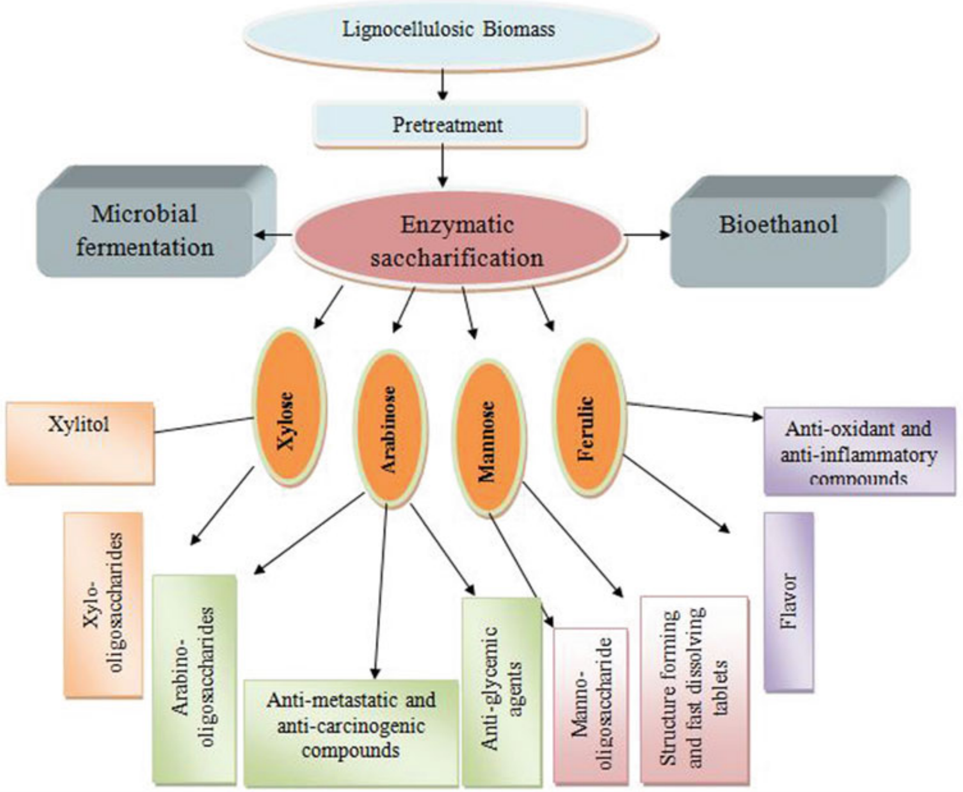

Fig. 1 Bioconversion of lignocellulosic biomass to value added chemicals

chemically or by microbial fermentation. Lactic acid has several industrial applications such as food, feed, pharmaceuticals, and cosmetics. It is mainly used as a precursor for producing biodegradable polyester called polylactic acid (PLA) (Novy et al. 2018; Ye et al. 2013). PLA is used to manufacture various products, including plastic cups, bags, packaging materials, and prosthetics (surgical implants) (Turner et al. 2015).

Microbial strains that potentially utilize xylose as well as glucose and ferment to lactic acid using renewable raw materials are of great importance for industrial biotechnology (Turner et al. 2015). Many reports highlight efforts to obtain such microbial strains that are capable of simultaneous consumption of xylose and glucose through mutagenesis and by introducing heterologous pathways of metabolism into conventional *S. cerevisiae* (Robak and Balcerek 2018).

The studies suggest that yeast can execute better than lactic acid bacteria (LAB) under convenient fermentation conditions, therefore, few yeasts have been engineered with a heterologous lactate dehydrogenase (LDH). As investigated by Kwak and Jin (2017), in spite of introducing a heterologous LDH, the engineered *S. cerevisiae* generated ethanol as a major product and low yield of lactic acid under fermentable sugars through its unusual regulatory system known as the Crabtree effect. The effect explains the phenomenon where some yeasts prefer fermentation over aerobic respiration even in sufficient supply of oxygen. In another study, production of lactic acid by Crabtree positive yeasts, LDH from *Rhizopus oryzae* was overexpressed in *S. cerevisiae* to compare the glucose and xylose utilizing capabilities; yet the production of ethanol (0.31 g g^{-1} glucose) was still greater than lactic acid (0.22 g g^{-1}).

In contrast, engineered *S. cerevisiae* generated higher lactic acid (0.69 g g^{-1} xylose) with insignificant ethanol (<0.01 g g^{-1} xylose) production under sole xylose culture conditions (Turner et al. 2015). Upon changing carbon source from glucose to xylose, Crabtree negative yeasts also showed improvement in the production of lactic acid with lower ethanol yield. Overexpression of *Lactobacillus helveticus* LDH in a native xylose utilizing yeast *S. stipitis* exhibited significant productivity of lactic acid (0.60 g g^{-1} xylose) and a considerable decline in ethanol yields (using 0.28 to 0.02 g g^{-1} xylose) under limited supply of oxygen, at 50 g L^{-1} xylose concentration (Kwak and Jin 2017).

However, reports suggest that only few strains of LAB can ferment xylose (Mussatto and Teixeira 2010). *Enterococcus mundtii* QU25, a strain of LAB has been studied to produce elevated yield of lactic acid homofermentatively via PPP from both glucose and xylose. With increase in xylose concentrations (25.8 g L^{-1}–100 g L^{-1}) QU25 generated more lactic acid (21.7 g L^{-1}) with minimal by-products consuming 50.2 g L^{-1} xylose. At this concentration, the maximal productivity of lactic acid (3.14 g L^{-1} h^{-1}) was attained; any decrease in concentration of xylose leads to lower lactic acid yields (Abdel-Rahman et al. 2016). *Bacillus coagulans* C106, a thermophilic strain, has also been reported with the ability to ferment xylose to lactic acid with a theoretical yield of 100% using PPP (Ye et al. 2013).

11.2 Bioethanol Production

Bioethanol also known as ethyl alcohol is one of the most studied biofuels. It is considered as a petrol substitute and less toxic fuel for transport vehicles (Rodrussamee et al. 2018) as its use can reduce Carbon dioxide (CO_2) emission (Selim et al. 2018). Bioethanol is a high octane number biofuel produced by fermentable sugars and is generally classified into first, second, and third generations. The first-generation bioethanol production utilizes food feedstock, primarily starchy materials. Whereas bioethanol of second generation is manufactured from LC biomass, such biomass is generally easily available and is more cost-effective. Since second-generation bioethanol is based on non-food feedstock, it does not compete with food supplies. Production of third-generation bioethanol is rooted on algal cultivation using waste streams from industries as substrate (Robak and Balcerek 2018). In comparison to other raw materials such as molasses and starchy substrates, LC biomass is considered as most economical (Singla et al. 2012).

The ability of microorganisms to utilize glucose, xylose, galactose, arabinose, and mannose is prerequisite to ethanol production from biomass (Hahn-Hägerdal et al. 2006). Other ideal attributes include the ability to display broad substrate specificity as well as “ethanol tolerance”, substrate, temperature, and inhibitory compounds in hydrolysates (Pasha et al. 2007). Generally, inhabitant xylose-fermenting yeasts, for example, *Pachysolen tannophilus* (Jeffries et al. 1985), *P. stipitis* (Toivola et al. 1984), *Scheffersomyces* (*Candida*) *shehatae* (Chandel et al. 2007), and *Kluyveromyces marxianus* (Nitiyon et al. 2016; Rodrussamee et al. 2011) can ferment both glucose and xylose.

Among several microorganisms, yeasts have shown to exhibit privileged yields of ethanol from xylose. So far, the most comprehensively studied xylose-fermenting yeasts include *Pichia stipitis, Pachysolen tannophilus,* and *Candida shehatae*. Among which *C. shehatae* and *P. stipitis* are the most desirable inhabitant producers of ethanol with near theoretical yield of 0.51 g ethanol g^{-1} xylose.

According to a recent report, *S. cerevisiae* and *P. stipitis* are two most potent model organisms in fermentation technology because of their higher productivity and ethanol yield. They have considerably higher tolerance to ethanol and certain inhibitors present in LC hydrolysates. Besides, they can utilize various carbohydrate rich substrates through fermentation processes (Selim et al. 2018; Vilela L de et al. 2015). Though these fermentation processes are influenced by various toxic substances and inhibitory compounds that restrict the enzymes activity resulting in failure to obtain desired products (Wikandari et al. 2019). The cofactor imbalance due to co-expression of XR and XDH is discussed in detail in previous sections. It is considered that this cofactor imbalance is the main reason for less efficient xylose fermentation for bioethanol production.

Two key approaches including cloning of XR and XDH and/or XI have been generally used to overcome this issue. Moreover, additional genetic modifications like (i) overexpression of enzymes required for conversion of xylulose into glycolysis intermediates, (ii) mutagenesis of aldose reductase (transforms xylose to xylitol), and (iii) overexpression of heterologous xylose transporters have also been implemented. Besides all these genetic approaches to improve xylose fermentation, ethanol yield by recombinant *S. cerevisiae* is still insignificant and simultaneous fermentation of xylose and glucose is yet another bottleneck.

In an effort to control the repressive effect of glucose over the utilization of xylose, Vilela et al. (2015) described heterologous expression of a XI gene (*xylA*) from *Burkholderia cenocepacia* into *S. cerevisiae* strain that exhibited anaerobic fermentation of xylose, without xylitol accumulation. Moreover, an evolutionary engineering strategy was manipulated through sequential batch fermentation on xylose to the *xylA*-expressing strain for improving xylose fermentation. The resulting yeast strain was capable of co-fermenting xylose and glucose, with enhanced ethanol production. In another study, comparison of the commercial strains with XI (from *Clostridium phytofermentans)* or XR/XDH pathway showed that recombinant strains of *S. cerevisiae* with both XI and XR/XDH pathways are the most efficient ethanol producers (Cunha et al. 2019). To further promote higher ethanol production from xylose, heterologous genes, *Sut*1 and *Sut*2 for sugar transporters were expressed, the customized version of *S. cerevisiae* could only transport xylose (Du et al. 2010). Figure 2 shows pathways to produce ethanol from xylose using either bacteria or yeast.

11.3 Xylitol Production

Xylitol is used as a sugar substitute with low caloric content for diabetic patients and has anti-carcinogenic properties (Takata et al. 2014; Mishra et al. 2013; Lee et al. 2013). A number of researches have been conducted on xylitol production from xylose using plant biomass as a source of raw material (Kwak et al. 2019).

Majority of xylose-assimilating yeasts synthesize xylitol by expressing *xyl*1 and *xyl*2 genes that encode XR and XDH,

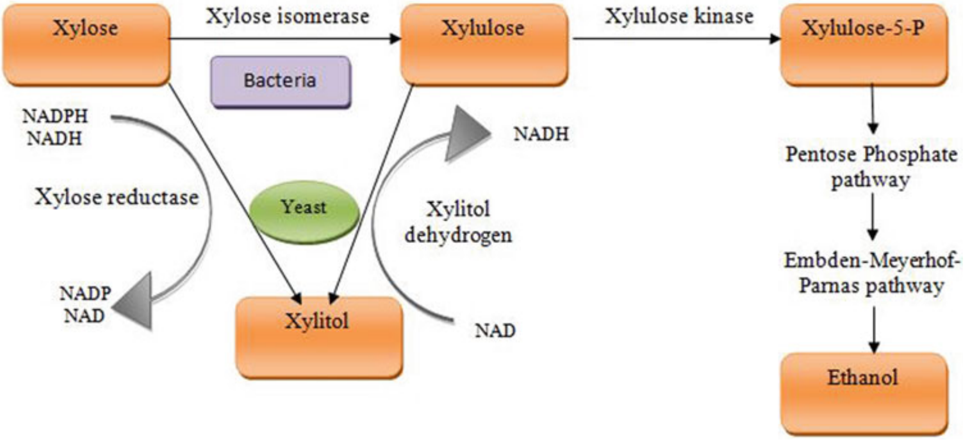

Fig. 2 Metabolic pathways from xylose to ethanol

respectively. XR reduces D-xylose to xylitol using NADPH as a cofactor, while XDH oxidizes xylitol to D-xylulose using NAD as a cofactor and hence yield of xylitol is reduced. In a subsequent reaction catalyzed by xylulose kinase, D-xylulose is further converted to D-xylulose 5-phosphate (Kwak et al. 2019).

Hallborn et al. (1991) cloned *xyl*1 gene from *P. stipitis* in *S. cerevisiae* for xylitol production. Since yeast cells oxidize xylitol to D-xylulose for the growth, it becomes a major limiting factor to obtain higher yields of xylitol, therefore, Ko et al. (2006) investigated the effect of blocking this step by disrupting the function of *xdh* gene of *Candida tropicalis*. The synthesis of xylitol was substantially enhanced and the strain was able to utilize glycerol as a co-substrate. In another study, RNA interference (RNAi) approach was used to reduce the XDH by 48% in *Trichoderma reesei*, consequently, the xylitol yield was improved (Wang et al. 2005).

Among naturally xylose utilizing yeasts, *Candida parapsilosis* and *C. guilliermondii* were reported to produce 0.74 g g^{-1} xylose (Kwak et al. 2019; Nolleau et al. 1993). Overexpression of XR in *C. tropicalis* from *Neurospora crassa* improved xylitol yield equal to 0.96 g g^{-1} xylose under cultural conditions of xylose-glucose (Jeon et al. 2012). Oh et al. (2013) reported an engineered *S. cerevisiae* with nearly 100% theoretical yield (1.00 g of xylitol g^{-1} of xylose) and 15% higher production than consecutive utilization of glucose and xylose.

11.4 ϒ-Valerolactone

γ-Valerolactone or gamma-Valerolactone (GVL), a multi-faceted renewable platform chemical that can be procured from cellulosic or hemicellulosic components of renewable LC biomass (Melero et al. 2017). GVL is an effective sustainable liquid with many advantages such as biodegradability, non-toxicity, stability, and renewability. It can be used as a feasible carbon source for green solvents and it can also serve as a forerunner for the manufacture of transport fuels.

Xylose being the major monomer present in hydrolysates obtained from hemicellulose that can also be utilized to produce GVL. Currently a multistep strategy is implemented to obtain GVL from xylose. Initially, xylose is converted to furfural, the reaction is further accelerated by mineral or solid acid which is catalytically hydrogenated to furfuryl alcohol (FAL). This is followed by the alcoholysis of FAL to LA through cascade reactions. LA is finally hydrogenated to GVL (Melero et al. 2017; Tang et al. 2014).

Captivatingly, GVL itself is also an exceptional solvent and is capable of transforming biomass into chemicals and fuels. According to an investigation, 95% yield was obtained when GVL was used as a solvent for the manufacture of phosphatidylserine (an industrially important component in pharmaceutics and functional food) from biomass (Tang et al. 2014). Additionally, GVL has also been proven to be a preferable substitute than ethanol as a fuel additive because of its higher energy content and lesser vapor pressure (Melero et al. 2017).

11.5 Furfural

Furfural is a naturally occurring dehydration product of xylose achieved from hemicellulose fraction of LC biomass. It is considered as one of the most significant value-added platforms for fuel production and other useful chemicals (Wang et al. 2020). It is applied for various purposes such as for the synthesis of flavoring agents, adhesives, fungicides, inks, and antacids (Machado et al. 2016). It can also be used to produce numerous other chemicals including solvents to selectively extract aromatics from oil and diesel. Furfural is converted to another biodegradable platform chemical, Tetrahydrofurfuryl alcohol (THFA), by catalytic hydrogenation (Takata et al. 2014). Traditionally THFA can be produced by the two-step process (Hoydonckx et al. 2007; Nakagawa et al. 2013) where xylan is first hydrolyzed followed by cyclodehydration of xylose units (Machado et al. 2016).

12 Conclusion

LC biomass is rich in hemicelluloses in which xylan is the main component. Xylan can be converted into xylose through various chemical and biological methods. Xylose can subsequently be utilized for the production of biofuels and chemicals. Hence, substantial effort has been made to develop microorganisms capable of efficient bioconversion of xylose. Advanced genetic approaches have been employed to the industrial strains such as *S. cerevisiae*, for the improvement of xylose fermentation by introducing heterologous xylose transporter and catabolic genes to reconstruct artificial pathways. Bioethanol and value-added chemicals, including lactic acid, xylitol, GVL, and furfural are manufactured from xylose by recombinant microorganisms with significant improvement in the productions through metabolic engineering. Regardless of the successive genetic engineering, there are still some limitations in xylose bioconversion, such as repressive action by glucose, restrictions in co-fermentation of glucose and xylose, and lower product yield. Further progress is required in order to suppress glucose inhibition and to explore new xylose transporters.

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Bioconversion of Hemicelluloses into Hydrogen

Janak Raj Khatiwada, Sarita Shrestha, Hem Kanta Sharma, and Wensheng Qin

Abstract

Hydrogen is a promising alternative to fossil fuels because of its environment-friendly characteristics. It has been used widely in varied sectors such as chemical production, electronic devices, food industries, desulfurization of crude oil, and steel industries. Due to its increasing use and demand, it is essential to develop a cheaper and energy-efficient source of hydrogen production. This review synthesizes and discusses various aspects of hydrogen production methods and processes, the challenges, and economic perspective for sustainable production of biohydrogen. Compared to electrolysis, thermochemical and electrochemical processes, the biohydrogen production is environment friendly and energy efficient. Various factors such as feedstock, pH, temperature, partial pressure of hydrogen, and hydraulic retention time are responsible for the biological process and yield of biological hydrogen production. This review suggests that lignocellulosic biomass is commonly available, cheaper and eco-friendly source of hydrogen production.

Keywords

Hydrogen • Biomass • Pretreatments • Biohydrogen production • Limiting factors

1 Global Energy Demand

The global energy demand increased by 2.9% in 2018 and the annual global energy consumption was estimated at 13,864 million tons of oil equivalent (in 2018). Fossil fuels are regarded as the major drivers of the industrial revolution leading to economic and technological changes in the recent years. In the total energy consumption, fossil fuel alone accounted 85% including oil (34%), natural gas (24%), and coal (27%). Remaining 15% are used from other forms of energy such as nuclear energy (4%), hydroelectricity (7%), and renewable resources (4%) (BP 2019). The high consumption of fossil fuel in recent decades is considered as a major factor for global warming. Also, the recent consumption trend indicates further growth in the increment of greenhouse gas emissions in future. In this context, overcoming the recent energy demand by lowering the emission of greenhouse gas has become a great challenge.

Several researches are ongoing worldwide to discover cheaper, eco-friendly, and alternative renewable energy sources which can minimize the world's carbon footprint. Recent studies revealed that alternative and renewable energy resources could be a better solution for sustainable energy production and energy security in the future because they mitigate greenhouse gas emission (Sharif et al. 2019). Renewable and alternative energy resources are easily available as compared to other energy sources and are derived from solar, hydropower, geothermal, wind, ocean resources, and solid biomass, and others (Ellabban et al. 2014). Compared to other sources of renewable energies, the conversion of biomass for energy production is one of the cheapest and promising alternatives. Moreover, the biomass is readily and widely available and is cheap in terms of investment costs and feasible technology (Macqueen and Korhaliller 2011).

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Large quantity of bio-wastes is produced from different sources including forestry, agriculture, industries, and household solid waste in the world. These biomasses are considered as waste materials particularly in the developing countries and creating several environmental issues (Chen et al. 2017; Worden et al. 2017). However, recent researches have indicated that they can be used as the energy sources to contribute in the global energy production such as bioethanol, biohydrogen, methane, and other value-added products (Limayem and Ricke 2012; Xu et al. 2019; Keskin et al. 2019). Therefore, this review provides recent progress and findings on biohydrogen production from lignocellulosic biomass with a special focus on hemicellulose and discusses the techno-economic bottleneck involved in hydrogen production from plant biomass.

1.1 Classification of Energy Sources

1.1.1 Biomass and Biofuels

Biomass originates from biological materials (plants or animals) that can be used in energy production. Lignocellulosic biomass is a reliable source of energy since the early age of human civilization. Fire is the major energy source from biomass and provides thermal energy to keep warm and be used for cooking food. There are several ways to produce energy from biomass, for example, burning biomass to produce heat in thermal plants (to run the steam engine and generate electricity), and turning feedstocks into liquid biofuels (ethanol) or biogas (hydrogen, oxygen, or methane) (Giampietro et al. 1997). Biofuels are fuel(s) either solid, liquid, or gaseous produced directly or indirectly from biomass (FAO 2004; Lee and Lavoie 2013). Biofuels are grouped as first, second, and third-generation biofuels based on the feedstock used and their technological innovation (Lee and Lavoie 2013).

1.1.2 First-Generation Biofuels

First-generation biofuels are derived from edible food like corn, sugar, and vegetable oil (Aro 2016). Bioethanol is a major by-product produced from the fermentation of edible crops like corn and sugars. Other feedstocks are widely used to produce first-generation bioethanol including barley, potato, sugar-beets, and sugarcane. The first-generation biofuels can blend with petroleum-based fuels and potential improvement on exhaust emissions (Mancaruso et al. 2011). Though the first-generation biofuels have significant positive impacts on environmental pollution and carbon emission, it is not a sustainable energy production because food security versus fuels is its major challenge. Still, it is claimed that biodiesel is not a cost-efficient emission reduction technology. Therefore, more cost-efficient alternative technologies are recommended.

1.1.3 Second-Generation Biofuels

Second-generation biofuels are derived from lignocellulosic biomass such as crop and forest residues, and municipal solid wastes (Begum and Dahman 2015). These biofuels are more sustainable because they are cheap and produced from abundant non-food plant materials. However, their production methods are still quite expensive and have several technical barriers during the bioconversion processes (Mancaruso et al. 2011).

1.1.4 Third-Generation Biofuels

Third-generation biofuels are produced by using algal biomass to manufacture diesel and gasoline (Neto et al. 2019). The microalgae (examples: *Nannochloropsis granulate*, *Spirulina maxima*) can provide different types of renewable biofuel like methane, biodiesel, gasoline, biohydrogen, and jet fuel. Thus, algae can provide a promising source of future fuel and other valuable products (Chowdhury et al. 2019).

2 Lignocellulosic Biomass

Lignocellulosic biomass is the most abundant plant material and is inexpensive, eco-friendly, and abundant renewable resource. It can be used in biofuels, chemicals, and polymer production (Li et al. 2007). There are three major components of lignocellulosic biomass: cellulose (40–60%), hemicellulose (20–40%), and lignin (10–24%) (Sharma et al. 2019). However, the composition of these three primary components varies based on plant type, age, cultivation, and climate conditions.

2.1 Cellulose

Cellulose is the most abundant and major structural component of the plant cell wall (Fig. 1). It is an organized fibrous structure consisting of D-glucose subunits connected by β-1,4 glycosidic bonds (Fengel and Wegener 1989; Pérez et al. 2002). This linkage in carbohydrate or polysaccharide makes cellulose as a straight chain polymer (also called as cellulose microfibrils) (Pérez et al. 2002). The microfibril structure of cellulose is composed of alternating crystalline and amorphous regions (Fengel and Wegener 1989; Nanda et al. 2014). The amorphous form of cellulose is susceptible to enzymatic decomposition (Kumar et al. 2009).

2.2 Hemicellulose

It is the second most abundant polysaccharide found in plant biomass (Fig. 1). Hemicellulose is composed of short lateral

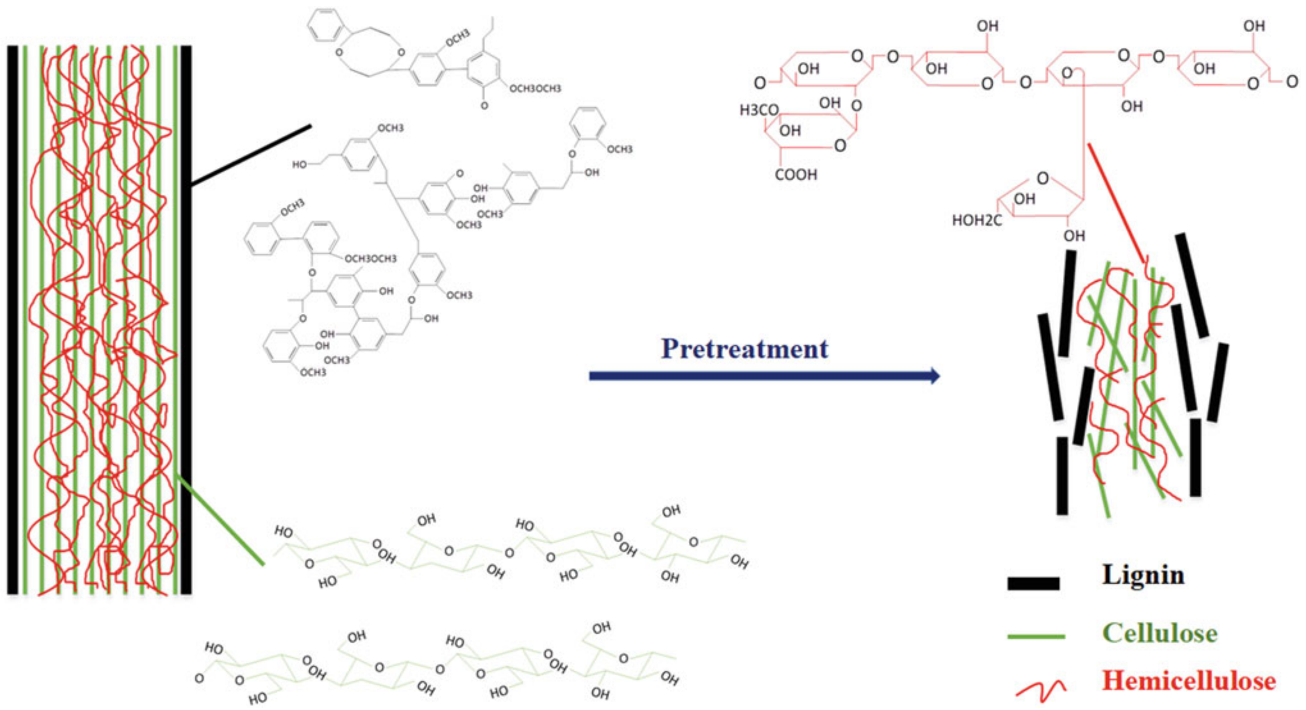

Fig. 1 Diagrammatic representation of the lignocellulosic biomass and the role of pretreatment in the bioconversion

chains of different hexose and pentose sugars (such as xylose, mannose, galactose, rhamnose, and arabinose) and uronic acids (Lin et al. 2015). Glucuronoxylan and glucomannan are the principal components of hardwood and softwood hemicellulose, respectively (Pérez et al. 2002).

2.3 Lignin

Lignin is a complex, branched phenolic polymer containing three phenylpropanolic monomers linked by carbon-carbon and aryl-ether bonds (Lu et al. 2017; Upton and Kasko 2016). Lignin accounts for 30% of total organic carbon found on Earth (Upton and Kasko 2016). It is an aromatic natural polymer found in all terrestrial and some of the aquatic plants (Guragain et al. 2015). It acts as a potentially renewable resource for energy and aromatic chemical production. The lignin provides structural support, impermeability, transport water and nutrients, and protection against chemical and pathogen attack (Polo et al. 2020; Bonawitz and Chapple 2010).

3 Bioconversion of Lignocellulosic Biomass

Each year several tons of lignocellulosic wastes are produced from different sources including forestry and agricultural biomass, paper and food industries, and municipal solid waste (Limayem and Ricke 2012; Dashtban et al. 2009). Even today, these biomasses are considered as waste materials in developing countries which are creating several environmental issues (Chen et al. 2017; Worden et al. 2017). However, recent data suggested that lignocellulosic biomasses can be successfully converted into biofuels (Putro et al. 2016). The global bioethanol production has dramatically increased since 2000 and reached up to 72.06 Billion Gallons per year in 2017 (EIA 2020) (Fig. 2). More than 84% of the global ethanol fuel production (22.86 out of 27.06 Billions of

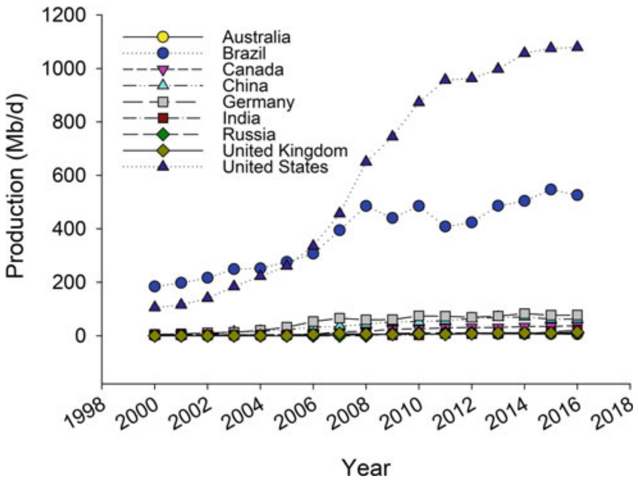

Fig. 2 Biofuel production by countries from 2000 to 2017 (*Data source* EIA (2020))

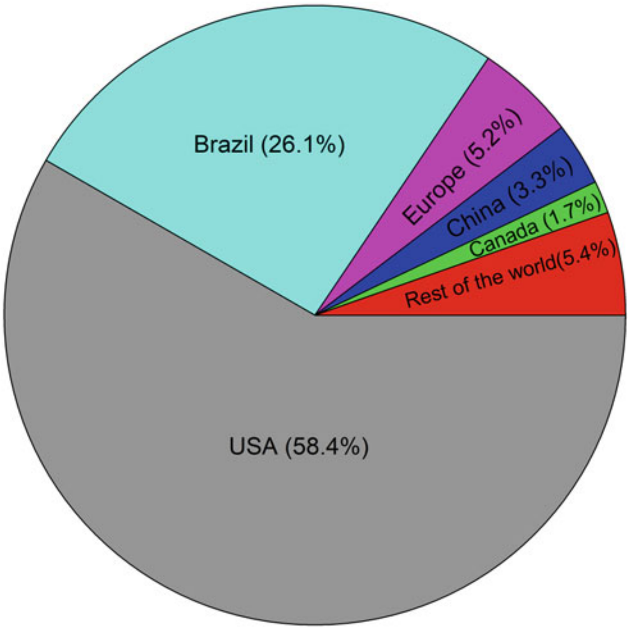

Fig. 3 Biofuel production by countries in the year 2017 (*Data source* EIA (2020))

Gallons) was concentrated in two countries, USA (15.8) and Brazil (7.06) in 2017 (EIA 2020) (Fig. 3).

4 Pretreatment

The lignocellulosic biomass has a property to resist against chemicals and biological degradation (Polo et al. 2020). The structural complexity of the plant cell wall hinders the pretreatment process (Fig. 1) (Jeoh et al. 2017). Pretreatment of biomass is an essential tool in the bioconversion processes in which the structure of cellulosic biomass is converted to be more accessible for enzymatic and microbial digestion (Galbe and Zacchi 2012; Zheng et al. 2014). In this process, the complex structure of carbohydrate polymers is converted into fermentable sugars. Several studies have been carried out for the enhancement of the digestibility process of lignocellulosic biomass for the efficient conversion of biopolymers to biofuel (ethanol, methane and, hydrogen) and other products (Sharma et al. 2019; Koupaie et al. 2019). The major goal of pretreatment is to disintegrate the lignocellulosic biomass into its three major components; cellulose, hemicellulose, and lignin. Broadly the pretreatment methods can be divided into physical, chemical, physico-chemical, and biological methods or their combinations (Table 1) (Xu et al. 2019; Sindhu et al. 2016).

5 Hydrogen as a Promising Source of Energy

Hydrogen is considered as a promising alternative source of energy. It can be generated from natural and bioresources (Jiang et al. 2019). It is a colorless, odorless, tasteless, and highly abundant gas. Hydrogen is a clean and non-toxic renewable energy (Hosseini and Wahid 2016). There has been increasing demand for hydrogen in different sectors, for example, in the production of chemicals, electronic devices, food industries, desulfurization of crude oil in oil refineries, and steel industries (Glenk and Reichelstein 2019; Nicita et al. 2020). It is reported that about 95% of current hydrogen production is based on fossil fuel (IRENA 2018; Thomas et al. 2018). The most common ways of hydrogen production are steam-methane reforming, non-catalytic partial oxidation of fossil fuels, hybrid form, and electrolysis (chlor-alkali) processes (Muradov 2017). However, these methods are highly cost-inefficient, requiring sophisticated technology for storage and distribution. Therefore, researchers are struggling to find the renewable and environmentally friendly sources of hydrogen production. Consequently, they have successfully uncovered the bioconversion process of lignocellulosic biomass (Xu 2007) and solid wastes (Lay et al. 1999) into hydrogen in the recent decades. In the initial stage of the conversion process, plant biomass and organic wastes are converted into methane by the application of chemical reactions and bacteria. Then organic matters are hydrolyzed and fermented into fatty acids, which are then converted into acetate and hydrogen.

Bioconversion of lignocellulosic biomass into hydrogen has several positive impacts in sustainable energy production, global energy use, and maintaining a sustainable environment. Following significant advantages of producing hydrogen as an energy resource can be highlighted:

- Hydrogen is clean and produces water vapor after combustion (Stern 2018).
- The combustion of hydrogen is about 50% more efficient than gasoline (Kim et al. 2018).
- Hydrogen gas has a higher energy yield (122 kJ/g) compared to other hydrocarbon fuels (Kapdan and Kargi 2006).
- Hydrogen battery can be used as future power for automobiles (T-Raissi and Block 2004).
- Hydrogen gas can be easily stored as a metal hydride such as magnesium hydride, sodium aluminum hydride, lithium aluminum hydride, palladium hydride, etc. (Jain 2009).

Table 1 Comparison of pretreatment methods of lignocellulosic biomass

Pretreatment	Functions	References
Physical pretreatment		
Milling	Breaks down the structure of lignocellulosic biomass, size reduction, decrease crystallinity of cellulose	Bai et al. (2018)
Pyrolysis	Decomposition of cellulose into H_2, CO, and other carbon residues at high temperatures (>300 °C)	Al Arni (2018)
Microwave	Breakdown of lignocellulose and increase the enzymatic process	Liu et al. (2018)
Extrusion	Disruptions of lignocellulose in high temperature (>300 °C)	Wahid et al. (2015)
Ultrasonication	Breakdown of the lignin layer and disrupt the amorphous cell	He et al. (2017)
Chemical pretreatment		
Acid	Breakdown lignin and other polymers under high temperature	Lloyd and Wyman (2005)
Alkali	Breakdown lignin and other polymers under high temperature	Sun et al. (2016)
Ionic liquids	Cations and anions help to solubilize the cellulose and lignin	Swatloski et al. (2002)
Organosolv	Separation of cellulose by dissolving most lignin and hemicellulose with or without addition of a catalyst	Yu et al. (2018)
Deep eutectic Solvents	Solubilize polysaccharides, accelerate cellulose extraction, nanofibrillation or nanocrystalization	Zdanowicz et al. (2018)
Physicochemical pretreatments		
Steam explosion	Hemicellulose degradation by the application of heat in the form of pressurized steam	Chen and Liu (2015)
CO_2 explosion	Disruption of hemicellulose and lignin, enhance enzymatic hydrolysis	Morais et al. (2015)
Liquid hot water	Hydrolyzes hemicellulose and breakdown of lignin at high water temperature and pressure	Zhuang et al. (2016)
Biological pretreatments		
Whole cell	Breakdown of lignin	Hammel and Cullen (2008)
Enzymatic pretreatment	Enzymatic degradation of lignin	Zámocký et al. (2014)

5.1 Thermochemical Routes for Hydrogen Production from Biomass

Broadly, there are two ways of hydrogen production from lignocellulosic biomass: they are thermochemical and biochemical methods (Fig. 4). Biochemical methods require starch or sugar enriched feedstock whereas various ranges of lignocellulosic biomass can be utilized in thermochemical methods (Basu 2013). Moreover, thermochemical methods are much energy and cost-efficient and faster compared to biochemical routes. Thermochemical process uses heat from various resources, such as natural gas, coal, or biomass to convert the lignocellulosic biomass into hydrogen. There are three types of thermochemical processes (1) Pyrolysis, (2) Liquefaction, and (3) Gasification. Three methods, feedstock used, condition, product yield, major advantages, and disadvantages are summarized in Table 2.

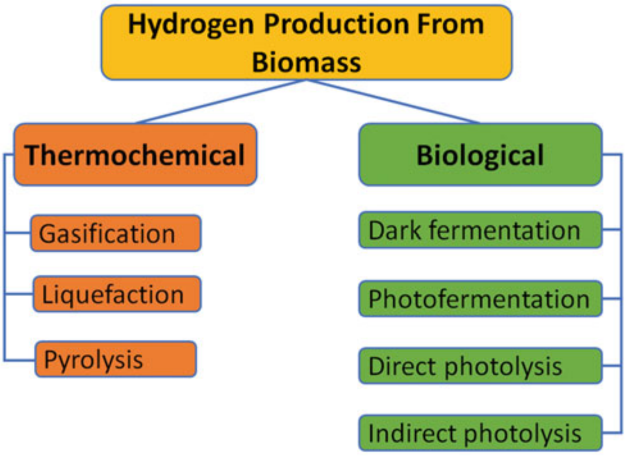

Fig. 4 Methods of hydrogen production from biomass

Table 2 Summary of pretreatments of biomass via pyrolysis and gasification

Method	Feedstock	Process condition	H_2 yield	Major advantages	Major disadvantage	References
Fast pyrolysis	Forest pinewood waste	500–600 °C	117 g per kg of biomass	Simple process	Lower yield of biofuel	Arregi et al. (2016)
Flash pyrolysis	Rice husk and sawdust	800 and 900 °C	0.267 Nm^3/kg	Easy handling process	Less economic	Sun et al. (2010)
Slow pyrolysis	Cellulose fibers and lignin	600 °C	Xylan—0.30%, Cellulose—0.08%, Lignin—0.33% of biomass	Low-value energy product	Not profitable	Giudicianni et al. (2013)
Air gasification	Pine sawdust	870 °C	High temperature favored higher H_2 production	Low-value energy product	Lower yield of hydrogen	Lv et al. (2007)
Air and oxygen/steam gasification	Pine wood blocks	886 °C	30.51% of total gas produced	Higher yield in low energy consumption		Lv et al. (2007)
Supercritical water gasification	Sawdust and municipal solid waste	375 °C and 22 MPa	0.12% of total biomass	Simple process	High processing costs	Castello et al. (2017)

5.1.1 Pyrolysis

Pyrolysis is the conversion of biomass or any carbonaceous feedstocks in anaerobic condition to produce charcoal, bio-oil, and biogas at a pressure of 0.1–0.5 MPa and a temperature of 500–900 °C (Ni et al. 2006; Bičáková and Straka 2012). The major purpose of the pyrolysis is to break down the polymeric molecules into shorter molecular weight compounds. Biomass pyrolysis is categorized into conventional (slow), vacuum, fast, and flash pyrolysis. The major differences between slow and fast pyrolysis are the heating rates (time) and maximum reaction temperatures (Al 2018). The differences in time and temperature significantly affect production of biofuels and other products. Slow pyrolysis produces primarily gas while fast pyrolysis generates biofuel (Brown et al. 2011; Demirbas 2016). Therefore, fast pyrolysis is cost, time, and energy efficient in the conversion of biomass. Pyrolytic decomposition of biomass can be illustrated by the following equation (Eq. 1) (Demirbas 2016):

$$\text{Biomass} + \text{Energy} \rightarrow H_2 + CO + CO_2 + \text{HC gases} + \text{Tar} + \text{Char} \tag{1}$$

i. Fast pyrolysis

The biomass feedstock is heated rapidly in anoxic condition. There are three main products of fast pyrolysis: bio-oil, gas, and char. Tar (47.13%) is the major product of fast pyrolysis followed by char (28.33%), losses (13.21%), and gases (11.33%) respectively at 653 K (Al 2018). The major gases include H_2, CH_4, CO, CO_2, and other depending on the feedstocks used for pyrolysis (Demirbas 2016).

ii. Slow pyrolysis

It is the conventional form of pyrolysis in which the production of charcoal or char is the major by-product. The plant biomass is heated slowly in an anaerobic condition to a relatively low temperature (about 400 °C) over an extended period (Basu 2013). According to Al Arni (2018) char (37.64%) is the major product of slow pyrolysis followed by tar (26.11%), gas (25.10%), and losses (11.15%) at 753 K.

iii. Flash pyrolysis

Flash pyrolysis is also called very fast pyrolysis. In this process biomass is rapidly heated (above 1000 °C/s) in an anoxic condition. The main product of the flash pyrolysis is biofuel (about 70–75% of biomass) with 15–25% of biochar residues (Basu 2013).

5.1.2 Gasification

In comparison to the pyrolysis processes, the gasification process aims to maximize the conversion of a solid biomass into usable gases. The gasification process converts organic biomass into hydrogen and other products without combustion. In this process, biomass is heated at high temperatures (>700 °C) provided with a regulated amount of oxygen and steam. This process produces carbon monoxide (CO), hydrogen (H_2), and carbon dioxide (CO_2) (Eq. 2) (Balat and Kırtay 2010). Biomass gasification takes place in a complex chain of chemical reactions. Usually, this process is completed through the following stages: drying, pyrolysis, char, and tar gasification. Different types of biomass materials such as waste wood, sawdust, and agricultural waste can be used to produce hydrogen via gasification (Basu 2013).

$$C_6H_{12}O_6 + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + \text{other} \tag{2}$$

5.1.3 Liquefaction

Liquefaction (hydrothermal liquefaction) is a process of conversion of lignocellulosic biomass into bio-liquid at a temperature of 280–370 °C and pressure of 10–25 MPa in the absence of oxygen (Gollakota et al. 2018). The major goal of this process is to break down the solid biopolymeric structure into liquid components (Elliott et al. 2015). During the conversion process many complex reactions take place and convert biomass into crude oil-like products (Behrendt et al. 2008). There are major two types of process mechanism based on the nature of feedstock namely dry feedstock (lignocellulose biomass) and wet feedstock (algal biomass) (Elliott et al. 2015). Lower hydrogen yield is the major limitation of this method.

5.2 Biological Routes for Hydrogen Production

There has been growing interest in bioconversion of waste products and biomass to produce biofuels and biohydrogen. Biohydrogen production is considered as an eco-friendly and inexhaustible process than electrolysis, thermochemical, and electrochemical processes (Kırtay 2011). In biological processes the feedstocks are catalyzed by microorganisms under atmospheric pressure and at an ambient temperature. Biohydrogen production methods are broadly categorized as light-dependent and light-independent processes (Ding et al. 2016). Light-dependent processes can be further classified into direct biophotolysis, indirect biophotolysis, and photo-fermentation. Light-independent processes are also called dark fermentation (Table 3).

5.2.1 Direct Biophotolysis

Biohydrogen production through biophotolysis is carried out by photosynthetic organisms such as microalgae and cyanobacteria (Eq. 3) (Eroglu and Melis 2011). In this process, autotrophs decompose water into hydrogen and oxygen in the presence of sunlight.

$$2H_2O \ \text{Sun light} \rightarrow 2H_2 + O_2 \tag{3}$$

Table 3 Review of biological hydrogen process and its prospects

Methods	Organisms	H_2 production	Advantages	Disadvantages	References
Direct biophotolysis	Cyanobacteria and algae	1.1 mmol/l-h	•H_2 production from hydrolysis •Lignocellulosic biomass as substrate Easy to operate	•Low H_2 production rate •Extremely light dependent •Low conversion efficiency from light Product contains CO_2 or O_2	Sun et al. (2019), Tamburic et al. (2011)
Indirect biophotolysis	Cyanobacteria	0.0114 kg H_2/kg biomass	•H_2 production from water and sunlight •Lignocellulosic biomass as substrate •Easy to operate	•Low photochemical efficiency •O_2 is inhibitory to nitrogenase	Sveshnikov et al. (1997), Hallenbeck and Benemann (2002)
Photo-fermentation	Photosynthetic bacteria	2.41 mol H_2/mol glucose	•Sunlight as source of energy •Lignocellulosic biomass as substrate	•Highly light dependent •Low H_2 production	Toledo-Alarcón et al. (2018), Ghirardi et al. (2000)
Dark fermentation	Obligate or facultative anaerobic fermentative bacteria	32 mmol/Lglucose	•H_2 can be produced without light •Wide spectrum waste can be used	•Low H_2 yield •Large production of by-product gases	Li and Fang (2007), Ghirardi et al. (2000)

The hydrolysis is carried out into two different photosynthesis stages: photosystem I (PSI) and photosystem II (PSII). In photosystem I (PSI), production of the reductant of CO_2 taken place whereas in photosystem II (PSII) split water into H_2 and O_2 (Bolatkhan et al. 2019). In direct photolysis, various green algae (such as *Chlamydomonas reinhardtii*, *Chlorococcumlittorale*, *Chlorella fusca*, *Platymonassubcordiformis*, *Scenedesmus obliquus*etc.) (Fan et al. 2016; Guan et al. 2004) and cyanobacteria (*Anabaena cylindrical, Oscillatoria brevis*, *Nostocmuscorum,* etc.) are widely used for hydrogen production (Das and Veziroglu 2008; Dutta et al. 2005).

Water is used as the primary feedstock in the direct biophotolysis method which is inexpensive and available everywhere. On the other side, hydrogen production is prohibited by the suppressive effect of oxygen as a by-product of photosynthesis and enzymatic catalysis which is the major drawback of this method (Table 3) (Sun et al. 2019). Moreover, this process yields less hydrogen and cost-inefficient in the industrial-scale production (Sakurai and Masukawa 2007).

5.2.2 Indirect Biophotolysis

Indirect biophotolysis is carried out in two steps: photosynthesis and fermentation. Firstly, the synthesis of carbohydrates takes place under the light (Eq. 4). Secondly, the hydrogen is produced from carbohydrates via anaerobic dark fermentation (Eq. 5) (Hallenbeck and Benemann 2002; Kossalbayev et al. 2020).

$$6H_2O + 6CO_2 \text{ Sun light} \rightarrow C_6H_{12}O_6 + 6O_2 \qquad (4)$$

$$C_6H_{12}O_6 + 12H_2O \text{ Sun light} \rightarrow 12H_{12} + 6CO_2 \qquad (5)$$

Cyanobacteria play a major role in the production of hydrogen in indirect biophotolysis processes. It possesses major enzymes such as nitrogenase and hydrogenase which helped in metabolic functions for the hydrogen (Hallenbeck and Benemann 2002; Kossalbayev et al. 2020).

5.2.3 Photo-Fermentation

In this process, lignocellulosic feedstocks are decomposed into hydrogen and carbon dioxide by using photosynthetic microorganisms such as *Rhodobacter* sp. in the presence of sunlight and organic acids. Photo-fermentation occurs under oxygen deficient condition with the optimal temperature of 30–35 °C and pH 7.0 (Eq. 6) (Argun and Kargi 2011). In this process wide range of organic wastes such as fruits and vegetable wastes or other lignocellulosic wastes can be used as substrate for the production of biohydrogen (Özgür et al. 2010; Fascetti and Todini 1995).

$$CH_3COOH + 2H_2O \text{ Sun light} \rightarrow 4H_2 + 2CO_2 \qquad (6)$$

5.2.4 Dark Fermentation

Dark fermentation is environmentally friendly and widely used method for biohydrogen production from organic feedstocks. This process is undertaken in a dark and anaerobic environment in which anaerobic bacteria convert carbohydrate-rich substrates into hydrogen (Toledo-Alarcón et al. 2018). This process is carried out by different groups of bacteria such as *Enteric* and *Clostridia* sp. (Khanna and Das 2013). In the dark fermentation, the first step is the glycolysis process in which glucose is fermented to pyruvate. Then, under the anaerobic environment, pyruvate is oxidized to acetyl-CoA, $CO_{2,}$ and H_2 (Li and Fang 2007). Compared to other biological production methods, dark fermentation process is cost-effective, higher hydrogen production rate, and faster conversion efficiencies. This process can utilize a wide range of organic feedstocks including municipal wastes, agriculture, and forest residues (Ghimire et al. 2015).

6 Metabolic Pathway of Hydrogen Production

Hydrogen can be produced via biophotolysis, photo-fermentation, and dark fermentation (Ding et al. 2016). Although biophotolysis by green microalgae and cyanobacteria is a highly desirable process, the photochemical efficiency is low due to oxygen inhibition on hydrogenase (Oh et al. 2013). Microbial fermentation (including dark fermentation and photo-fermentation) could be one of the potential alternatives to produce biohydrogen. However, except for the glucose, lignocellulosic biomass has not been studied extensively for the hydrogen production due to structural complexity of plant biomass. Usually, a pretreatment of lignocellulosic biomass is an essential step before hydrolysis to convert a complex biopolymer into fermentable sugars (glucose and xylose). Hydrolysis of cellulosic biomass is catalyzed by synergistic effect of cellulase-endoglucanase, cellobiohydrolase, and β-glucosidase to form glucose, whereas the hemicellulosic components are catalyzed by hemicellulolytic enzymes such as endo-xylanase, exo-xylanase, and β-xylosidase to form xylose (Sharma et al. 2019). These sugars can be utilized further in hydrogen production. However, the hydrolysis of lignocellulosic biomass often produces some inhibitory compounds such as phenolic and other aromatic compounds, levulinic acid, aliphatic acids, and furan aldehydes, etc. which inhibit the microbial growth and hinder the downstream processing of bioproducts (Jönsson et al. 2013; Jönsson and Martín 2016). Thus, a direct bioconversion (without pretreatment) of cellulosic and hemicellulosic biomass for hydrogen production is gaining popularity due to its environmental and economic benefit. Some thermophilic

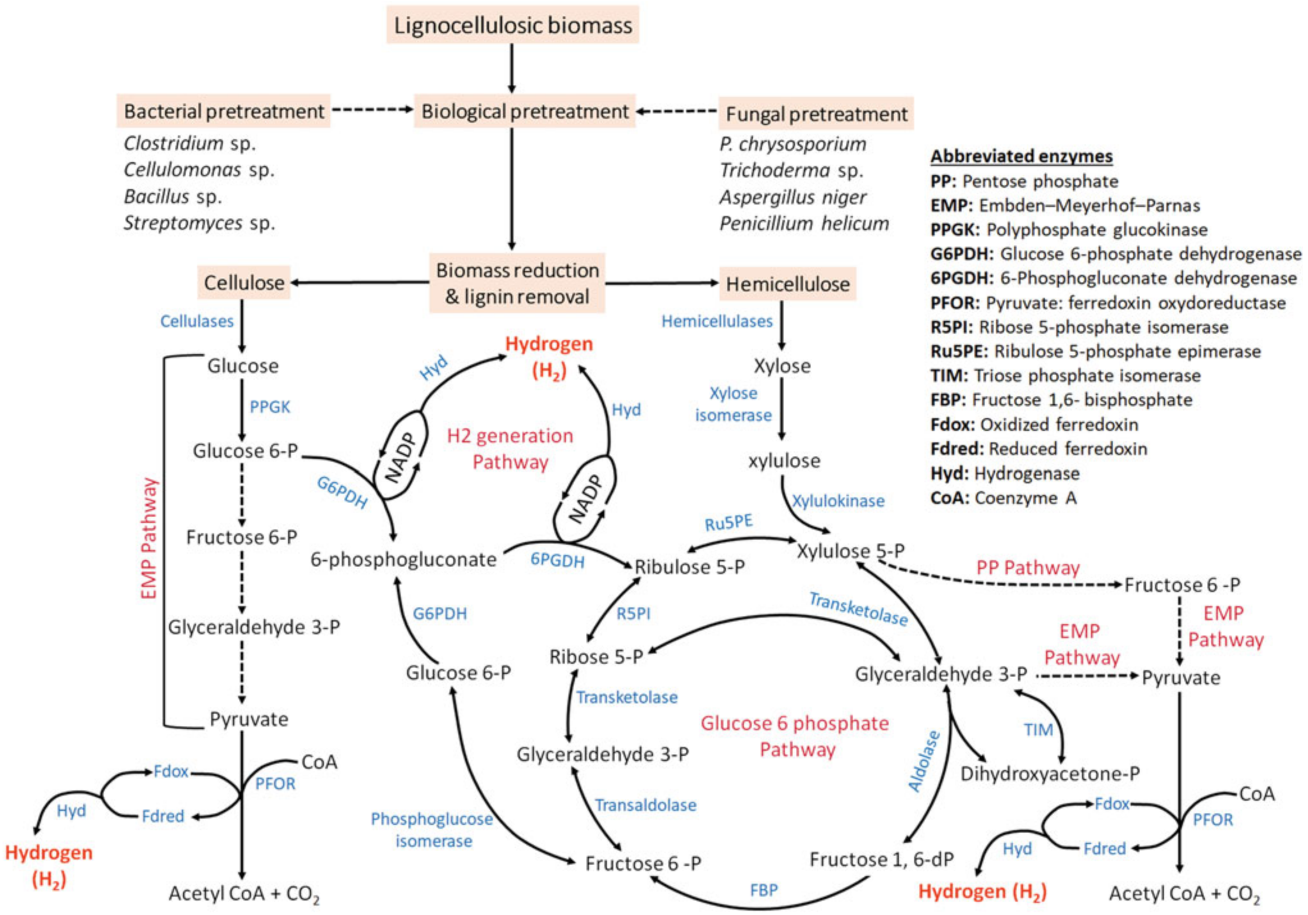

Fig. 5 Major metabolic pathways of hydrogen biosynthesis from lignocellulosic biomass (adopted and modified from Rollin et al. (2015)). The enzymes and pathways are in blue and red-colored text, respectively. The dashed arrows indicate the multi-steps metabolic pathway. Few representative bacteria, fungi, and abbreviated enzymes are included in the figure legend

bacteria including *Clostridium* sp., *Caldicellulosiruptor saccharolyticus, Thermoanaerobacterium* sp., *Thermotoga-maritima* sp. *Pyrococcusfuriosus* sp., etc. can produce hydrogen directly from various plant polymers (Cao et al. 2014; Ren et al. 2008; Willquist et al. 2011; Verhaart et al. 2010). When grown in polymeric biomass, these bacteria utilize various hydrolytic enzymes and hydrogenases for hydrogen production (Oh et al. 2013). Based on the literature reviewed (Rollin et al. 2015; Reginatto and Antônio 2015; Yu and Takahashi 2007), we reconstruct the potential metabolic pathways for hydrogen production (Fig. 5). Reginatto and Antônio (2015) outlined the hydrogen production through fermentation pathways using *Escherichia coli* and *Enterobacteriaceae* and several enzymes via Embden–Meyerhof–Parnas (EMP) pathway to form pyruvate. The pyruvate is further catalyzed by ferredoxin oxydoreductase and converted into acetyl-CoA and then to acetate with the release of hydrogen and carbon dioxide under anaerobic conditions. The enzyme hydrogenase plays a key role at the final stage of hydrogen production. Rollin et al. (2015) proposed another hydrogen generation pathway from lignocellulosic biomass in which bioconversion cellulosic and hemicellulosic biomasses in hydrogen production are resulted in formation of monomeric sugars—glucose and xylose produced after hydrolysis of plant biomass. These sugars are subjected to phosphorylation by the action of polyphosphate. The nicotinamide adenine dinucleotide phosphate (NADPH) is further catalyzed by dehydrogenases and hydrogenase to produced hydrogen. Here the nonoxidative pentose phosphate pathway and partial glycolysis pathways recycle the ribulose, 5-xylulose, and 5-phosphates to glucose 6-phosphates that ultimately used in the production of hydrogen (Rollin et al. 2015).

7 Factors Affecting Hydrogen Production in Dark Fermentation

7.1 Feedstock

Organic feedstocks play a major role in the production of biohydrogen from dark fermentation methods. Glucose and sucrose rich feedstock are model substrates for biohydrogen production (Ghimire et al. 2015). Still, complex substrates such as municipal solid waste, forestry and agricultural biomasses (such as dead wood, corn stalks, wheat straw, and rice straw) and wastages from food processing industries (e.g., cheese whey, oil mills, and animals dungs) have been widely used in dark fermentation process to produce hydrogen (Keskin et al. 2019; Kargi et al. 2012; Mohammadi et al. 2011; Chen et al. 2012).

7.2 pH

pH is a major factor that regulates the enzymatic functions thereby affecting the metabolic pathway of organisms to produce hydrogen (Ghimire et al. 2015). In the dark fermentation process, several facultative organisms have been used to produce hydrogen via glycolysis (Tao et al. 2007). This enzymatic pathway of the hydrogen production is highly sensitive to the pH. Tao et al. (2007) reported that maximum hydrogen yield at medium pH level (pH = 6). Thus, pH level significantly affects the hydrogenase enzyme activity. If the medium concentration becomes acidic, pH level gets reduced which directly shifts enzymatic metabolism towards the conversion of acid into alcohol. At the lower pH level, hydrogen yield decreases sharply due to the production of acidic metabolites such as carboxylic acid, acetic acid, and formic acid. Similarly, Zagrodnik and Laniecki (2015) reported the reduction of the production of H_2 with increasing pH level.

7.3 Temperature

Temperature regulates the bacterial growth, rate of biohydrogen production, and microbial metabolisms in anaerobic fermentation processes. The selection of optimal temperature and organisms used for the fermentation process depends on feedstock types. Due to the complexities of the lignocellulosic biomass, there is considerable variation in operating temperature. Thus, optimal temperature selection is important based on bacteria/organisms used during fermentation. Organisms (anaerobic bacteria) that have been used for dark fermentation are classified into different groups (such as psychrophiles, mesophiles, thermophiles, extreme thermophiles, and hyperthermophiles) based on the optimal temperature in which particular organism perform higher microbial activities and also accelerate the bioconversion rate of feedstocks (Levin et al. 2004; Alvarado-Cuevas et al. 2015; Boileau et al. 2016). Among them, mesophilic condition (temperature range: 25–45 °C, e.g. *Clostridium saccharobutylicum*) is the most favorable temperature range for the fermentative biohydrogen production (Li and Fang 2007). In contrast, thermophilic (45–65 °C) and extreme-thermophilic (65–80 °C) bacteria can perform effectively during fermentation of the diversified feedstock such as buffalo manure, cheese whey, and sludge (Ghimire et al. 2015; Verhaart et al. 2010; Pakarinen et al. 2008). However, biohydrogen production from extreme-thermophilic conditions requires higher energy input (Hallenbeck 2005).

7.4 Hydrogen Partial Pressure (HPP)

HPP is a pressure created by hydrogen gas inside the reactor system (Hawkes et al. 2007). When hydrogen started to accumulate inside the reactor, the partial pressure of hydrogen increases and subsequently decreases the production of hydrogen. Consequently, metabolic pathway of hydrogen production shifts and starts to the accumulated other byproducts such as ethanol, acetone, and lactic acid, (Ghimire et al. 2015; Hawkes et al. 2007). Lee et al. (2012) reported that reduction of the partial pressure during the hydrogen metabolism in dark fermentation increases the production of H_2.

7.5 Hydraulic Retention Time

Hydraulic retention time (or fermentation time or hydraulic loading) is the average number of time (days) that a feedstock remains in a storage unit (digester/bioreactor). Hydraulic retention time is calculated by dividing bioreactor volume (gallons) by the feed volume (gal/day) (Kim et al. 2013). Higher hydrogen production is highly correlated with shorter retention time (Zhang et al. 2013).

8 Conclusion

Lignocellulosic biomass has been extensively used for biohydrogen production. It consists of biopolymer components such as cellulose, hemicellulose, and lignin. Glucose and xylose are the final products after the appropriate pretreatment of hemicellulose or lignocellulosic biomass. Different pretreatment methods, for example, physical, chemical, and biological have been employed to convert the complex structure of carbohydrate polymers into fermentable sugars. Biological pretreatments of lignocellulosic feedstock are the most desirable methods compared to conventional pretreatment methods which are cost-inefficient and produce undesirable inhibitors. Among the different methods of hydrogen production, the biological route is cheaper and eco-friendly. Biological hydrogen production process is highly affected by several factors such as feedstock, pH, temperature, the partial pressure of hydrogen, and hydraulic retention time. Further improvement in genetic engineering and biotechnologies are needed for more efficient and cost-effective biological pretreatment and low-cost conversion of hemicellulose into hydrogen and other value-added products.

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Bioconversion of Food Waste into Bioplastics

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Abstract

Food waste is defined as a significant loss in natural resources, such as losses in land, water, energy, and labor. World government agencies have declared that Brazil significantly contributes to food waste. The main causes of food waste are a lack of qualification and preparation for the harvest, inadequate producer knowledge, improper transport and storage conditions, climate changes, improperly installed supply centers, and consumer's waste. Food waste can be minimized by valorization of these residues through value-added products. For example, the waste of these resources can be reduced through their bioconversion into bioplastics. Thus, several processes used to transform food waste, e.g., soybeans residues, rice and cassava husks (starch), natural fibers (cellulose), and shrimp husks (chitin/chitosan) into biodegradable plastics are presented, which focus on various technologies, different compositions, physicochemical and biological properties, and thermal and mechanical behaviors from the biofilms produced, and their potential applications. The use of these feedstocks for bioplastic generation is currently a challenge for food waste valorization by these companies, and it can provide modern society with an ecofriendly, sustainable, and renewable biomaterial.

Keywords

Applications • Composition • Feedstocks • Packaging • Properties • Structures

1 Introduction

Plastic is the result of an organic synthesis process that utilizes fossil sources. Due to its particular properties, it is the most consumed material in the world, with over 300 million metric tons of plastics produced annually worldwide (Walker and Rothman 2020; Singh and Sharma 2016). However, its prolonged degradation rate is of great environmental concern. In addition, petrochemical resources are limited, and oil exploration and production have harmful impacts on air, soil, surface water, groundwater, and several ecosystems (Tsang et al. 2019).

An alternative sustainable to using petrochemicals for synthetic polymers is bioplastics production (Rieger et al. 2012). Bioplastics are a generalized term for polymeric materials with a biomass source (Rudin and Choi 2013). However, it is not simply a designation for biodegradable materials or compostable plastics. Thus, for these materials certain properties can be expected, such as durability, conformability, flexibility, transparency, mechanical resistance, and acting as a gas barrier (Araújo et al. 2018). Consequently, plastic derivatives obtained from biomass have gained greater interest in the development of biomaterials for food packaging and biomedical products (Rocha et al. 2020).

Manufactured bioplastics are not yet competitive with conventional plastics, due to the higher cost of bioplastic synthesis. In addition, their precarious mechanical properties are brittle after thermoforming, such as with starch-based

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bioplastics (Kato 2019; Lopez-Gil et al. 2014). However, adequate processing and post-treatment conditions may favor some bioplastic characteristics including their mechanical and tensile strengths (Jiménez-Rosado et al. 2020). Specifically, using heat treatments can improve the mechanical properties of the obtained structures, for example, bioplastics based on soy proteins (Alashwal et al. 2020).

The primary characteristic of a bioplastic is its biological or biomass base (Chua et al. 1999). Thus, another problem can be mitigated when bioplastic is produced, i.e., the safe destination of food waste (Tsang et al. 2019). Food production generates thousands of agroindustrial waste tons in the processing of different cultures (Colen et al. 2019). A large part of these wastes have no direct applications, impacting the environment through their inadequate treatment, e.g., burning and burial or other disposal methods of these residues (Conke and Nascimento 2018). Biomass generation in Brazil from agricultural and/or agroindustrial residues in 2015 were 768 million tons and 130 million tons, respectively, with a growth projection for 2030 of 1,196 million tons and 207 million tons, representing an increase of approximately 55 and 59%, respectively (Moraes et al. 2017).

Food waste in Brazil is related to several factors, including harvesting, inadequate preparation, inappropriate handling and food transport, storage, and Brazilian cultural habits (Henz and Porpino 2017). Therefore, changing habits and developing of new technologies related to food residue use is vital (Landim et al. 2016; Marcheto et al. 2008). Bioplastics production resolves food waste-related environmental issues by utilizing the renewable and biodegradable resources of commonly used materials (Mclellan et al. 2019).

Therefore, numerous studies have demonstrated the usability of food residues in biological conversion for bioplastics production (Araújo et al. 2018; Alashwal et al. 2020; Zhang et al. 2020; Yamada et al. 2020; Dinesh et al. 2020; Teigiserova et al. 2019; Karan et al. 2019). Biodegradation functionality is an advantage that can be used in many of these bioplastic creation processes (Emadian et al. 2017).

With the advancement of biological processing techniques, it is possible to convert nearly all biomass from food waste, whether of vegetable origin (green engineering) or animal origin, into bioplastics (Agnihotri et al. 2020). This conversion allows for energy generation systems and feedstocks for biodegradable plastics to fall under the broad concept of bioeconomics (Karan et al. 2019). Once inedible food waste becomes a reality of food processing, it can promote the use of stable feedstocks for future chains, where bio-based compounds with value-added products are produced, and can partially replace synthetic chemical production (e.g., organic acids, dyes, enzymes, chemicals, and bioplastics) (Bhaskar et al. 2018).

This chapter discusses the main compositions and structures of the substrates that produce bioplastics from food waste, whit an emphasis on (a) cassava husks, (b) rice husks, (c) shrimp husks, and (d) natural fibers (Fig. 1). These food waste feedstocks are commonly found in the State of Maranhão (northeast region), Brazil. The physicochemical, biological, thermal, and mechanical characterizations of these residues and their potential applications as bioplastics are presented.

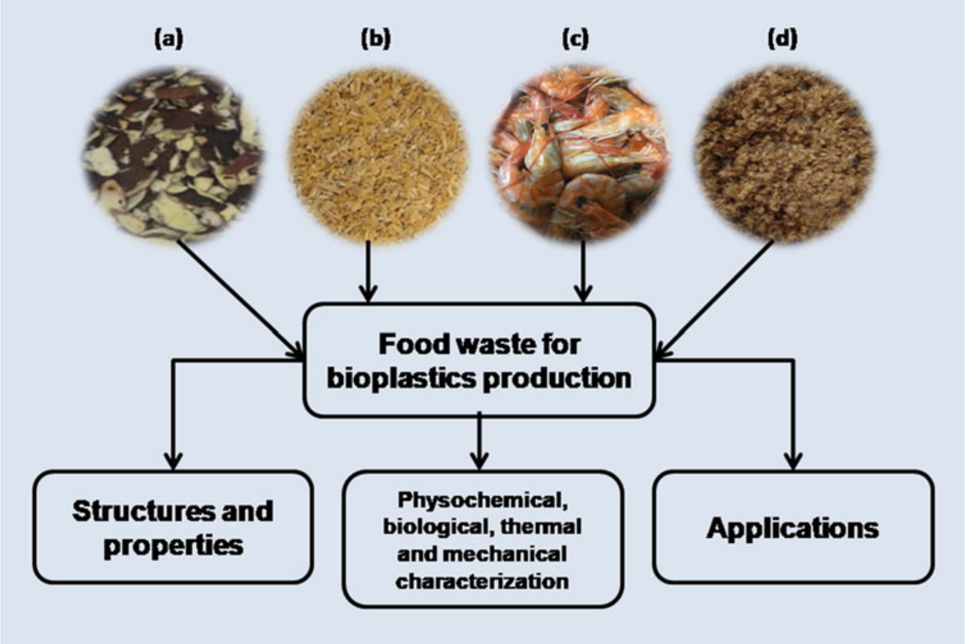

Fig. 1 Illustrative scheme for representing the main feedstocks (food waste) used in this study for bioplastics production and the approaches presented about them: **a** cassava husks, **b** rice husks, **c** shrimps husks, and **d** natural fibers (*açaí* seeds or coconut shell)

2 Main Substrates for Bioplastic Production from Food Waste

The compilation of all waste data illustrates its aggravation of environmental problems. Much of this negative environmental impact stems from the human need to feed may be a better fit here depending on the intended meaning (Tsang et al. 2019; Quested et al. 2013). Organic waste is responsible for the production of leachate, which contaminates the soil and groundwater in landfills. Organic matter decomposition produces CO_2 and methane, gases that contribute to the greenhouse effect (Tsang et al. 2019; Quested et al. 2013; Reisinger et al. 2011; Rubia-García et al. 2012).

The food industry must create a waste generation plan to decrease the quantity of waste produced, and to properly route byproducts. Therefore, the environmental management of food production is the most important challenge for the future.

The reuse of byproducts is more economical. For example, less energy, water, time, labor, fertilizers, and pesticides are wasted. In addition, one-third of the product that was previously wasted becomes an added-value product (Martínez et al 2012). Therefore, waste management in the food industry remains an unresolved problem and a top-priority issue.

As an alternative to these residues, there is a growing interest in their applications as matrixes in the development and/or reinforcement of bioplastics. This is because synthetic polymers are derived from petroleum, a nonrenewable natural resource that has a great environmental impact from its extraction and refinement Ashter (2016), unlike materials that are derived from renewable resources, i.e., from resources that can be recovered (Morin-Crini et al. 2019).

Scientific interest in the development of degradable biopolymeric films over the last decade is due to environmental concerns related to the irregular disposal of synthetic plastics (Ashter 2016; Callister and Rethwisch 2012). However, these materials can be diversely applied in health care, as electronic sensors, structures, coatings, and for the development of new products and technologies (Mano et al. 2007; Teixeira et al. 2018; Romani et al. 2017; Lemos et al. 2017).

The use of polysaccharide films (primarily using food residues such as rice husk, soy, cassava, and shrimp) has been suggested for use on food surfaces to protect them from weather and to preserve their physical and chemical characteristics, and nutritional values (Piñeros-Hernandez et al. 2017).

According to Jafari et al. (2015) and Garavand et al. (2017), bioplastic-forming polysaccharides are mainly sourced from agricultural resources, for example, starch, cellulose, and chitosan.

2.1 Structures, Compositions, and Properties

This next subsection highlights the design, constitutions, and characteristics of the feedstocks that present great potential utilization as bioplastic.

2.1.1 Shrimp Shells

Bioplastic packaging manufacturing, which is predominately used in the food industry, can be combined with fishery residues, such as shrimp shells that are rich in chitosan. The addition of chitosan to films can help maintain film integrity when it is applied to food products (Susilawati et al. 2019). However, chitosan is obtained from the deacetylation of chitin. According to Santos et al. (2020), chitin is principally removed from the exoskeleton of arthropods and is considered to be the second more numerous natural polysaccharides, after cellulose, and the two presenting exceedingly resembling chemical structures. Chitin can be obtained in the form of water-insoluble solid, organic solvents, and diluted acid mixtures, and it may be utilized as a flocculant or an adsorbent in water treatment.

Chitin functions as a fibrous component and is nearly always associated with proteins, forming oligoproteins that interact with constituents, such as carbonates and phosphates Susilawati et al. (2019). The structure of chitin can be modified by removing the acetyl groups through a chemical reaction at a high temperature in a concentrated alkaline solution and. When the chitin deacetylation is greater than 60–65%, the resulting copolymer is chitosan (Casadidio et al. 2019) (Fig. 2).

Chitosan has functional amine groups and primary and secondary hydroxyl groups; therefore, chitosan has a high chemical reactivity because it can form hydrogen bonds and become an ideal mixer (Setiani et al. 2013).

Chitosan shows hydrophobic character (waterproof material) and antimicrobial effects (Rochima et al. 2018), as it can repress the development of microorganisms, e.g., *Escherichia coli, Shigella dysenteriae, Salmonella typhimurium*, and *Candida* (Santos et al. 2020), which makes it even more of a significant research field for the food industry. Chitosan can complement the characteristic deficiencies of bioplastic packaging based on starch (Oktavia et al. 2015).

2.1.2 Rice Husks, Soy Residues, and Cassava Between-Husk

Starch, which is the most important type of bioplastic polysaccharide, can be extracted from cassava, rice, and soybeans (Susilawati et al. 2019; Bansal et al. 2018; Cruz et al. 2020). This is mainly due to amylopectin levels that can affect the stability of bioplastics and amylase, which influence tensile strength and flexibility. The proportions of

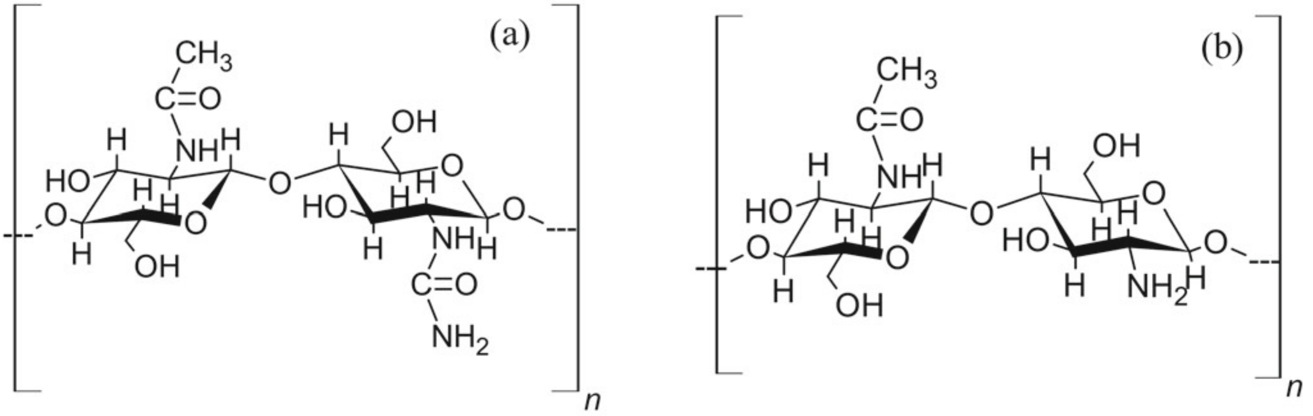

Fig. 2 Chemical structure: **a** chitin, and **b** chitosan *Source* Adapted from Casadidio et al. (2019) and Yang et al. (2019)

amylase and amylopectin play an imperative part in the bioplastic mechanical characteristics; amylase results in most favorable properties for bioplastics than amylopectin does because of its linear structure. Moreover, starch comprises of water residue that too collaborates to its mechanical characteristics and decreases the glass transition temperature (Khalil et al. 2019). The starch obtained from these sources is easily degraded by microorganisms, such as decomposing bacteria, breaking the polymer chain into its monomers (Dhanapal et al. 2012).

The polymers are in the form of granules from 1 to 100 μm in diameter, and they are primarily composed of amylose chains, corresponding to linear fractions with α-1,4 glycosidic bonds, and amylopectin, which represents branched glycan with α-1,6 bonds (Zhu et al. 2017) (Fig. 3). However, there are great morphological and structural variations and in the amounts of amylose, amylopectin, protein, and lipids in starch plant species, resulting in different physicochemical properties (Perotti et al. 2014).

Amylose is a low-branched carbohydrate with a molecular weight of 105-106 units of anhydroglucose. Amylopectin is a multiple, highly branched polymer with a high molecular weight of 107–109 anhydroglucose units. Waxy starch contains little or no amylose, while high amylose starch contains more than 50% of the linear polymer (Basiak et al. 2017).

Bioplastics made from these sources have thinner structures and higher tensile strength values (Nugroho et al. 2013; Ravindra et al. 2018; Soekamto et al. 2017). Edible starch-based films exhibit low water resistance that can affect their physical and/or mechanical properties. This is due to the low solvency of the ramified amylopectin, which provokes accumulation and high dissolvability at elevated temperatures and exhibits a feeble obstacle in opposition to components with little polarity (Podshivalov et al. 2016), which results in starch biofilms fragility due to the hydrophilic character of amylopectin. In spite of the fact that polysaccharides present numerous focal points, particularly the capacity to decrease pollution and contribute to eco-friendly production, they moreover present some disadvantages, for example, sensitivity to moisture and fragile mechanical properties. These troubles must be overcome to enhance their properties. Alternatively, polysaccharides can be added to biopolymers, such as hydrophobic and antimicrobial materials or incorporated into other materials, e.g., lipids, nanoclays (Müller et al. 2011), and lignocellulosic fibers, which can be adopted as a promising strategy.

One usable fiber is that from rice husks, which is rich in cellulose (Cruz and Crnkovic 2019). Rice husks consist of approximately 57% cellulose; therefore, they also have the potential to be used as raw materials in bioplastics manufacturing, thus increasing the bioplastic mechanical resistance (Johar et al. 2012).

2.1.3 Natural Fibers

Bioplastics exhibit properties that hinder their use in other areas, such as in packaging and plastic bags, because of their high solubility in aqueous media, leaching tendency, and low mechanical resistance. Therefore, the use of natural fibers to reinforce these bioplastics can be investigated to improve the properties of these polymeric matrices, while taking into account the physical and chemical processes used in these fibers to ensure adequate dimensions improve the fiber ratio matrix (Paixão et al. 2019).

Vegetable fibers are the primary agricultural residues (Albimante et al. 2013), and they offer several advantages, such as being easily modified by chemical agents and resistant to mechanical properties. Brazil is one of the main agricultural producers (Food and Agriculture Organization of United Nations (FAO) 2018), thus, the country produces large amounts of biomass residues that can be used in polymeric matrix cargoes.

There are many applications for lignocellulosic fibers in the production of bioplastics (Jamróz et al. 2019), the

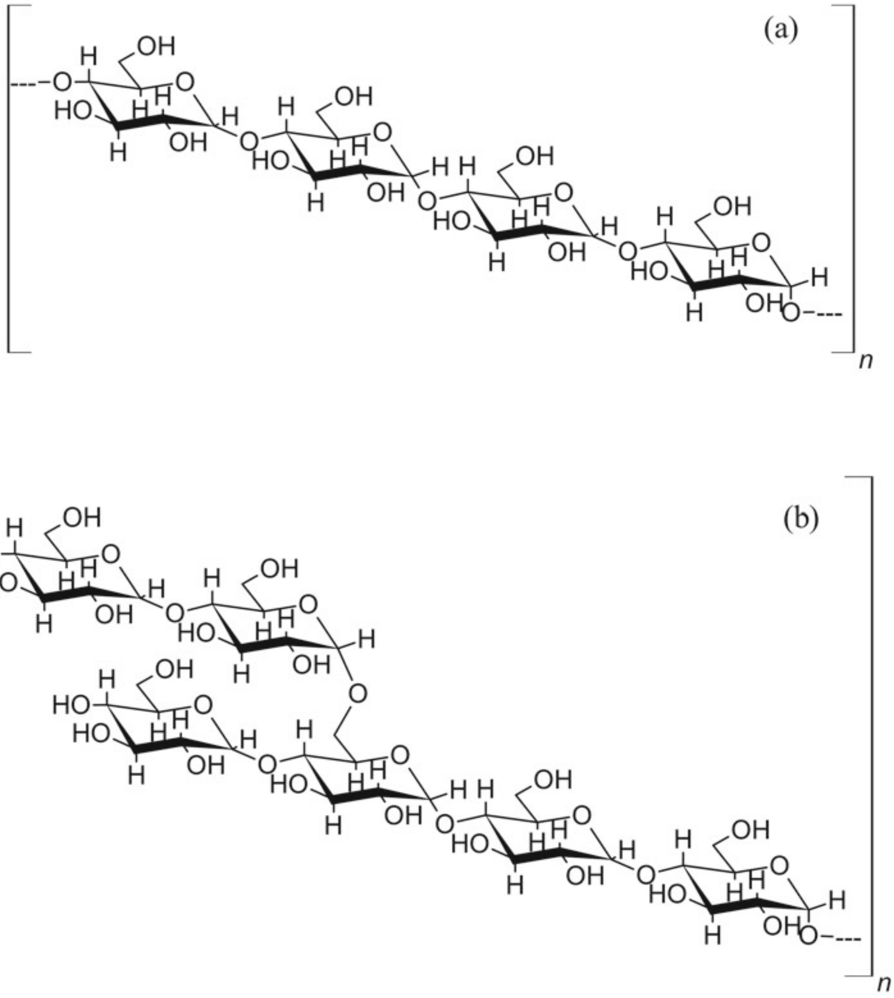

Fig. 3 Basic structures: **a** amylase, and **b** amylopectin *Source* Adapted from Tsang et al. (2019)

application of these charges generally has a better effect in the micro- and nano-proportions. The fibers can be added to matrices at these scales in a more controlled manner with greater homogeneity. Technologies have been developed to obtain these fibers as nano- or micro-charges either integrally or constituently (Paixão et al. 2019).

Fibrous residues from the different plants are available for polymeric composite elaboration and bioplastic applications. The fibers may be defined according to the portion of the vegetable that these are extracted: fibers from the bark, fibers, seeds, core, or reed. Bamboo, jute, kenaf, linen, sisal, hemp, coconut, and sugarcane bagasse are the most commercialized fibers worldwide, especially, bamboo and sugarcane bagasse fibers, with 30 and 75 million tons traded annually, respectively (Faruk et al. 2012).

The conditions of climate, weather, and vegetable cultivation influence not only the structure and morphology of fibers, but also their chemical composition. The primary plant fiber components are cellulose, lignin, and hemicellulose (Fig. 4). The variation of these components varies for each vegetable; cellulose-rich fibers, such as kenaf, linen, rice husk, and sisal are preferable for polymeric matrices (Johar et al. 2012; Faruk et al. 2012).

Cellulose and lignin effect singular roles in the bioplastic fabrication. Generally, cellulose enhances the mechanical property of the bioplastics; however, lignin betters the thermal stability, reduces the water uptake, and ensures the sufficient dispersion of cellulose in the bioplastics (Ma et al. 2015; Yang et al. 2019). Both cellulose and lignin can affect bioplastics Liu et al. (2014). Hemicellulose and lignin are used as reinforcements in polylactic acid (PLA)-based bioplastics (Agustin-Salazar et al. 2018).

Various researches have related on the addition of natural fibers to polymeric compositions according to their geographic distributions and cultural employments worldwide (Pickering et al. 2016; Väisänen et al. 2017; Müller et al. 2017).

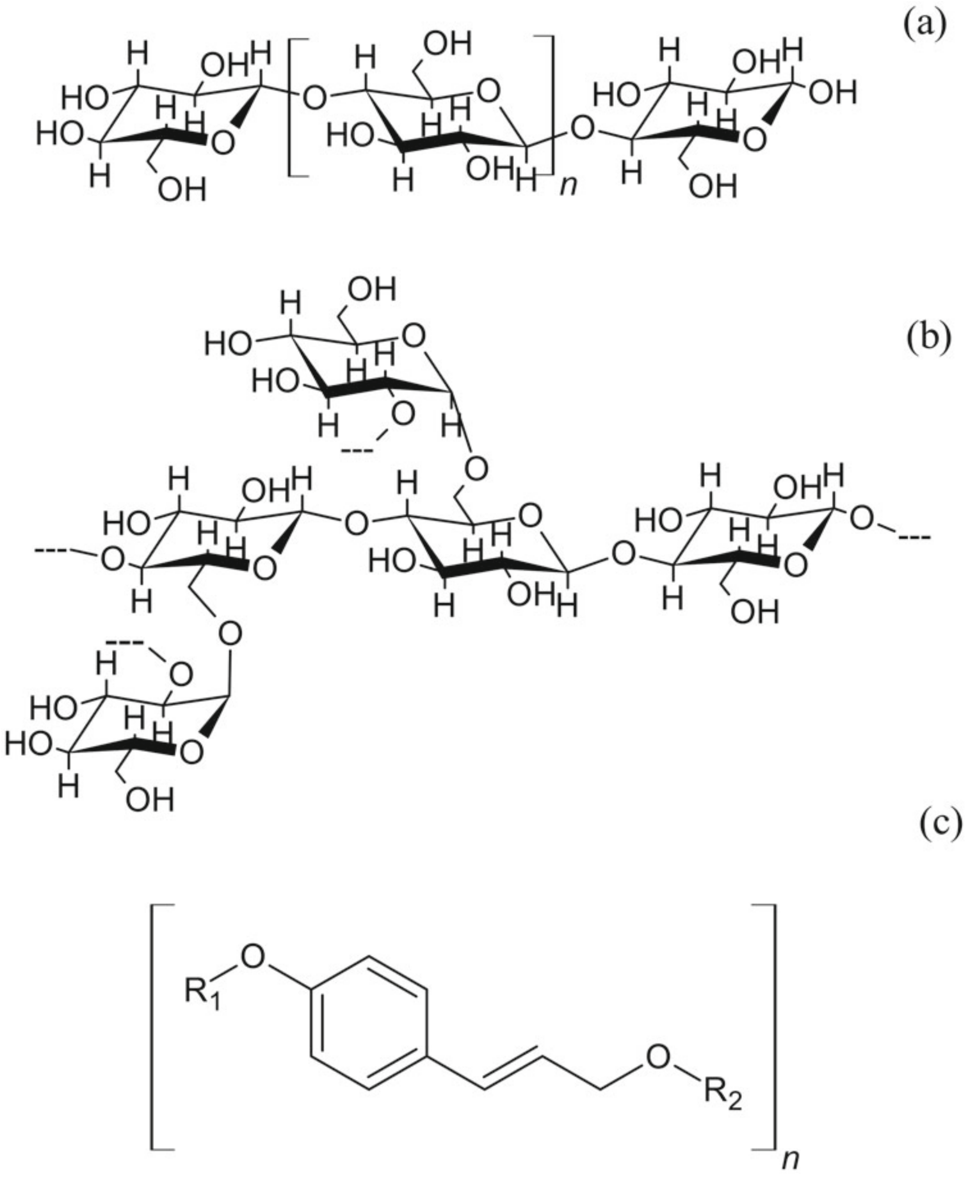

Fig. 4 Basic structures: **a** cellulose, **b** hemicellulose, and **c** lignin *Source* Adapted from Tsang et al. (2019)

3 Property Characterizations of Bioplastics Produced from Food Waste

Modern society has developed increasingly sustainable products, given the great concern for the waste disposal in the environment (Freitas Netto et al. 2020). Bioplastics developed from natural resources, e.g., cellulose, chitin, and starch, are viable substitutes for nonrenewable polymers, with advantages, for example, biodegradability, biocompatibility, few toxicity, and cost (Hossain et al. 2018). However, biopolymer technology is not yet fully developed, and some parameters, e.g., mechanical properties and adaptations to industrial processes must be improved (Santos and Tavares 2015).

Bioplastics are formed by changing biopolymers structures (Chen and Patel 2012). Starches (polysaccharides) of tuberous roots, such as cassava, carrots, and potatoes or cereals (corn, soy, and rice) mixed with vegetable residues (coconut fiber, wood sawdust, and cassava peel), and common thermoplastics are based on many bioplastics (Rosa et al. 2001).

The complete characterization of bioplastics is critical as these can potentially replace non-biodegradable materials for packaging manufacturing. Essential parameters are described in biopackage studies.

3.1 General Characteristics of the Residues Utilized

In this study, it is proposed using various residues (shrimp, rice, and cassava husks, soybean residues, and natural fibers) for the bioplastic production. Therefore, it is necessary to understand the fundamental characteristics of these residues, which are widely discussed in the literature.

3.1.1 Husks of Shrimp, Rice, Cassava, Soybean Residues, and Natural Fibers

Bioplastics, which are derived from biomasses, have gained attention for the development of food packaging materials (Shah et al. 2019). Chitosan is currently the most favored biopolymers that may be attributed to their biocompatibility, biodegradability, non-toxicity, antioxidant, antimicrobial, and anticancer features (Wahid et al. 2019). Additionally, it is a low-cost matter achieved from aquatic resources, such as sea fruits rinds (Vilela et al. 2017; Xie et al. 2017). Chitin is an essential structural biopolymer, which consists of a large fraction of insects and crustaceous exoscaffold (Mitelut et al. 2015; Darbasi et al. 2017).

Cellulose-based bioplastics created through physicochemical modification or chemically modified cellulose is commonly employed (Bilo et al. 2018). The cellulose utilized includes that from peanut husks, citrus fruit shells, and corn straw. Fresh cellulose does not present the same physicochemical characteristics as those of thermoplastics (Tsang et al. 2019). However, these plastic features may be added to cellulose fibers through some mechanical pretreatments. In addition, the esterification of the hydroxyl groups with acid in the cellulosic structure ascertains the bioplastic features, such as fluidity, resistance, and durability that can be equivalent to those of the common plastics (Hps et al. 2016).

Numerous studies (Paixão et al. 2019; Costa et al. 2017; Mali et al. 2010; Batista et al. 2005; Bastioli 2005) have been conducted to characterize the functional properties of starch biofilms. According to Mali et al. (2010), starch is an abundant feedstock worldwide, with many possibilities for chemical, physical modification, genetic, and origin-resistant film, and coatings applications. In addition, starch biofilms have potential applications for the food, agricultural, and pharmaceutical sectors, and in various sectors where biodegradability is required (Batista et al. 2005; Bastioli 2005).

3.2 Technological Characterizations of the Bioplastics Produced by Food Residues

Biofilm characterization is critical for verifying behavior, such as considering the parameters presented in Fig. 5 for food coatings.

3.2.1 Physicochemical Properties

Physicochemical characterizations of feedstocks are essential for understanding the product behavior in the formulation of biofilms. To analyze bioplastics properties, the moisture content, color, solubility in water, acid, and oil; weight; thickness; opacity; and water vapor permeability (WVP) must be determined.

Silva et al. (2020) developed and characterized biodegradable corn starch films, containing the flour byproducts of sprouts. The authors observed that the characteristics of the proximate composition of the flour can affect the technological attributes of the biofilms. For Cazón et al. (2017), several components can serve as a basis for bioplastic formation, e.g., polysaccharides (fibers, starches,

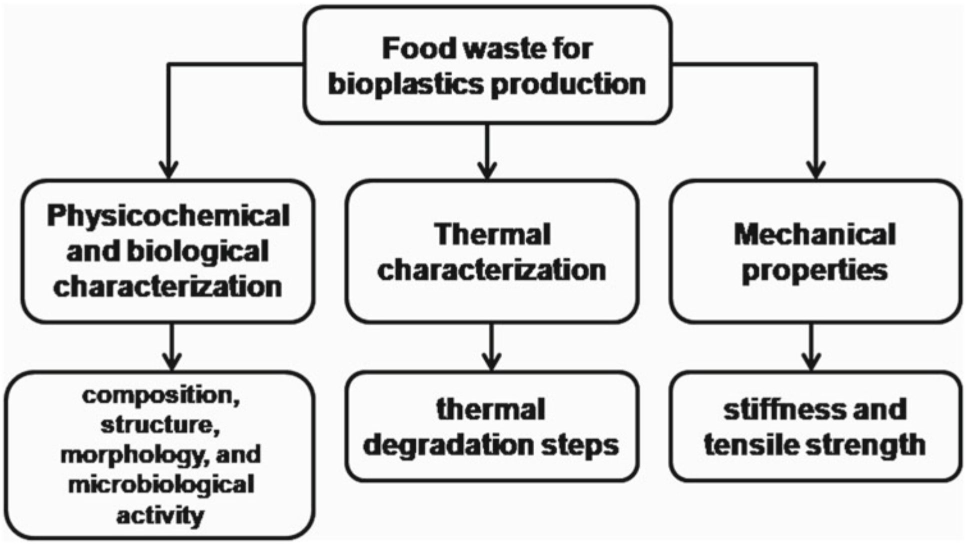

Fig. 5 Schematic representation of the main physicochemical, biological, and thermal characterizations, and the mechanical properties applied to food waste for bioplastics production

and pectins), lipids (waxes, acylglycerols, and fatty acids), and proteins. Flours with high fiber content that are obtained from vegetable residues can be used in bioplastics, resulting in several benefits for these products, e.g., increasing the mechanical properties and thermal stability, and decreasing the water adsorption (Crizel et al. 2018).

The increase in the proportion of flour byproducts of sprouts provided an increase in opacity, but did not interfere in the grammage or acid solubility values. Biofilms with greater weights, also offer greater mechanical resistances, i.e., a greater resistance to mechanical deformations (Almeida et al. 2013). Biodegradable films with sprout flour byproducts are also suitable for packaging or coating products with low levels of moisture and acidity, in addition to foods with high-fat contents. In addition, the appearance of the bioplastic illustrates a sufficient adaptation to market trends for alternative and biodegradable packaging (Silva et al. 2020).

The solvability of chitosan-based biofilms in aqua is a fundamental feature, and water resistance is a *sine qua non* condition for food packaging biofilms (Pavoni et al. 2019). Piyada et al. (2013) observed that the large water resistance of the Ch-ge-Q film (chitosan-gelatin-quercetin), which contains gelatinous chitosan, was maybe because of the relation and miscibility of the amino group inherent in the gelatin and chitosan with the quercetin phenolic component.

For the food packing biofilms, water vapor permeability is an essential factor, and it is utilized to assess the biofilm ability to decrease the humidity transport involving the food and the ambient surrounding the packing (Aguirre-Loredo and Velázquez 2016).

Food can easily deteriorate in environments with high moisture contents if it is not sufficiently stored and/or protected. The increase in moisture can lead to undesirable effects, e.g., sensory alteration, nutrients loss, and the appearance of microorganisms that facilitate the degradation of food (Reis and Schmiele 2019).

In 2020, (Yadav et al. 2020) studied the structural characteristics of chitosan and gelatin, including quercetin-starch, and they discovered characteristics of the biofilms with a base on chitosan-gelatine that contained complexes based on quercetin-starch. In addition, they found that to keep the fresh food, the PWV range must be kept as low as possible. This PVW behavior verified in the Ch-ge-Q biofilm is related with the attendance of hydroxyl and amino species in the chitosan skeletons that can supply linkage sites for water atoms (Souza et al. 2017). The biofilm infiltration of water vapor occurs through 2 (two) ways: adsorption and desorption. Because of the occurrence of biofilm hydrophilic character, the water vapor was simply adsorbed, and the dispersion stage was substantially enhanced (Souza et al. 2017).

3.2.2 Mechanical Properties

Tensile Strength and the Young's Modulus

The tensile resistance of the chitosan-based biofilms is straight associated with the molecular mass and deacetylation grade (Mujtaba et al. 2019). The dehydration temperature and relative air moisture too make an important function in the mechanical and hurdle features of chitosan-based biofilms (Vlacha et al. 2016). According to Pavoni et al. (2019), the tensile strength of the chitosan biofilms created with acetic acid increases when stored at ambient temperature (≈23 °C). This increase depends on the tensile strength time, and it can be described means of the conformational changes in the chitosan atoms and by reducing the free polymer volume (Liu et al. 2017). A recent study (Darbasi et al. 2017) claimed that the tensile strength and stretching at breakdown increased for chitosan-based biofilms, including propolis essence. These chitosan-based biofilms (Ch-ge-Q) can be used to rise the food product conservation times.

The rice straw nanofibers demonstrated the greatest strength with a Young modulus of approximately 1200 MPa (Siripatrawan and Vitchayakitti 2016). This improvement in the Young modulus was associated with the fiber nature and hard linkages formed among the chitosan and charges used in the experiments (maximum charge of 50 kN), ensuring an efficient charge transfer from the matrix to reinforcement fiber (Elhussieny et al. 2020). Hence, the chitosan reinforced with cellulose and/or nanocellulose extracted from rice straw residues is a favorable solution to replace plastic bags for food packaging (Welden 2020).

3.3 Biological Properties

The decay test is an important indicator of the biodegradability of composite products. Dehghan et al. (2019) verified that the bamboo flour amount exerted a significant effect on the degradation of the composite manufactured after 60 days of incubation. In general, the lowest weight loss achieved for all three types of fungi (*G. trabeum*, *T. versicolor*, and *C. globosum*) was obtained for the pure polymer. Therefore, the mixed composite was biodegradable when exposed to wood decomposition fungi, while the high-density pure polylactic acid composite was completely resistant to deterioration through microbiological action Dehghan et al. (2019).

Chitosan is a natural biopolymer, which exhibits sufficient antimicrobial action contra several types of living organisms, e.g., *gram-positive* and *gram-negative* bacteria, filamentary fungus, and yeasts (Kumar et al. 2020).

Hosseinnejad and Jafari (2016) demonstrated that the antimicrobial chitosan properties and mechanisms involved remain unclear, but the most acceptable ones include the

(1) connection of negative charge microbiological cellule pellicles with amine species and positively charged with chitosan that alters the barrier properties and leads to intracellular content leakage and cell death (Pan et al. 2015); (2) the second method is based on the chelating features of chitosan, and (3) the molecular mass of chitosan may too affect its anti-microbiological actions (Verlee et al. 2017).

Chitosan selectively connects to metals, limiting several metabolic enzymes in microbial cells, blockading acting centers, and decreasing its development. Therefore, the antimicrobial function of chitosan is primarily caused by its molecular mass, deacetylation degree, and other physicochemical properties (Kumar et al. 2019).

Nevertheless, in particular for food conservation and packing applications, additional improvements in the antimicrobial characteristics of chitosan are advantageous, to improve its antimicrobial features, natural antimicrobials, and their nanostructures (e.g., metal nanoparticles and metal oxides) were used Matharu et al. (2018).

3.4 Measuring Thermal Properties Using Thermogravimetric Analysis and Differential Scanning Calorimetry

Thermal stability is a determining factor in the functional properties of biofilms produced from food waste. This is because the application heat on different surfaces can change the biofilm structural parameters, which influence the functionality and stability of the bioplastics (Muralidharan et al. 2020).

In a study on the thermal characterization of corn starch bioplastics, containing sprout flour byproducts conducted by Silva et al. (2020), these noticed that the different components and concentrations found in biofilms presented various capabilities during heating. For all the manufactured films, three mass loss peaks were evidenced, with two endothermic peaks (heat absorption): one in the glass transition region and the other in the fusion region, and an exothermic peak (heat release), which can be explained by the plurality of ingredients and complex reactions that occur at high temperatures (Silva et al. 2020). The glass transition and melting temperatures of different materials are relevant for estimating the barrier properties of oxygen and water vapor, measuring the storage and transport conditions, using them in the industrial processes (Oluwasina et al. 2019). Therefore, the manufactured bioplastics can also be used in foods that do not undergo thermal processing at high temperatures, because there is a low transition temperature that can modify the components (Santana et al. 2018). According to Yamada et al. (2020), the insights recommended that the soybean protein is thermally stabilized by the effect with the 1% formaldehyde aqueous solution–methanol (HCHO), and the bioplastic produced demonstrated a thermal stability below 200 °C, due to the configuration of a 3D (three-dimensional) association with methylene containing cross-linkages with peptide chains. The authors concluded that soy proteins with HCHO reactions may make a significant function in the application of biodegradable resources, e.g., throw away objects, industrialized pieces, and unconventional plastic substances.

In a study developed by Dehghan et al. (2019), the addition of bamboo flour to the high-density polylactic acid (PLA) composites resulted in an efficient raise in the glass transition temperature of the composites. A slight increase in the transition temperature compared to that of the pure polymer represents a change in the softness and flexibility of the bioplastics (Yamada et al. 2020). It was also observed that the crystallinity degree of the composites increased compared to that of the pure polymer, which is possibly due to the presence of coupling agents in the composite structure (Velasco et al. 1996). This coupling agent is the result of an increase in the crystalline core, which directly leads to an increase in the crystal development around the fibers and an increase in the polymer crystallinity degree (Velasco et al. 1996). These factors significantly improve the connection between polymer chains and biopolymer fibers.

4 Applications of Bioplastics Produced by Food Waste

Plastic composes a variety of products in various fields due to its properties as a polymeric material. Plastics have become a worldwide concern due to their increasing levels of production and use. Food waste represents great losses of various resources such as land, labor, and water. The Food and Agriculture Organization (FAO) (2018) defines food waste as quality and quantity losses resulting from consumer behavior and retailer marketing (Bilo et al. 2018).

The production of synthetic plastics from irreversible processes is a large environmental problem. Therefore, due to their similar functions, bioplastics are a sustainable alternative to the concern to environmental contamination by synthetic materials of low degradability (Tsang et al. 2019).

4.1 Rice Straw Bioplastics Applied in Packaging

Cellulose is the most appreciated biopolymer, and it is present in wood, cotton, and rice straw (Spadetti et al. 2017). It consists of glucose units bound by a glycosidic bond. Cellulose fibers have several advantages, e.g., low cost, availability, renewability, low density, low thermal expansion, and water insolubility. Moreover, cellulose nanofibers obtained from horticulture have been studied because of their abundance and annual sustainability (Riva et al. 2018).

Therefore, the nanocomposite fibers from rice straw can be used to increase the resistance of nanocomposites, when unified in polymeric matrices because of their high aspect ratio, which is associated with structures interconnection abilities (Riva et al. 2018).

Rice straw is a material rich in cellulose (around 47%), hemicellulose (approximately 27%), and lignin (below 24%) (Mohammad et al. 2018; Garrote et al. 2002). It is the main feedstock for ethanol production Saha (2003). From the rice crop, 1.5 kg of straw can be generated from each 1 kg harvested biomass. However, in several countries, rice straw is usually burnt or discarded in rivers and lakes, contaminating and polluting air, water, and soil Binod et al. (2010). Nowadays, many agricultural byproducts and other inedible food residues, e.g., potato peels, sugarcane bagasse, shrimp husks, eggshell, and lignocellulosic fibers are used to produce ecofriendly materials (Sangon et al. 2018; Tiimob et al. 2017; Chiellini et al. 2001). Rice straw residues can be easily handled as they do not require separation from other residues (Moro et al. 2017).

There are numerous bioplastic applications from food packaging to medical care. Food packaging is a significant material (Dominguez-Escriba and Porcar 2010), it must be resistant to contact with oils and water. Bioplastics have the function of protecting food from exposure to the ambient and ensuring its quality and durability (Gilbert et al. 2017). Despite the improvements achieved in research, there are still some challenges to be overcome. Properties, such as thermal variability, water vapor, fragility, and resistance to melting must be optimized. The difficulties previously mentioned have encouraged research on bioplastic functionality improvements. The use of cellulose, nanoparticles, and chemical modifications are some of the mechanisms employed to reduce the limitations of bioplastics (Siracusa et al. 2008; Sartore et al. 2015). On the other hand, to create a low-cost bioplastic with mechanical characteristics same as those of synthetic plastic materials, e.g., polyethylene and polypropylene is very difficult.

From rice straw, bioplastics rich in cellulose can be produced. After pretreatment with trifluoroacetic acid (TFA), the cellulose present in the rice straw is extracted to produce bioplastic (Sartore et al. 2016). TFA is an organic acid solvent for cellulose (Bayer et al. 2014). Furthermore, it can be simply recycled via distillation and added to other organic solvents, for example, water.

4.2 Soy Protein Bioplastics Applied to Commercial Polyethylene

Artificial plastics produced from petroleum have several beneficial properties, e.g., in cost terms, ease of processing, and mechanical strength, and are produced globally in large quantities (Zhao et al. 2007). These artificial plastics have applications for several types of products, such as industrial components and throw away materials. However, as plastics are primarily derived from petroleum, due to the overuse of this resource, carbon dioxide, and other toxic compounds are released into environment during production, and this is a major problem.

In addition, synthetics plastics, such as polyethylene, polypropylene, and polyvinyl chloride present low degradability in environment and may remain for hundreds of years (Emadian et al. 2017; Thompson et al. 2009; Hester and Harrison 2018). Plastic waste polluting the ocean is also a major global contamination problem (Thompson et al. 2009; Luckachan and Pillai 2011). Therefore, an alternative to using plastic is the artificial plastic or bioplastic, which is composed of natural biopolymers (Thompson et al. 2009; Hester and Harrison 2018). Bioplastics are biopolymers produced from renewable biomass sources, such as wood, natural rubber, carbohydrates, food waste, and proteins (Picó and Barceló 2019; Xu et al. 2019; Lambert and Wagner 2017). In addition, biopolymers are easily obtained from nature, so there are no costs compared to synthetic polymers. Biopolymers are not dangerous to humans and are ecofriendly materials. Therefore, bioplastics composed of biopolymers, for example, starch Brodin et al. (2017), agarose Sagnelli et al. (2016), casein Awadhiya et al. (2016), lignin Sutermeister and Browne (1939), and keratin Kai et al. (2016) are great alternatives to synthetic plastic.

Soybean is one of the more cultivated plants in the world, especially in East Asia, where it is consumed as tofu (unfermented food), but also as miso and soy sauce (fermented food). However, soybeans contain good fat (20%) and protein (35%) contents (Ramakrishnan et al. 2018; El-Shemy 2013). Therefore, soybeans are used worldwide for oil. Ungreased soybeans contain many proteins. The residues of ungreased soybeans are largely discarded, even though they are used for human and as animal feed (Ramakrishnan et al. 2018). Degreased soybeans have been utilized to prepare cellulosic materials (Visakh and Nazarenko 1998), glycerol (Paetau et al. 1994), polyacrylamide (Tian et al. 2012), and graphene (Xu et al. 2015). However, the treatments applied to produce the cellulosic material from degreased soybean are complex. Therefore, to green chemistry to prepare bioplastics by a simple process is an ideal way to minimize contamination.

Soybean protein is basically composed of lysine and arginine, neutral amino acids, such as glycine, valine, alanine, and leucine, and also aspartic and glutamic amino acids (Jiang et al. 2016). The carboxyl or amino acid groups in the residues are modifiable functional groups. In particular, under moderate conditions, formaldehyde reacts with amino groups to produce methylol, and forming a methylene cross-link, e.g., N-CH_2-N (Yamada et al. 2020; Taira 1973;

Klockenbusch et al. 2012; Hopwood 1969). Therefore, degreased soybean, which contains lysine and arginine, reacts with HCHO in aqueous solutions and produces reticulated soybean. In addition, bioplastics, which are derived from this crop, are biodegradable and can be used in agricultural materials like straw and seedling pots.

4.3 Shrimp Waste Bioplastic Applied to Food Packaging Bags

There is growing interest regarding the use of biocomposite materials for various manufacturing purposes, because of their biodegradability, low carbon emissions, and low cost (Elhussieny et al. 2020). Chitosan is used in several applications, e.g., pharmaceutical, agricultural, and water and effluents treatment (McGhee et al. 1975). It is obtained from the chitin found in crustacean exoskeletons (Cristiano 2017). The extracted chitosan quality depends on the chitin deacetylation degree, which is controlled by modifying the time and temperature of the deacetylation process (Hossain and Iqbal 2014). Deacetylation is considered an important parameter that determines several physicochemical and biological chitosan properties, including its degradation rate (Antonino et al. 2017). Thus, the effect of different reaction times on the chitosan deacetylation degree can be explored. In addition, chitosan can be reinforced to overcome some of its physical and mechanical limitations (Marjan et al. 2016). Natural fibers (cellulose fibers) are used as reinforcement fillers in several polymers (Nevena et al. 2016).

Chitosan reinforced with natural fillers is a promising material to replace synthetic food packaging. Food packaging made from polyethylene is obtained from a nonrenewable source, petroleum, and requires up to 1,000 years decomposing (Ismail et al. 2011). As the production of large quantities of bags is associated with this long decomposition time, because plastic bags represent an ecological problem (Baxter 2018).

Food packaging bags made of natural materials, e.g., chitosan, do not present these negative environmental impacts. Synthetic food packaging bags are typically made of polyethylene. These materials exhibit a high resistance to humidity, and they are lightweight. However, their long degradation time causes an enormous problem regarding waste (Hacker et al. 2019). One of the most significant types of plastic pollution are the plastic bags used in supermarket shopping. In Egypt, 2% of urban residues are disposed in landfills, 8% is composted, 88% is disposed of in open areas, and 2% is recycled. Plastic pollution in Egypt occurs because of the lack of alternatives for composting this material (AbouHagra 2017). Most plastic waste accumulates on the streets or in illegal dumps, causing environmental and public health problems.

The experimental and characterization stages begin with the extraction of the chitosan from the shrimp bark residues. Then, the deacetylation degree of the extracted chitosan is controlled.

4.4 Cassava Waste Bioplastic Applied to Biodegradable Films

Millions of tons of plastics are produced every year worldwide, and the resulting environmental impact caused increases daily. Thus, producing biodegradable plastics from renewable sources has been the most viable alternative. Starch is a biopolymer matrix with great potential for the development of biodegradable packaging (Shah et al. 2016).

Starch is an important polysaccharide in nature (La Fuente et al. 2019; Junfeng and Jianjun 2011). Because it is obtained from natural sources, the cost is reduced and it is widely applicable. Consequently, starch is an extremely versatile material that is used in the food, paper, textile, chemical, and pharmaceutical industries (La Fuente et al. 2019). Starch sources are limited in nature, so improving the mechanical properties of biodegradable films is interesting to make the material even more versatile.

From the different starch modification possibilities, ozone processing is the most environmentally correct, as it follows all safety standards (Kaur et al. 2012). Ozone reacts with starch, which due to its oxidizing power, reduces the molecule size, and increases carboxyl and carbonyl content (Castanha et al. 2017). Consequently, different properties can be achieved from molecular modifications in size, load, and chemical and electronic affinity. Corn, sago, wheat, potatoes, and cassava are examples of some starch sources that can be modified by ozonation process (Castanha et al. 2017, 2019; Çatal and Ibanoglu 2012; Chan et al. 2009, 2011; Klein et al. 2014).

The molecular and granulometric structure of compounds that have the amino group are affected by ozonation of several forms. For example, cassava has granules less than 50 micrometers (polygonal and spherical forms), and potato starch contains larger and smaller granules (spherical and oval ways) (Hung et al. 2017).

Therefore, reassembly behaviors are influenced by different molecular sizes and electrical charges from starch sources. These molecular changes favor the film production process. Consequently, the properties of films produced with modified ozone starches are unpredictable and depend on factors, e.g., sources, reactors, and processing conditions. Thus, from the starch present in cassava, it is possible to produce biodegradable films by the ozonation method, for assessment the material conditions, such as its mechanical, hurdle, and functional features, and morphology, crystallinity, and color.

5 Final Considerations

There is a worldwide consensus that the use of different synthetic plastics, which are produced entirely by nonrenewable sources, is a great societal concern. Food waste is another major global issue, even though there is widespread hunger, especially in underdeveloped or developing countries.

This study evaluated some food residues feedstocks (e.g., cassava, rice, and shrimp husks, and natural fibers), which may be used for bioplastics production. Feedstock compositions and structures, and the main characterization techniques of the physicochemical, biological, thermal, and mechanical properties must be optimized in an ecological, sustainable, and renewable way to solve the two largest environmental problems currently faced by society.

Finally, the food industry, government agencies, and the populations of large cities require a global plan for the management and food waste generation to decrease the quantity produced and properly converting by-product into value-added products. Finding efficient solutions to these socioenvironmental and economic problems are an important challenge for future generations.

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Treatment and Bioconversion of Manure Effluents

Joseph K. Bwapwa

Abstract

Bioconversion of manure effluents can be considered as a promising and environmentally friendly option for the treatment of manure effluents. These conversion processes may be sustainable and beneficial for the farming and agricultural industry. Physical treatments, including daily spreading, liquid effluent storage, solids separation, odour control and lagoon treatment, can be undertaken before biological or chemical treatments. They do not involve major transformation when it comes to the nature of the manure effluents and its content. They are generally used for conditioning the liquid or solids from the effluent. Chemical treatments of manure effluents are undertaken to improve the removal efficiency of solids, pathogens and odours. They are effective and used with the addition of coagulating agents and pH regulator to significantly improve the quality of the final product being treated from manure effluents. In this review, the main focus is on bioconversion processes. They involve biological reactions and microorganisms activity under defined operating conditions. Aerobic and anaerobic digestion are described as the major biological processes to be explored for manure effluents treatment. They constitute the basis of most processes. Bioconversion involves processes such as composting, biodrying, gasification, cofiring, pelletization, methanol and syngas production, and many others. The majority of these processes lead to the generation of by-products, such as fertilizers and biogas, which can be used in the farming and agricultural activities. Heat generation, clean fuels or renewable energy resources are also generated from manure effluents and they may be useful in the energy sector. Furthermore, many other emerging applications using manure effluents, such as microalgae production, aquaculture, bedding, soil reclamation, are still being developed; they will also contribute to the expansion of the field of bioconversion of manure effluent soon.

Keywords

Bioconversion • Manure effluents • Anaerobic digestion • Aerobic digestion • Biodrying • Composting • Pelletization

1 Introduction

Manure effluents are mainly made of various organic components which may be useful in many applications by producing organic nitrogen, organic phosphorus, biofertilizers and biogas via conversion processes (Gajdoš 1998; Khalid et al. 2011; Chew et al. 2019). These processes can be physical, chemical or biological. Manure effluents are mainly generated by farming and agricultural activities (Saggar et al. 2004). These activities are vital in many countries because of their contribution to the economy and wellbeing of the populations. For most countries agriculture and farming provide healthy and affordable food to consumers; however, the nature of their wastes may harm the environment. There is, therefore, a tremendous need for a remedial strategy that can help recycle the wastes and their reuse (Wato et al. 2020; Gontard et al. 2018). Open space, wildlife habitats and aquifer recharge are known as very significant ecological gains that are linked to farming. On the other hand, additional nitrates in the groundwater, pathogenic molecules in the potable water and surplus of nutrients, biological oxygen demand (BOD) and solid residues in surface waters can harm the environment (Wato et al. 2020; Burkholder et al. 2007; Hubbard et al. 2004). Furthermore, farming can affect the surroundings with generation of odours, global warming gases and acid rains (Marszałek et al. 2018; Singh and Singh 2017). It is an obvious fact that our modern society has

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acknowledged most of these damaging effects, and remedial actions to protect the environment are more than a necessity today. Therefore, to maintain a sustainable industrial and economic development, there is a need to be fulfilled in terms of the expansion and optimization of alternative technologies or processes. This will allow a productive and sustainable farming as well as a cost-effective agriculture, while at the same time minimizing the negative effects on the environment. Also, it is important to mention that treatment of manure effluents can improve farm profitability (Joshi and Wang 2018; Dennehy et al. 2017). By processing manure effluents there is an option to decrease ammonia emission (Chadwick et al. 2020; García-González et al. 2019). Treatment of manure provides many benefits and the payback time is short (Hanifzadeh et al. 2017; Thu et al. 2012). Some of the key benefits amongst many are reduced ammonia emission as mentioned before, less storage capacity requirement and more efficient transports. There is an extensive diversity of farms for which the differences are based on environmental challenges and resources. There are number of farms with more advantages than other. These advantages include easy access to finances, skilled human resources, effective managing capacity, water and land assets (Altieri 2002). The farm position and management are directly linked to environmental challenges for any farming operation (Altieri 2002).

It is important to stress on the fact that larger farming operations generate bigger quantities of manure and higher amounts of nutrients at any site.

Consequently, the possibilities of point source pollution are also increased (Miner and Moore 2000). Studies should be undertaken with the aim to develop, validate and optimize technologies with the ability to decrease the volumes of manure and concentrate the nutrients through improved water management within the farming operations. Therefore, the following should be required: more effective use of feedstuff resources by the animals within a farming environment, effective separation of phases for the manure effluent to get both liquid and solid phases separately and undertaking cost-effective manure aeration.

Manure effluents may contain non-soluble and gradually biodegradable suspended solids. The increase of suspended particles can decrease light diffusion into a water body (Busato et al. 2020; USEPA 2002; Timmerman and Hoving 2016). They also contain phosphorus (P) and nitrogen (N) nutrients which are the main sources of eutrophication in surface waters (Busato et al. 2020; Murry et al. 2019). As a result, the dissolved oxygen content is reduced in water bodies to those levels that are insufficient for aquatic life. This could cause a rise of the destructive effects of algal blooms that are discharging contaminants while dying and harshly affecting wildlife and human beings. Besides, ammonia (NH_3) is a known toxic substance to marine life from the fast biodegradation of organic nitrogen (N_2) in wastewater (USEPA 2002; Amenu 2014). Pathogens in manure effluents can impact negatively on various freshwater resources; this includes potable water and marine life (USEPA 2002; Nemerow et al. 2009). Consequently, appropriate disposal of manure effluent is vital for public protection and prevention of water contamination including the preservation of aquatic life and wildlife (Ebner 2017; Goss and Richards 2008; Takahashi et al. 2020). Bioremediation and bioconversion of manure effluents may be specific to each country depending on various aspects linked to environmental and manure type (Murry et al. 2019; El-Sheekh et al. 2016). There are many options that can be undertaken by the farming industry for successful bioremediation of manure effluents. Various methods depend on local environmental conditions, the nature and type of manure effluents and requirements for effluent discharge (Murry et al. 2019; Vanotti et al. 2020; Liu and Wang 2020). Effluents from farming and agricultural industries are treated by similar processes and operations compared to the ones used in a conventional wastewater treatment plant. Additional treatment steps are undertaken depending on the origin, nature and content or quality of the generated effluents (USEPA 2002). Bioconversion processes of manure effluents can be undertaken in bioreactors. Their operational mode can be achieved in batch, continuous or semi-continuous. Additionally, various configurations of bioreactors are used depending on the feedstock nature. The technology deals with the conversion of solid to a gas phase as well as aqueous phase bioprocesses. Bioconversion processes of manure are known to be environmentally friendly alternatives. A range of cost-effective by-products is generated using affordable biocatalysts under achievable operating conditions. More studies are still needed for the optimization of emerging bioconversion processes. This chapter focuses on various treatments and bioconversion technologies for manure effluents to preserve the close environment from any negative effects due their handling or discharge.

2 Manure Handling Processes

2.1 Physical Treatments

There are many alternatives for manure effluent management; before the conversion process which can be chemical or biological, physical treatment processes can be undertaken for the separation of solid and liquid fractions, handling or conditioning. This section presents some of them in terms of their advantages and disadvantages.

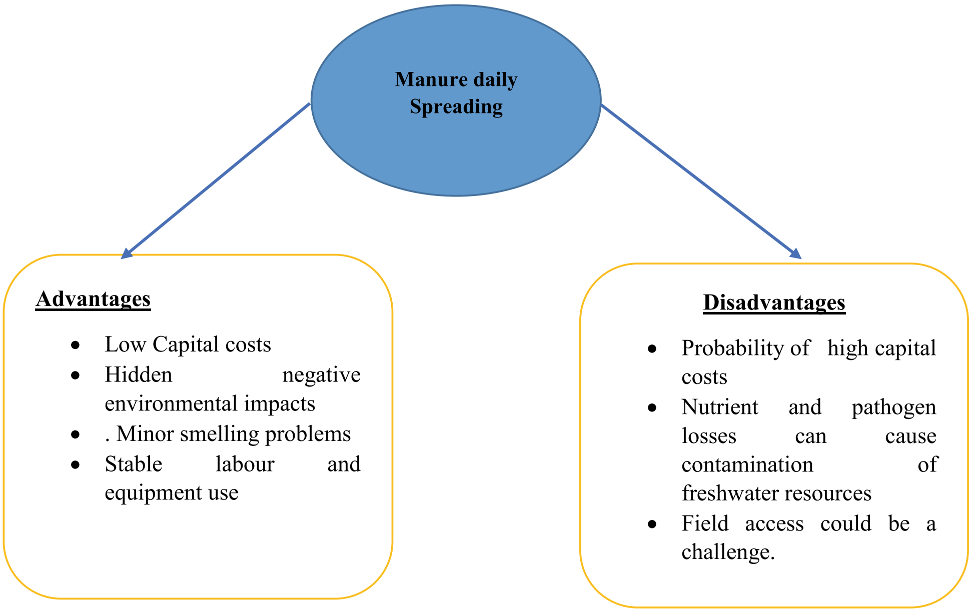


Fig. 1 Summary of advantages and disadvantages of daily spreading operation

2.1.1 Daily Spreading

A large number of farms are using this option. The spreading of manure is undertaken on a daily basis as they are generated during the year (Petersen 2018; Wright 2017). Figure 1 presents a summary including the strengths and the weaknesses of this operation. The process has the reputation of being cost-effective with flexibility in the management (Polprasert and Koottatep 2017). It is a practice that is done on a daily basis by many farmers as mentioned earlier. Nutrients management to decrease the use of fertilizer can be challenging unless efficient procedures are used (Drinkwater et al. 2017). When the practice of spreading is completed nearby the manure source, the soil absorbs excess of phosphorous which causes its contamination and reduce mobility of other minerals in the soil due to excess of phosphorous. Another consequence of high levels of phosphorous in the soil is the contamination of groundwater by migration of phosphorous. Although smelling problems are usually not a major concern on sites under spreading operation, runoff and leaching losses in saturated conditions may contribute to the discharging of nutrients to a watershed (Kleinman et al. 2017).

2.1.2 Liquid Effluent Storage

This operation is completed when there is a need to decrease dissemination of manure during high losses times and periods when fields are not accessible. Effluent storage is mandatory in various areas and usually supported for all areas. Figure 2 presents a summary involving the strengths and weaknesses of the liquid storage operation.

The storage of solid particles of manure and the manure effluents for the spreading at a correct time may decrease the nutrients discharging to a watershed; it has an advantage of protecting the water resources and soil from pollution (Chadwick et al. 2020; Rosov et al. 2020). Nutrients monitoring done by spreading from storage to decrease the use of fertilizers is a very effective and sustainable process (Svanbäck et al. 2019). Records keeping and spreading trends for each site are very important to be assured of the uniformity of coverage. There is a possibility of cost savings both in the reduction of fertilizers usage and operational use of processing plant from the process of spreading manure from storage (Fournel et al. 2018). Odour generation is a major concern when dealing with storage of manure.

2.1.3 Solid Separation

The separation of liquid effluent and solids from manure is an important operation when it comes to physical treatment. This separation is completed with the use of a filtration system used for solid/liquid separation such as a sedimentation tank or a filter-press. The physical separation between the solid and liquid fractions of manure effluents generates 30% dry matter (DM) from the solid fraction while the liquid represents only 4–8%. Figure 3 presents a summary of some advantages and disadvantages related to the separation of the solids from manure effluents. The separation and hauling of solids fraction has the potential of allowing the spread of almost 20% of phosphorus (Kumaragamage and Akinremi 2018). There are various types of separators available on the market that are very efficient in the way of performing the separation process. Many of them need additional water to operate adequately. However, screw press separator operates with no added water and it can generate a satisfactory dry product.

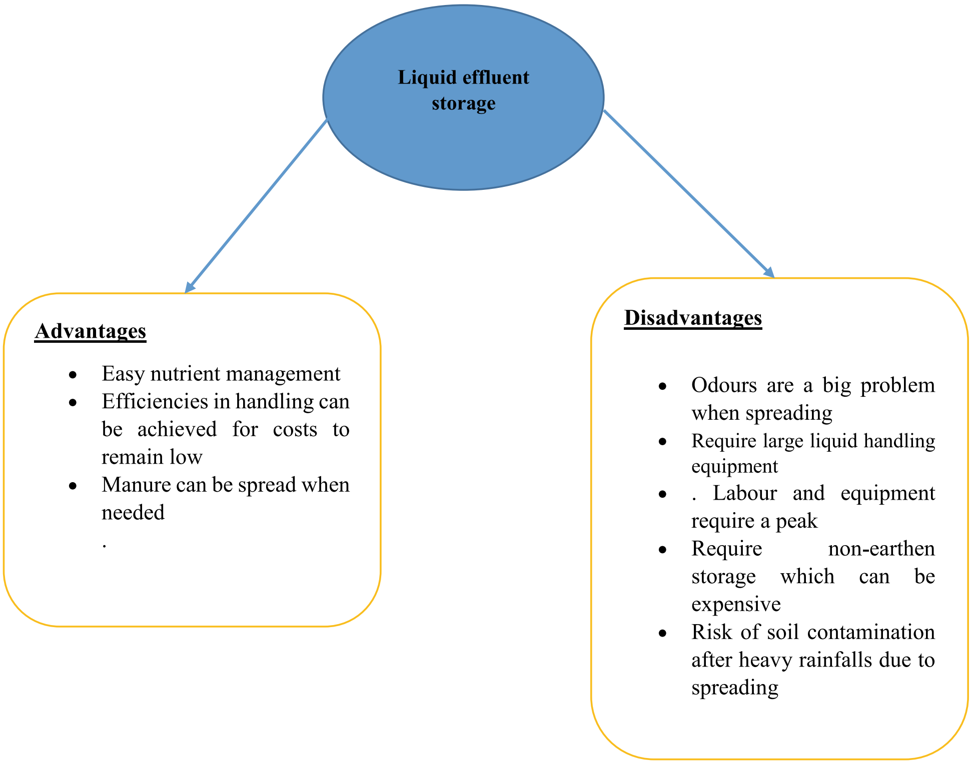


Fig. 2 Summary of advantages and disadvantages of liquid storage for manure effluents

Advantages

- Easy nutrient management
- Efficiencies in handling can be achieved for costs to remain low
- Manure can be spread when needed .

Disadvantages

- Odours are a big problem when spreading
- Require large liquid handling equipment
- . Labour and equipment require a peak
- Require non-earthen storage which can be expensive
- Risk of soil contamination after heavy rainfalls due to spreading

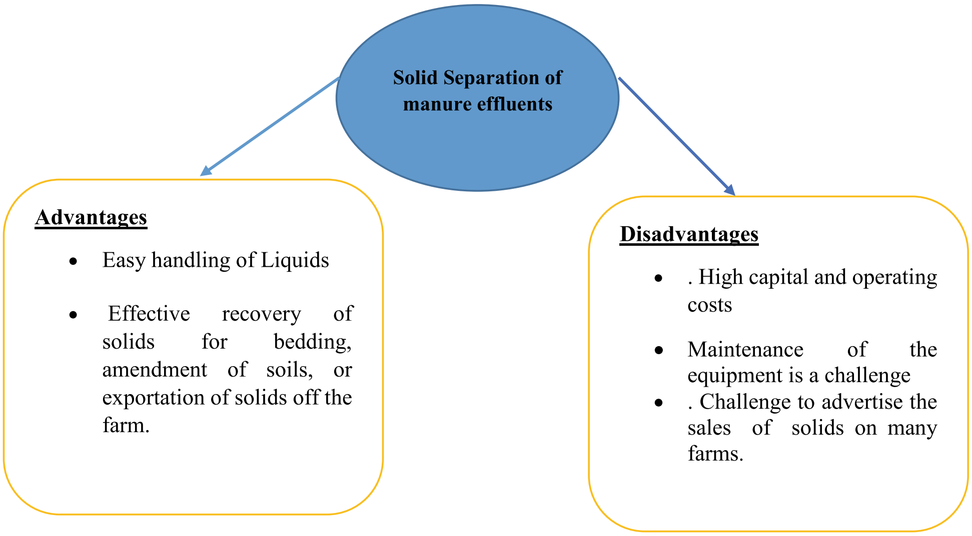


Fig. 3 Advantages and disadvantages for solids separation from manure effluents

Advantages

- Easy handling of Liquids
- Effective recovery of solids for bedding, amendment of soils, or exportation of solids off the farm.

Disadvantages

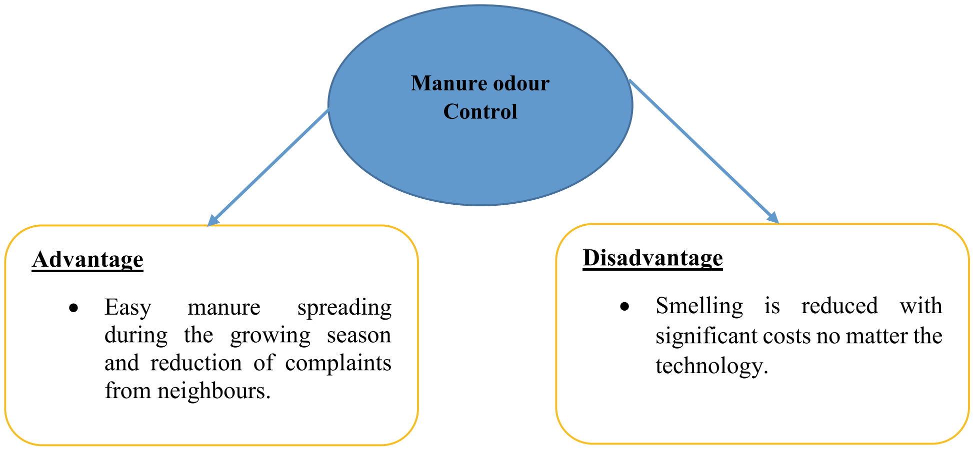
- . High capital and operating costs
- Maintenance of the equipment is a challenge
- . Challenge to advertise the sales of solids on many farms.

2.1.4 Odour Control

The control of odour for stored liquid manure is a major need whenever it comes to manure effluent management (Liu and Wang 2020; Kleinman et al. 2017). Chemical and biological treatments are tested and proposed in order to deal with the issue of smelling or odour generation from manure effluents. Figure 4 presents a brief summary related to strengths and weaknesses of this operation.

2.1.5 Lagoon Treatments for Solids Settling

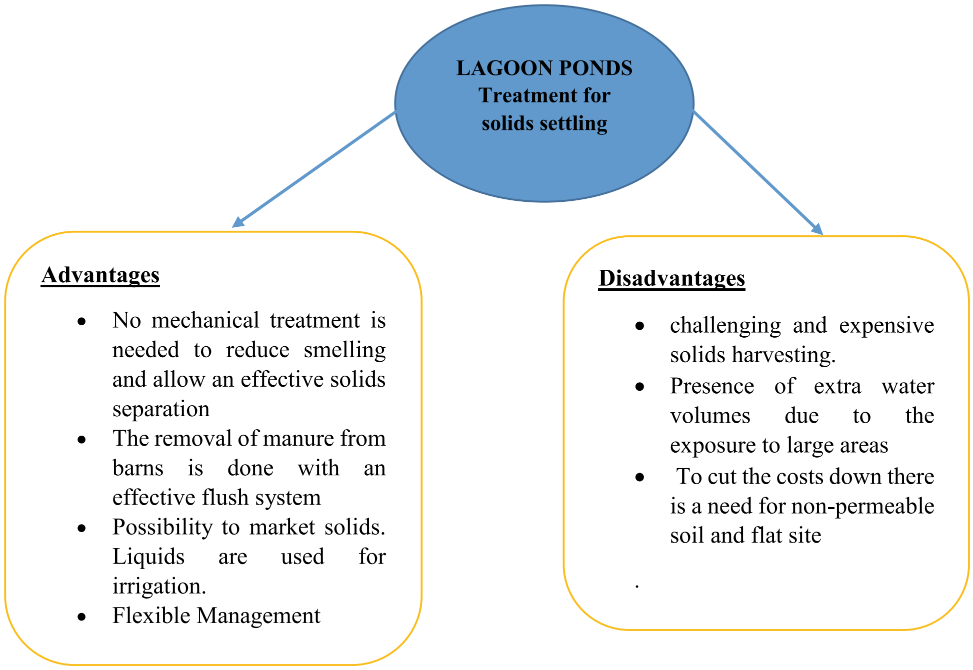
In this treatment manure is diluted; consequently, solid particles will settle down in large narrow pool. There will be a flow of the effluent as flush water to a facultative lagoon. This constitutes a recycling process in which more manure will be diluted. The removal of liquid and solid fractions out of the lagoon treatment system is done periodically depending on the extent of the system loadings. A patented



- Easy manure spreading during the growing season and reduction of complaints from neighbours.

- Smelling is reduced with significant costs no matter the technology.

Fig. 4 Advantage and disadvantage of odour control for manure effluents



- No mechanical treatment is needed to reduce smelling and allow an effective solids separation
- The removal of manure from barns is done with an effective flush system
- Possibility to market solids. Liquids are used for irrigation.
- Flexible Management

- challenging and expensive solids harvesting.
- Presence of extra water volumes due to the exposure to large areas
- To cut the costs down there is a need for non-permeable soil and flat site

Fig. 5 Advantages and disadvantages of lagoon treatment for solids settling from manure effluent

process named 'Bion' uses a well-controlled shallow pool for the separation of solid particles from manure in a stable pond system. The solids will thereafter be subjected to harvesting, drying and screening. At the end of these processes they will be vended soil amendment applications. Lagoon treatment contributes to the recycling of biologically active liquid by allowing the movement of effluents in a pond. This is normally achieved by flushing the ban's alleys. Lagoon treatment is considered as physical process when it deals with solids settling of manure effluents. It is also a biological process because both anaerobic or aerobic biodegradation take place during the treatment course. Therefore, there are two types of lagoon treatments that can be used for manure effluents depending on the manure effluent type and environmental conditions: anaerobic lagoon and aerobic lagoon (Khalil et al. 2016). Figure 5 summarizes the advantages and disadvantages of lagoon treatment for solid settling when dealing with manure effluent.

3 Chemical Treatment

Manure effluents can be treated chemically with the aim of improving solids removal, eliminating pathogens, eradicating smell and protecting the public health in preventing the spread of diseases. In the type of treatment, coagulant agents are added to significantly increase dewatering capacity of manure. Coagulants carry together solid particles from manure effluents to allow a fast settling. Carrying small particles together can also improve solids removal by filtration. Because of the corrosive and extreme slippery nature, coagulants should be handled with care (OSU 2000). Increasing pH around 12 for half an hour is generally done when dealing with chemical treatment. Lime is normally used to increase the pH of the manure effluent. The use of lime to increase the pH may also present a limitation. In most cases there is a direct loss of ammonia in the form of emissions from the manure. These emissions have negative impacts on the human health by causing irritation, burning and lung damage. Therefore, it is not appropriate to add lime to manure effluents in areas that are not properly ventilated or confined (OSU 2000). Chemical treatment method eliminates most of the pathogens present in the manure; consequently, odours are eliminated and the spread of disease will be limited.

4 Bioconversion Processes of Manure Effluents

4.1 Anaerobic Digestion and Aerobic Digestion

Bioconversion processes for manure effluents are mainly based on biological treatment; they involve aerobic or anaerobic digestion by using naturally occurring microorganisms in manure effluents to generate useful products such as methane, carbon dioxide, treated effluent, biomethanol and bioethanol. Aerobic digestion allows the decomposition of manure effluents or any biodegradable wastes in the presence of oxygen. It can be undertaken in aerobic lagoons which stabilize the manure by addition of oxygen as mentioned earlier. Aerobic digestion consists of one step containing one process through which microorganisms are allowed to convert manure effluents to carbon dioxide and water. They have an advantage of limiting the generation of odours; they are smaller than anaerobic lagoons; however, they require regular maintenance and are energy-demanding (Tallou et al. 2020; Loyon 2017).

Anaerobic digestion is known as one of the most used technologies for biodegradable wastes, including manure effluents, because of its effectiveness and the nature of manure/biodegradable wastes which are well adapted to anaerobic digestion. Anaerobic digestion is a process dealing with the biodegradation of manure/wastes by living organisms in the absence of oxygen. It can be achieved in anaerobic digesters or lagoons (Tallou et al. 2020; Loyon 2017; Yao et al. 2020). Digesters decompose manure effluents or any biodegradable waste into a biogas that can be used in energy applications (Bharathiraja et al. 2018). Anaerobic lagoons may be enclosed for gas collection. Uncovered anaerobic lagoons are generally hundred times greater than anaerobic digesters (OSU 2000). Biological treatment of manure effluents deals with microorganisms in manure to modify its properties under operating conditions. Anaerobic digestion is made of four main steps described as follows: hydrolysis, acidogenesis, acetogenesis and methanogenesis. In the last phase (methanogenesis) the manure is transformed into biogas by living organisms. Biogas is a mixture of CH_4, CO_2, N_2, H_2, CO, O_2 and H_2S. Between 60 and 80% of the biogas is made of CH_4, and the rest is made mostly of CO_2. Generally, N_2, H_2, CO, O_2 and H_2S are detected in trace amounts (Roos 1997). Methane (CH_4) in biogas is comparable to natural gas. After scrubbing it is possible to use it in combustion engines to run generators for electricity production (Rozdilsky 1997). The electricity can be used on the farm or it can also be sold to the close community if there is an available market for it. Biogas may also be used for other needs on site as source of energy for boilers, heaters, refrigeration, cooking and lighting. Furthermore, nitrogen (N_2) is transformed into ammonia (NH_3) during digestion. NH_3 is one of the key components needed to produce commercial fertilizers. The anaerobic digestion of manure effluents generates a uniform and predictable product. Furthermore, anaerobic digestion can also generate solids by-products with a wide range of applications. These solids by-products can be used as substrates in compost aiming to provide sources of carbon and nutrients. Figures 6 presents the advantages and disadvantages for anaerobic digestions for manure effluents.

There are numerous sorts of digesters. They are designed with particularities related to types of manure/biodegradable wastes and operating conditions. Table 1 presents a summary of different types of digesters used for anaerobic digestion of manure.

4.2 Composting of Manure

This is an aerobic biodegradation of manure/ organic wastes under thermophilic conditions between 40 and 65 °C (UNL 1998). It is an established on-farm manure technology. In this process organic matter present in manure is subjected to biodegradation or decay process which is taking place in a pile. Due to the fact that oxygen is important in the composting process, the pile must be mixed frequently to integrate oxygen and to be assured about the composting of the less disintegrated material at the pile's edge (Purdue 1996). It should be done when there is no reheating of the pile after its mixing (Purdue 1994). The energy released during the biodegradation process increases the compost temperature in order to speed up the decomposition of organic matter and allow the evaporation of water. This will result in a dried and stabilized compost within 3 to 6 months. The main limitation on composting is the condition for a dry bulking amendment required to generate a suitable porosity in

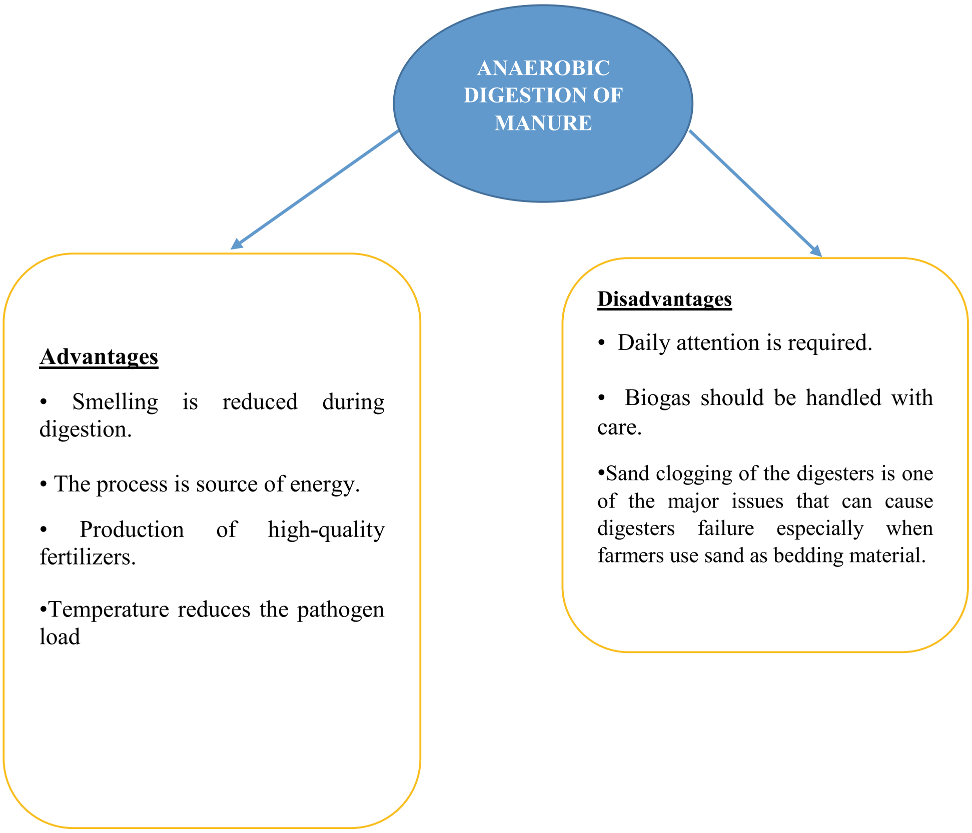


Fig. 6 Advantages and disadvantages of anaerobic digestion for manure effluents

Advantages

- Smelling is reduced during digestion.
- The process is source of energy.
- Production of high-quality fertilizers.
- Temperature reduces the pathogen load

Disadvantages

- Daily attention is required.
- Biogas should be handled with care.
- Sand clogging of the digesters is one of the major issues that can cause digesters failure especially when farmers use sand as bedding material.

Table 1 Summary of some digesters used for manure treatment

Digester	Characteristics	References
Complete-mix digester	Convenient for organic wastes having 3–10% solids content	USEPA (1997a)
Plug-flow digester	No mixing, and it can be loaded with manure that can have 11–14% solids content. There is an addition of a new ‘plug’ on daily basis which gradually drives off the old manure down the tank	USEPA (1997b)
Covered lagoon digester	It is made of a floating impermeable cover placed over the surface of a manure treatment lagoon. Covered lagoons can be used at both swine and dairy operations. It operates better when the manure is handled as a liquid and in the warm climate	USEPA (1996)
Loop digester	It is convenient for solids-rich suspensions. A loop digester generally operates with 11–13% total solids slurry	Rozdilsky (1997)
Advanced integrated pond system	They are simple in their design and very reliable. Biogas is collected from the cover. Effluent discharge is achieved into a second pond which should be a reliable algae growth media	Rozdilsky (1997)
Anaerobic Sequencing Batch Reactor (ASBR)	Anaerobic reactor uses the following steps: filling, reaction, settling, decanting. During the filling phase, the basin receives influent wastewater. Odours, nutrients, COD, BOD, suspended solids are removed in the manure effluent. The system is capable of effective removal of N_2 and P. Capital and operating costs may be higher	Mahvi (2008)

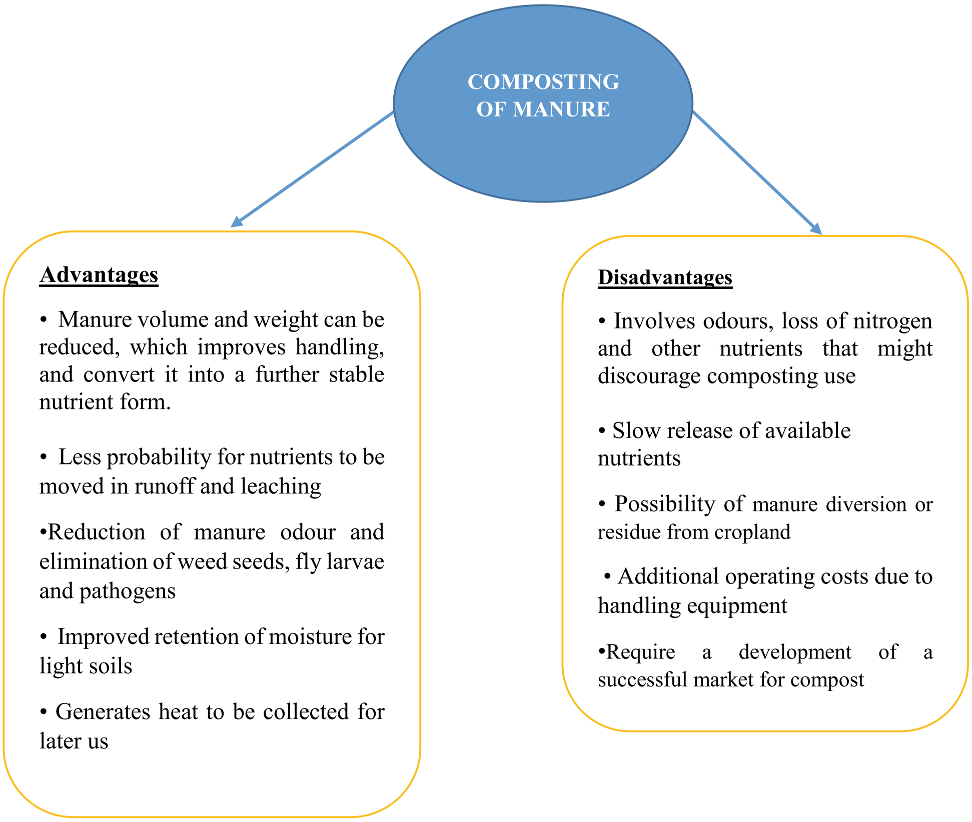


Fig. 7 Advantages and disadvantages of composting manure effluents

COMPOSTING OF MANURE

Advantages

- Manure volume and weight can be reduced, which improves handling, and convert it into a further stable nutrient form.
- Less probability for nutrients to be moved in runoff and leaching
- Reduction of manure odour and elimination of weed seeds, fly larvae and pathogens
- Improved retention of moisture for light soils
- Generates heat to be collected for later us

Disadvantages

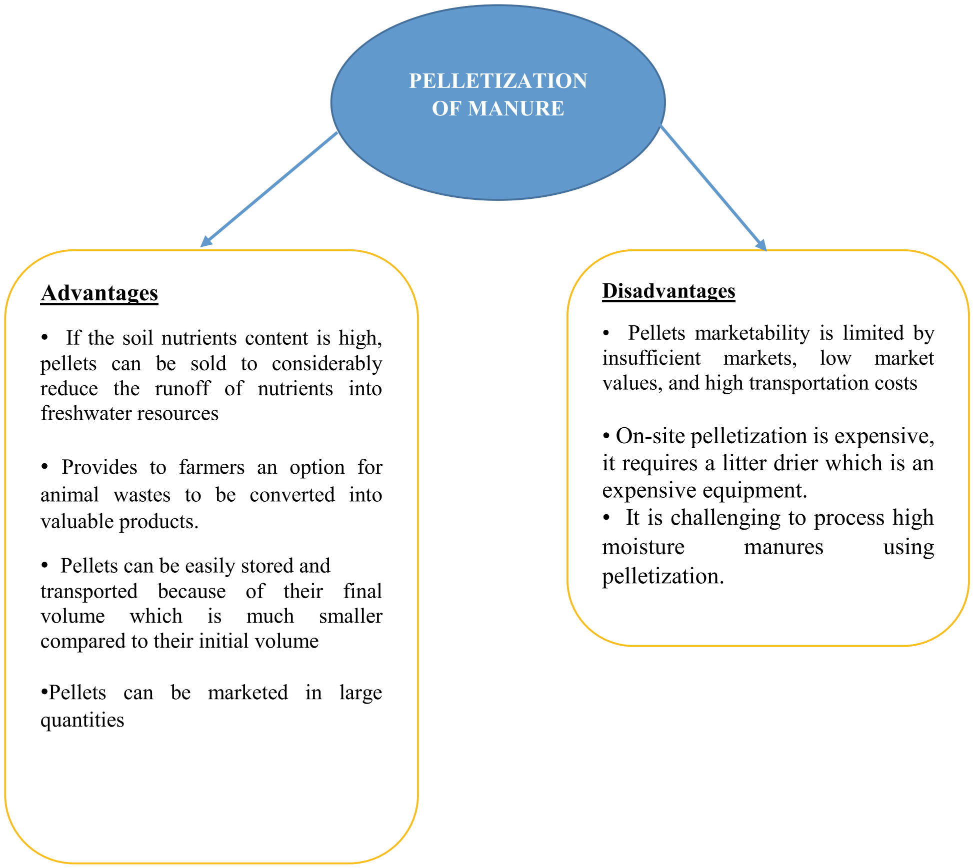
- Involves odours, loss of nitrogen and other nutrients that might discourage composting use
- Slow release of available nutrients
- Possibility of manure diversion or residue from cropland
- Additional operating costs due to handling equipment
- Require a development of a successful market for compost

manures with high moisture content. This condition can be removed with the use of solids separation technology. The final product which is the compost is known to be odourless with little moisture percentage, and a fine textured substance may be used as a fertilizer or used in nurseries and gardens (UNL 1998). It is also an important source of N_2, organic molecules and nutrients. Nitrogen (N_2) in compost is not freely accessible as it is the case of N_2 in manure effluents. Furthermore, the levels of K, P, and micronutrients in the compost are equal to or greater than the one in manure effluents. The most important factors influencing the composting rate and its effectiveness are described as follows: carbon to nitrogen (C:N) ratio, water content, temperature, aeration rate and the physical texture of organic matter representing the particle size. The optimum temperature for composting is around 56 °C. Despite the fact that the internal part of the pile may normally reach this temperature, the external part does not. Consequently, the pile must be mixed as mentioned before to ensure the effectiveness of manure composting (Purdue 1994). Moisture is a key factor requiring maintenance for optimal composting. At higher levels of moisture, cavities are packed with liquids and subsequently preventing aeration. Therefore, drying is from time to time indispensable. This helps in getting an optimum moisture percentage and eventually raising the effectiveness of composting (Purdue 1994). The addition of a bulking ingredient may assist in reducing moisture (UNL 1998). At lower levels of moisture, the microbial action is delayed or prevented. The C:N ratio is fundamental in order to ensure that the needed quantities of C and N_2 are accessible for microorganisms because they use carbon as a source of energy and nitrogen as a nutrients source. In the event the ratio C:N is smaller than 20:1, N_2 will outflow as NH_3; in case the amount of carbon is higher, the biodegradation rate may decline (Purdue 1994). The ideal ratio should be 30:1; the optimum C:N ratio should be maintained to stop the loss of N_2 and to make sure that composting process can be fast (Purdue 1994). Aeration is an important process because it helps maintain effective composting. The biodegradation rate is higher with small particles due to the fact that they have a large surface area providing living organisms with more sites for degradation (Purdue 1994). Figure 7 summarizes the advantages and disadvantages of this technology.

4.3 Pelletization of Manure

This process deals with solids manure after separation from the liquid fraction. The solid fraction of the effluent is a raw manure that is rich in nutrients and can be transformed into a high-grade, pasteurized, pelletized organic fertilizers.

Fig. 8 Advantages and disadvantages related to pelletization of manures



Advantages

- If the soil nutrients content is high, pellets can be sold to considerably reduce the runoff of nutrients into freshwater resources
- Provides to farmers an option for animal wastes to be converted into valuable products.
- Pellets can be easily stored and transported because of their final volume which is much smaller compared to their initial volume
- Pellets can be marketed in large quantities

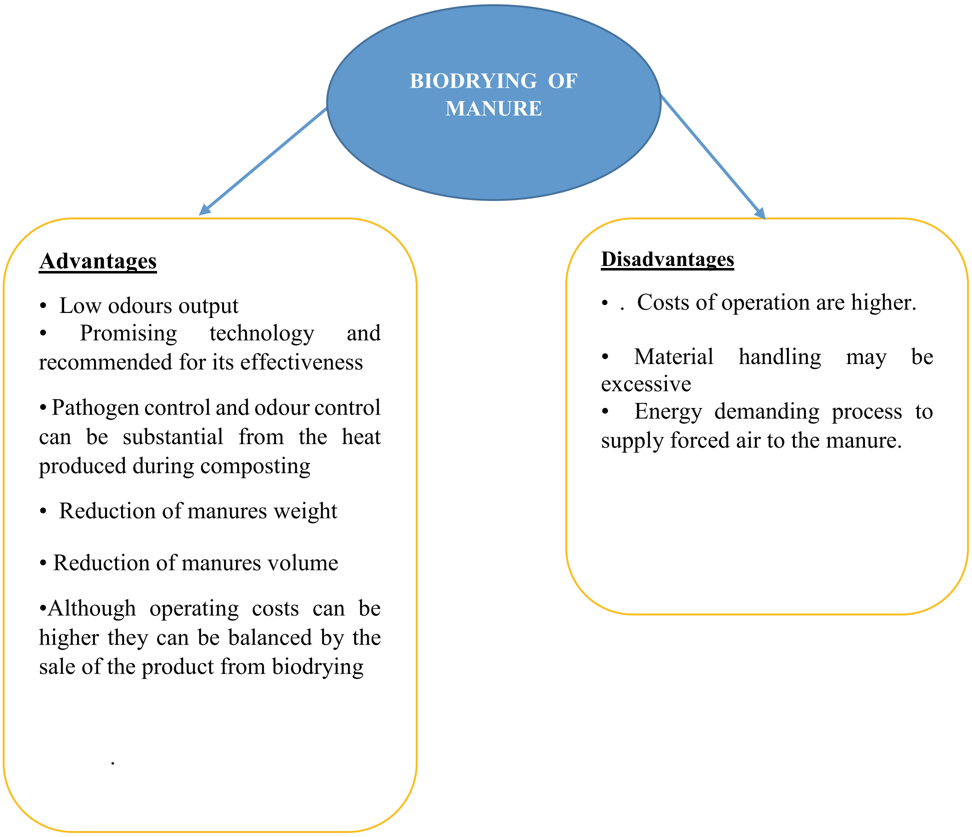
Disadvantages

- Pellets marketability is limited by insufficient markets, low market values, and high transportation costs
- On-site pelletization is expensive, it requires a litter drier which is an expensive equipment.
- It is challenging to process high moisture manures using pelletization.

Extrusion process is completed after pasteurization in order to convert new manure into a dry one without pathogens and to handle it easily; this is a final product that may serve as a fertilizer, amendment of soils, additive to animal feed or energy applications (USPEA 1998). Finally, compaction of manure under well-defined operating conditions at higher pressure and temperature is undertaken; this is followed by a compression into a die to make pellets. Figure 8 presents some advantages and disadvantages related to pelletization.

4.4 Biodrying of Manure

The aerobic disintegration of drying the manure/compost mixture or any organic waste with forced air constitutes a process called biodrying (Moharir et al. 2019). This option is achieved by reusing dry compost as the adjustment to composting under moderate temperature in a forced air environment. Managing the drying process is a serious aspect to be considered in this process. The process can make available a certain amount of energy to decrease 12% DM manure to a 60% DM residual. Forced air current used for composting, under a roof, with the flow of air monitored cautiously may assist in optimizing this process. Composting works effectively when the original moisture level is lower than 70%. Biodrying process may possibly allow the composting of many types of manure with minor adjustment. The compost will be compacted at half in volume and its weight will be reduced to one-sixth from its original size. This is possible because of loss of water and the sublimation due to the transformation of solids to gas. Pathogens and odour monitoring will be an important aspect to be considered in this situation. The heat generated through the composting process has revealed that there is substantial reduction of pathogens viability. This aerobic contribution of composting will subsequently end up in generating an insignificant amount of odour if managed appropriately (Bernal et al. 2017). The storage and dissemination of high solids product would decrease the probability of runoff and remove the possibility of the storage system failure. Even though the air control/temperature feedback system may need automation for the optimization of the removal of moisture, the system will still be satisfactory with regard to managing the skills of the majority of farm operators. Solid handling of odourless product will have the capacity to make the spreading of manure more flexible. Biodrying is a common process used in conversion of manures and has been recommended in many cases with results that are conducive (Moharir et al. 2019). Figure 9 presents the advantages and disadvantages of biodrying of manures.



Advantages

- Low odours output
- Promising technology and recommended for its effectiveness
- Pathogen control and odour control can be substantial from the heat produced during composting
- Reduction of manures weight
- Reduction of manures volume
- Although operating costs can be higher they can be balanced by the sale of the product from biodrying

Disadvantages

- . Costs of operation are higher.
- Material handling may be excessive
- Energy demanding process to supply forced air to the manure.

Fig. 9 Advantages and disadvantages related to biodrying of manures

4.5 Gasification of Manures

Gasification is a process that uses heat for the conversion of manure into a clean fuel gas. This is an endothermic procedure converting manure into a gas with low or medium heat of combustion (Watson et al. 2018; Widjaya et al. 2018). It is achieved with various types of gasifiers such as low-pressure gasifiers, fixed bed gasifiers and fluidized bed gasifiers. There are numerous types of gasification processes available; they depend on the type of biomass, manure or any other matter (Watson et al. 2018; Widjaya et al. 2018). The conversion of manure into a gas provides a remarkable flexibility in the way that energy is being produced. The gasification process can be completed in a fast way called pyrolysis. This is a catalytic process in which volatile components of the manure are vaporized during heating at a temperature around 600 °C or more (Watson et al. 2018; Widjaya et al. 2018). The char and ashes constitute the non-vaporized by-products from pyrolysis. Char being the fixed carbon fraction from pyrolysis can be gasified with oxygen, steam and hydrogen after pyrolysis (Watson et al. 2018; Widjaya et al. 2018; Guo et al. 2020). A fraction of the char which is not burned is finally burned to discharge the heat needed for the endothermic reactions during gasification. Manure effluents present an opportunity to produce clean and renewable fuels from the gasification process if the relevant catalysts are used and the optimum operating conditions are established. Figure 10 summarizes the advantages and disadvantages of gasification of manure.

4.6 Methanol Production from Manure

Methanol is an alcohol made from natural gas, biomass or organic matter. Biodegradable wastes including manure constitute the raw material that can be converted to methanol. It is called biomethanol when made from these sources. Methanol can be considered as a liquid fuel because it burns much like gasoline. It is generally used as gasoline fuel additives and in the manufacturing of many chemicals. It can also be considered as a promising source of energy in the transportation sector (fuel). Generally, methanol is produced from synthesis gas (syngas) which is a mixture of CO, CO_2 and H_2 at 50–100 bar with temperature in the range between 250 and 300 °C, using copper and zinc-based catalysts or any other relevant catalysts. These catalysts are already active at 200 °C and selective towards the formation of H_2 and CO_2. This is achieved through the anaerobic digestion or gasification of the manure, biodegradable solid wastes or any other feedstock (El-Mashad et al. 2011; Nanda et al. 2016; Blug et al. 2014; Noor and Kamarudin 2014). Briefly, the process is achieved in two stages: First, the

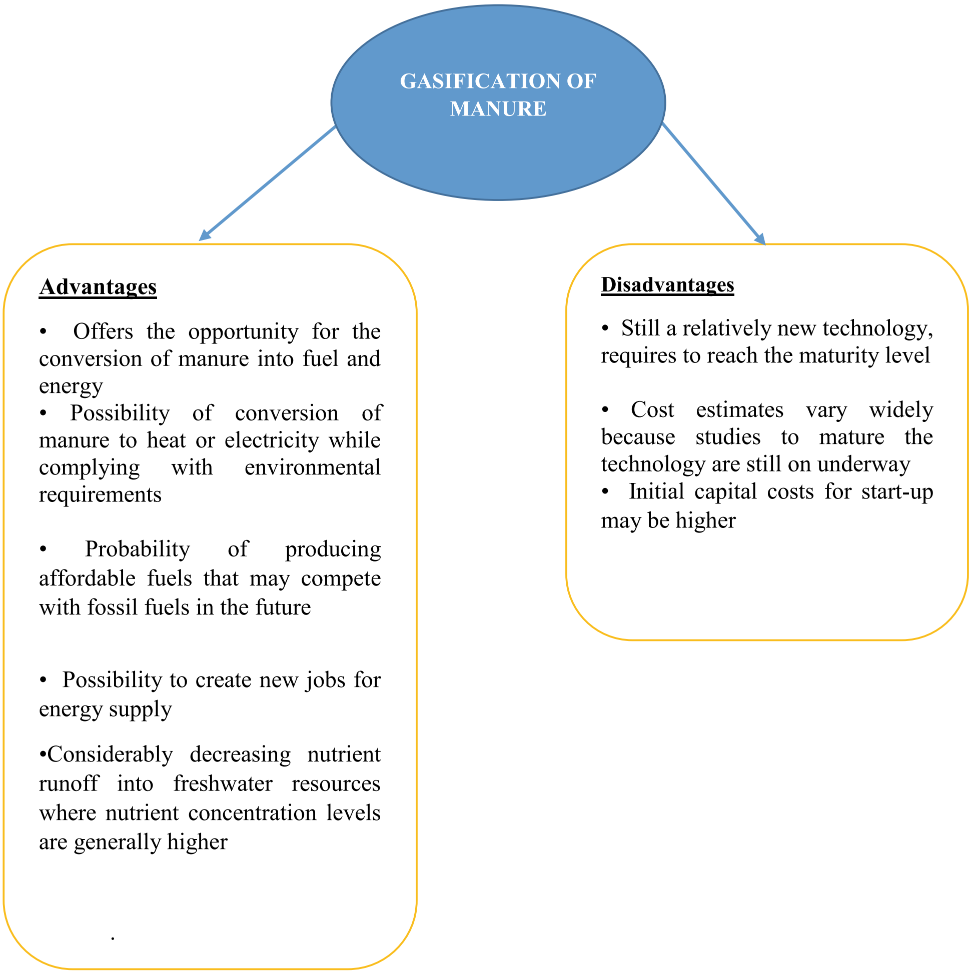


Fig. 10 Advantages and disadvantages related to gasification of manures

Advantages

- Offers the opportunity for the conversion of manure into fuel and energy
- Possibility of conversion of manure to heat or electricity while complying with environmental requirements
- Probability of producing affordable fuels that may compete with fossil fuels in the future
- Possibility to create new jobs for energy supply
- Considerably decreasing nutrient runoff into freshwater resources where nutrient concentration levels are generally higher

Disadvantages

- Still a relatively new technology, requires to reach the maturity level
- Cost estimates vary widely because studies to mature the technology are still on underway
- Initial capital costs for start-up may be higher

manure or feedstock is transformed into a syngas stream from the gasification process. Secondly, the synthesis gas is converted to methanol via the use of catalysts as mentioned earlier. The synthesis of methanol from manure or any feedstock is an exothermic process; for that reason, the extra energy can be used to generate electricity needed in the process (Noor and Kamarudin 2014; Belete and Ayza 2015). The storage and transportation of methanol are done in similar way as it is for gasoline and diesel. They are even easier compared to other transportation fuels. Methanol usage eases the reliance on non-renewable energy alternatives while resolving issues concerning manures and other biomasses used for energy production (Ak and Demirbas 2016). Figure 11 presents a summary of advantages and limitations related to methanol production from manure.

4.7 Cofiring of Manure with Base Fuel

This is a simultaneous combustion of manure and a base fuel which can be wood, coal or any other base fuel. It is identified as a promising option regarding the use of manure in heat and electricity generation (Tillman 1999). The heat generated from cofiring may be useful in steam or power plants where boilers are producing high pressured steam for the generation of electricity. The boiler takes in energy from the combined combustion of manure and base fuel to heat water and convert it into steam. Some technologies using boilers have been assessed with the cofiring process (EREN/DOE 2000). Stoker-grate firing systems with animal manures are now commercialized. Cofiring is achieved with wood shavings, straw, or both, rather than coal with manure (Antares Group Incorporated et al. 1999).

Generally, the key components in the costs of a cofiring process are the base fuel costs and the capital costs of adapting the processing plant where cofiring is being undertaken (Plasynski 1999). Costs are affected by the accessibility of a site for yarding, biomass storage, drying facilities and the boiler types. The boiler efficiency is always significant after the adjustment of combustion output regarding the mixture of the new fuel mixture. This implies that the efficiency of biomass combustion to electricity will

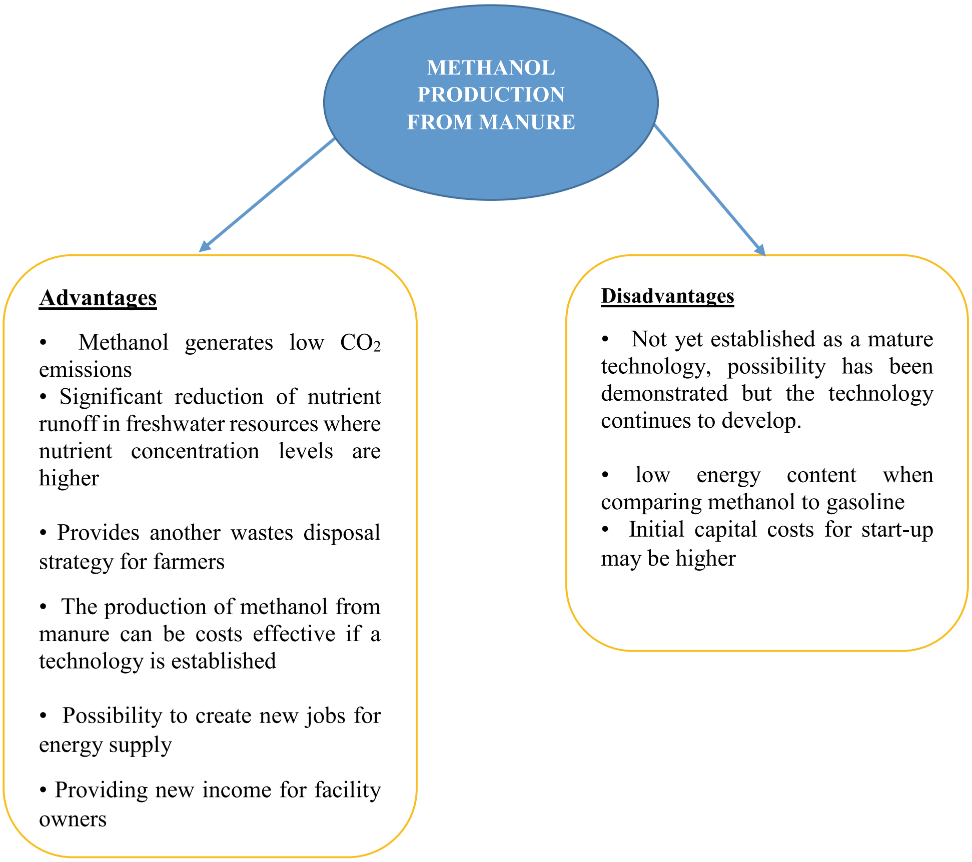


Fig. 11 Advantages and disadvantages related to methanol production from manure

METHANOL PRODUCTION FROM MANURE

Advantages

- Methanol generates low CO_2 emissions
- Significant reduction of nutrient runoff in freshwater resources where nutrient concentration levels are higher
- Provides another wastes disposal strategy for farmers
- The production of methanol from manure can be costs effective if a technology is established
- Possibility to create new jobs for energy supply
- Providing new income for facility owners

Disadvantages

- Not yet established as a mature technology, possibility has been demonstrated but the technology continues to develop.
- low energy content when comparing methanol to gasoline
- Initial capital costs for start-up may be higher

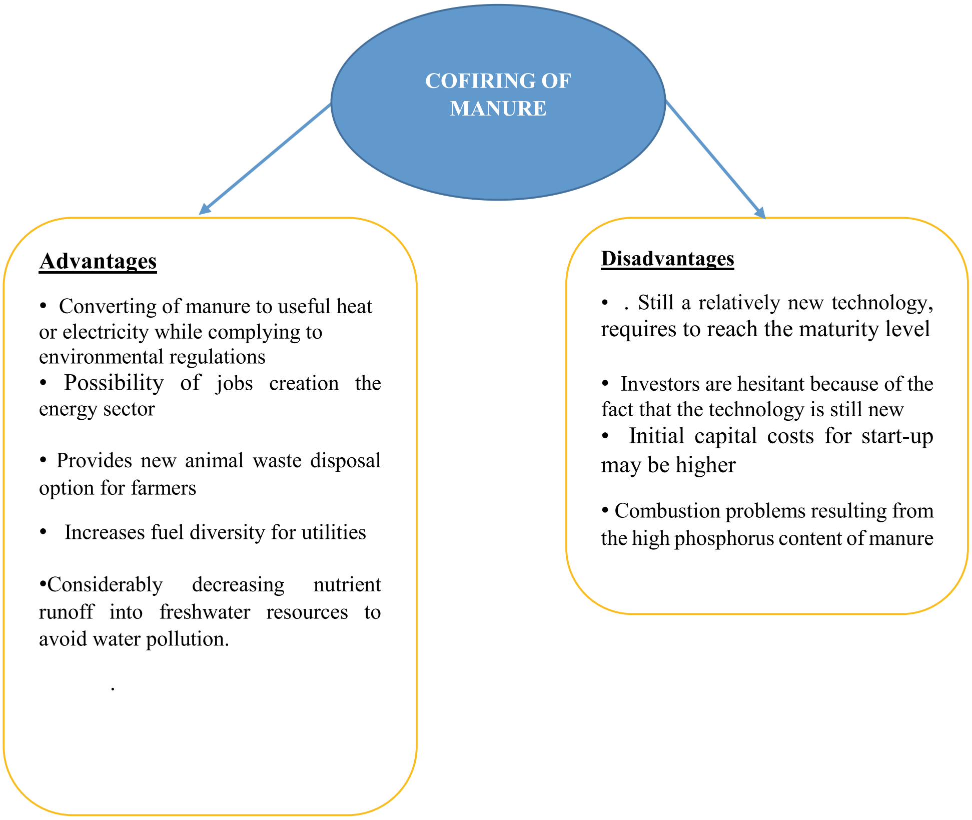


Fig. 12 Advantages and disadvantages related to manure cofiring

COFIRING OF MANURE

Advantages

- Converting of manure to useful heat or electricity while complying to environmental regulations
- Possibility of jobs creation the energy sector
- Provides new animal waste disposal option for farmers
- Increases fuel diversity for utilities
- Considerably decreasing nutrient runoff into freshwater resources to avoid water pollution.

Disadvantages

- . Still a relatively new technology, requires to reach the maturity level
- Investors are hesitant because of the fact that the technology is still new
- Initial capital costs for start-up may be higher
- Combustion problems resulting from the high phosphorus content of manure

Table 2 Emerging applications of manure effluents

Applications	Characteristics	Reference
Algae production	Biological process in which algae or any photosynthetic microorganisms are cultivated using the nutrients in manure for their growth. In this process a crop of microalgae is produced and harvested biomass can be used as a fertilizer. Also, high-protein animal feed supplements can also be produced from this application. The product can be sold and a clean effluent can be generated from the process	ACFA (2000a)
Aquaculture	Using manure in aquaculture is cost effective. Combining manure with high-protein feed reduces the growth of aquatic organisms. Therefore, it is recommended to use manure on its own in aquaculture	ARS (1998)
Bedding or Litter	The solids from manure effluents can be used as bedding or litter after separation with the liquid fraction. Litter is a combination of various feedstocks including manure. It is used by farmers as an affordable fertilizer for cropland	Purdue (1996)
Building/construction material	Cow manure can be processed into fiberboard to be used in the construction industry	Belsie (2000) ISU (2000)
Soil Reclamation	Increases the content of organic matter in the soil. The structure of the soil is also improved when doing soil reclamation with manure or other organic wastes, water retention of sandy soils can be increased, contribute to slow release of nutrients, and supports the development of beneficial soil microorganisms	ACFA (2000b)

be close to the range between 33 and 37% of the coal firing (DOE 2000). Figure 12 presents the advantages and disadvantages of cofiring of manure and base fuel.

4.8 Emerging Technologies for Manure Conversion

Many options developed in the previous sections relate to the technologies that are generally used for conversion of manure effluents for the last few decades. There are emerging technologies which are growing and they could be soon competing with the existing ones. Table 2 presents some emerging applications for the conversion of manure effluents that can be used.

5 Conclusion

Bioconversion of manure effluents may be considered as a promising and environmentally friendly option. The conversion options are identified as effective and they can be beneficial for the farming and agricultural industry. They deal with the issue of waste management in the farming and agricultural environment. Many studies are underway for optimizing the existing and developing the emerging bioconversion processes. Some of these processes end up in the production of clean and renewable energy. Consequently, bioconversion of manure effluents can generate various by-products which are useful for the farmers and energy industry.

There are many ways to convert manure effluents. Some of the processes are physical, chemical or biological. Bioconversion of manure effluent involves biological reactions in bioreactors. Bioconversion technology involves bioprocessing phases that can be liquid, solid or gas. In this study the main focus was on bioconversion of manure effluents and their outcomes. Prior to the bioconversion processes, an overview of physical treatments for manure effluents can be undertaken depending on the applications, the types of manure and the objectives. These physical treatments include daily spreading, liquid effluent storage, solids separation, odour control and lagoon treatment. These processes do not involve major transformation when it comes to the nature of the manure effluents and its content. They are generally used for conditioning the liquid or solids from the effluent. The final product from these treatments can be either the liquid or the solids fraction of the manure effluent. It is obvious that the final product can be used for relevant applications such as daily spreading and solids separation in the farming environment depending on the needs. Also, chemical treatments can be undertaken generally when there is a need of improving the removal efficiency for solids, pathogens and odours. There are effective methods being used in farming activities with the addition of coagulating agents and pH regulator to significantly improve the quality of the final product being treated from manure effluents.

They can be costly because of the amount of chemicals to be used and may cause contamination of the manure if used in excess.

The main focus being bioconversion as mentioned earlier, aerobic and anaerobic digestion are among the major processes used in the biological conversion of manure effluents or manure only as solid waste. These two processes are well known for their effectiveness under specific operating conditions. This can be possible with the use of oxygen or without oxygen for aerobic and anaerobic digestion respectively. It is very essential to stress on the fact that anaerobic digestion has a large ground of applications for bioconversion of manure effluents. It is generating by-products such as biogas and hydrogen to be used in the energy sector. However, aerobic digestion is also important in the treatment of manure effluents because it generates clean effluent and CO_2. Composting is an aerobic treatment that is used to process manure or any other organic feedstock at thermophilic temperatures. It is known as an on-site and reputable process for manure treatment. In this process organic matter present in manure is subjected to a decay which is taking place in a pile. Composting can effectively reduce manure odour, remove completely the weed seeds and pathogens, and it can also improve the retention of moisture for light soils. Biodrying is also another aerobic process using forced-air for drying manure or compost mixture. The merit of the process is such that odour, volume and weight of the manure are reduced including the availability of handling equipment for solid particles on many farms; however, the operating costs may be higher. Pelletization of solids manure is achieved through an extrusion technique. The manure being rich in nutrients is converted into high-grade, pasteurized, pelletized organic fertilizers. This process provides a great option to farmers in order for them to deal effectively with wastes management and avoid the contamination of neighbouring freshwater resources from nutrients runoff. However, the marketability of pellets is limited coupled with high transport costs. Gasification or pyrolysis is also a sustainable and effective conversion process; undertaken at around 600 °C with the assistance of biocatalysts/catalysts for the conversion of manure into clean fuel. It is generally a two-step endothermic process because after pyrolysis the char undergoes a gasification with oxygen, hydrogen and steam, to collect as much gas from the manure. The fraction of unburned char will produce enough heat for endothermic gasification reactions. From this process clean fuel, electricity and heat can be produced while complying with environmental regulations. Furthermore, from gasification or anaerobic digestion of manure, it is possible to produce methanol. In this regard syngas is produced first, followed by its synthesis to generate methanol. The process can be cost-effective, however, initial capital costs are higher. Cofiring process is also a conversion process that combines the combustion of manure and a base fuel to produce heat that can be useful for power plants or steam plants. Cofiring manure and base fuel have recorded some success and show promise for the future. The process can also generate electricity by using a pressured steam from a boiler into a turbine. However, the technology is still new and many studies should be completed before reaching the maturity level.

There are also applications dealing with microalgae production, aquaculture, use of manure in building industry, manure bedding or litter and soil reclamation using manure which are considered as emerging technologies. Their growth could add up on the list of bioconversion processes for manure effluents once they reach the commercial stage with a certain level of maturity.

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Application of Hemicellulose in Biohydrogen Production

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Abstract

This chapter discusses the sources, the structure and the characteristics of hemicellulose, methods of biohydrogen production, pretreatment methods of lignocellulose material and the steps involved in the bioconversion of hemicellulose to hydrogen gas. The depletion in fossil fuel reserves, coupled with high dependency on its usage, tends to create a crisis in energy around the globe. Moreover, the rise in fuel price, along with the increasing demand resulting from high population density, has led to more research for alternative sources of energy. The environmental pollution (such as the emission of greenhouse gases and ozone layer depletion) resulting from utilizing fossil fuel and its related products is another source of concern to the research community as it constitutes harm to mankind. Hydrogen gas has a lot in stock for the global energy demand, because of its high energy content. It is renewable and eco-friendly. Hydrogen gas can be produced from biological materials like hemicellulose.

Keywords

Hemicelluloses • Biohydrogen • Biophotolysis • Dark fermentation • Photo fermentation • Lignocellulosic pretreatment

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1 Introduction

Considering the detrimental effects of fossil fuel usage on the environment and energy depletion, it is necessary to produce clean-burning and renewable energy that can replace fossil fuel energy sources (Cao et al. 2014). Bio-based economy is a strategy employed to lower the environmental pollution the world is facing currently from using fossil fuel products (Farhat et al. 2017; Bugge et al. 2016). Products generated from renewable resources represent a better option as opposed to products based on depleting non-renewable supplies, and allows a move toward enhanced energy security and less environmental effects (Jönsson et al. 2013) through a reduction of greenhouse gas emissions (Wu et al. 2013).

Lignocellulosic biomass is the most abundant raw materials for biohydrogen generation and its usage does not compete with food production. It is the only renewable energy source of carbon. Lignocellulosic biomass is made up of cellulose, hemicellulose and lignin as main components as well as pectin, protein and minerals in small amounts (Zhou et al. 2017). Hydrogen gas is the most promising energy of the future that is generated from various resources and can easily be stored. It is a clean carbon dioxide-free gas (Wu et al. 2013). Also, it has the highest energy content when compared with other gaseous fuels with a value of 122 kJ/g and is 2.75 times higher than hydrocarbon fuels (Argun et al. 2008). It has been described as an energy carrier which does not imply it being an energy source (IRENA 2018).

Bioconversion is the conversion of organic materials such as plant or animal waste (usually referred to as biomass) into usable products or energy sources by biological processes or agents. Utilizing plant wastes as recycled feedstock is a means for reducing the reliance on fossil oil (Delbecq et al. 2018; Aresta et al. 2012). Biomass is an important raw material for the sustainable generation of bioenergy and chemicals, with lignocellulosic biomass being the most copious in supply. Lignocellulosic biomass plays a major

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role in substituting fossil oil. Half of it is made up of cellulose while three-tenths is hemicellulose, with the remaining containing more of lignin. The biomass-derived glucose feedstock is a major operating cost driver for hydrogen gas production via fermentation (Maness et al. 2005; Giuseppe et al. 2019). Among the various renewable energy sources, biohydrogen is gradually gaining research interest due to its high efficiency. Several methods are readily available to generate biohydrogen from lignocellulosic biomass such as direct biophotolysis and dark fermentations (Kusmardini et al. 2018). The share of hydrogen in the energy market is increasing with the implementation of fuel cell systems and the growing demand for zero-emission fuels (Milne et al. n. d) making microbial hydrogen production route an important approach.

2 Hemicellulose

Hemicellulose is an important component present in wood materials in native softwood and hardwood. The main hemicellulose is galactoglucomannan and glucuronoxylan, respectively (Willför et al. 2005a, b; Li et al. 2013). Hemicellulose belongs to a group of heterogeneous polysaccharides which are formed through biosynthetic routes different from that of cellulose. It can also be seen as cell wall polysaccharides that are not characterized as being either cellulose or pectin (Zhou et al. 2017). Table 1 shows the characteristic that differentiates hemicellulose from cellulose. They represent around 33% of dry mass of cell walls depending on the plant feedstock used (Pauly and Keegstra 2010; Pauly and Gille 2013). They are the second most abundant polysaccharides in nature contributing 30% of dry weight of the total lignocellulosics. Several agricultural residues such as corn fiber, wheat straw and sugarcane bagasse contain about 20–40% hemicelluloses (Peng and Wu 2011). It is a part of wood fractions that consists of polymerization (Mansor et al. 2019; Rowell et al. 2005). They are heterogeneous polymers of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose) and uronic acid.

2.1 Hemicellulose Structure

The detailed structure of hemicellulose and its abundance vary widely between species and cell types (Scheller and Ulvskov 2010). Structurally, hemicellulose links lignin and cellulose together. Figure 1 describes the structure of hemicellulose in comparison with cellulose and lignin and their various percentages in lignocellulosic biomass (Amin et al. 2017). Its polymer is branched with several forms of sugar such as pentoses, hexoses and sugar acids. Its major bonds are 1.4 that links ß-D-pyrosyl unit (Hendriks and Zeeman 2008; Glazer and Nikaido 2007). Hemicellulose includes xyloglucans, xylans, mannans and glucomannans and beta-(1—3, 1—4)-glucans (Scheller and Ulvskov 2010). Xylan is the basic constituent of hemicellulose but it is not the only carbohydrate species present in hemicelluloses (Zhang et al. 2015). It is a mixture of polysaccharides that are made up of mostly sugars such as glucose, mannose, xylose and arabinose and methylglucuronic and galacturonic acids (McKendry 2002).

Table 1 Difference between hemicellulose and cellulose

Properties	Cellulose	Hemicelluloses	References
Structure	Crystalline and strong	Random, amorphous structure with little strength	Li (2014), Peŕez et al. (2002)
Response to hydrolysis	Resistant to hydrolysis	Easily hydrolyzed acid or base or myriad hemicellulase enzymes	Li (2014)
Degree of polymerization	1000 units	100–200 units	Peŕez et al. (2002)
Sugar present	Only glucose	Glucose and several others	Peŕez et al. (2002)
Degree of orderliness	Presence of ordered state	Absence of highly ordered state	Li (2014)
Molecular weight	Higher molecular weight	Lower molecular weight	Peŕez et al. (2002)
% dry weight	About 45% dry weight of wood	About 25–30% dry weight of wood	Peŕez et al. (2002)
Structure description	It is a straight chain polymer with no coiling or branching	It is branched with short-sided chains that is made up of diverse sugars	Li (2014, Peŕez et al. (2002)
Stability	High stability because of high degree of polymerization	Low stability	

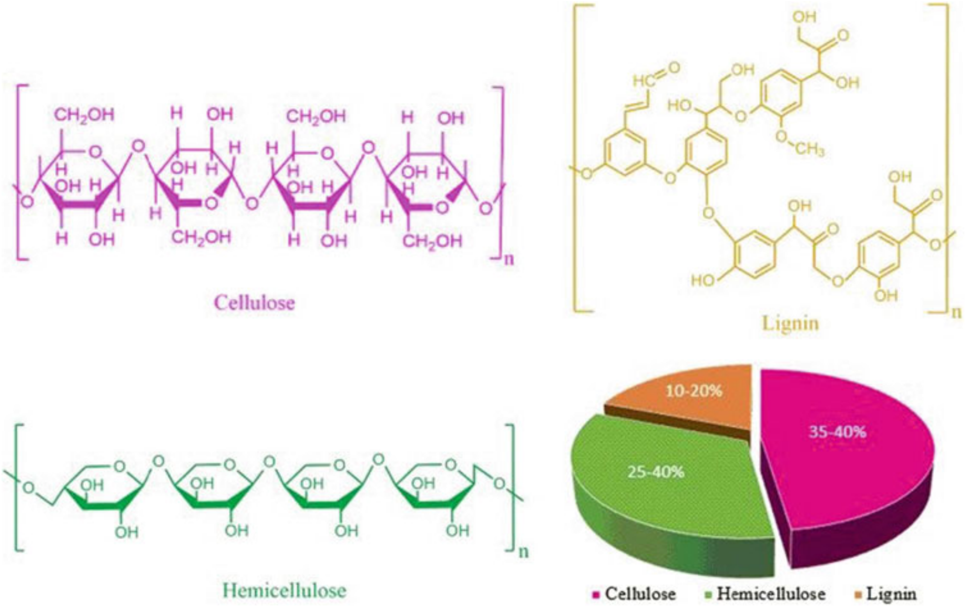


Fig. 1 Structure of hemicellulose in comparison to cellulose and lignin

3 Pretreatment Process for Lignocellulosic Biomass

This is the first and key step in processing of lignocellulosic biomass that helps in their modification to make it accessible for further processes or reactions in order to convert it into biofuel. This involves altering of the structural and compositional complexity of lignocellulose biomass to enhance hydrolysis and better yield of fermentable sugars (Pullammanappallil 2013). Figure 2 depicts the effect of pretreatment on the structural components of lignocellulosic biomass. Lignocellulose materials are usually degraded under certain pretreatment conditions. And several pretreatment techniques have been documented in literature and they are grouped under major headings as physical, chemical, physicochemical and biological pretreatment. Figure 3 shows a detailed classification of the various pretreatment techniques for lignocellulosic biomass. And the product obtained from any of the above-mentioned techniques is dependent on the operational conditions of the entire pretreatment process. The physical method tends to increase the reactive surface area of the lignocellulose biomass by reducing the size into smaller particles, thereby reducing the degree of crystalline creating easy accessibility for enzymes. This method is energy intensive and therefore involves lots of cost (Sun and Cheng 2002). Chemical methods employ chemical substances in the form of acid, alkaline, ionic liquid and organic solvent in altering the complex structure of lignocellulose biomass to their constituent components like cellulose, hemicelluloses and lignin or their reducing sugar equivalent (Zhang et al. 2016; Elgharbawy et al. 2016; Kumar and Sharma 2017). Physiochemical method employs both techniques in physical and chemical methods in pretreatment of lignocellulosic biomass. This method is quite effective because it improves lignin removal and increases hydrolysis efficiency (Apilak et al. 2019). Biological methods employ the use of enzymes and microorganisms in degrading the lignocellulosic biomass. This method is slow and eco-friendly. The detailed benefits and limitations of the four classes of pretreatment techniques are documented in the literature (Kumar et al. 2009; Mosier et al. 2005; Hassan et al. 2018; Seidl and Goulart 2016; Zhao et al. 2009; Avellar 1998; Zhang et al. 2007; Teymouri et al. 2005; Wang et al. 2009).

The choice of pretreatment method to be used must satisfy the following conditions:

i. Avoid size reduction biomass
ii. Preservation of hemicellulose fraction
iii. Less formation of degradation products
iv. Less energy use
v. Use of cheap catalyst and/or cheap catalyst recycle and regeneration of high value lignin co-products (Kumar and Sharma 2017; Wyman 1999).

There are several extraction methods that have been explored in the literature for extracting hemicellulose from its raw materials/sources such as alkaline peroxide extraction, liquid hot water extraction, steam treatment, microwave treatment, ionic liquid extraction, alkaline extraction and dilute acid treatment (Nguyen et al. 2000; Egües et al. 2012; Hasegawa et al. 2004; Palm and Zacchi 2003; Froschauer et al. 2013).

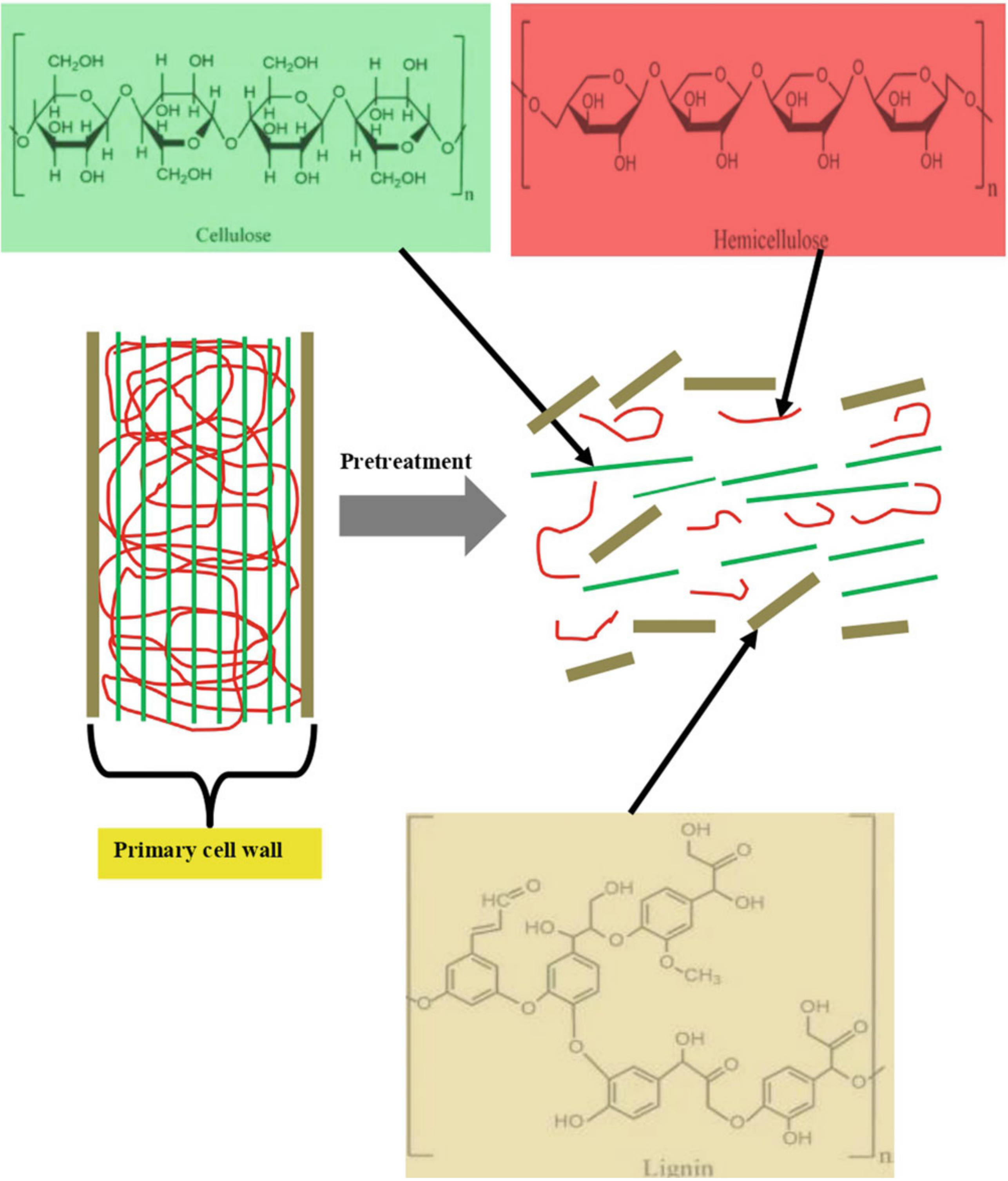
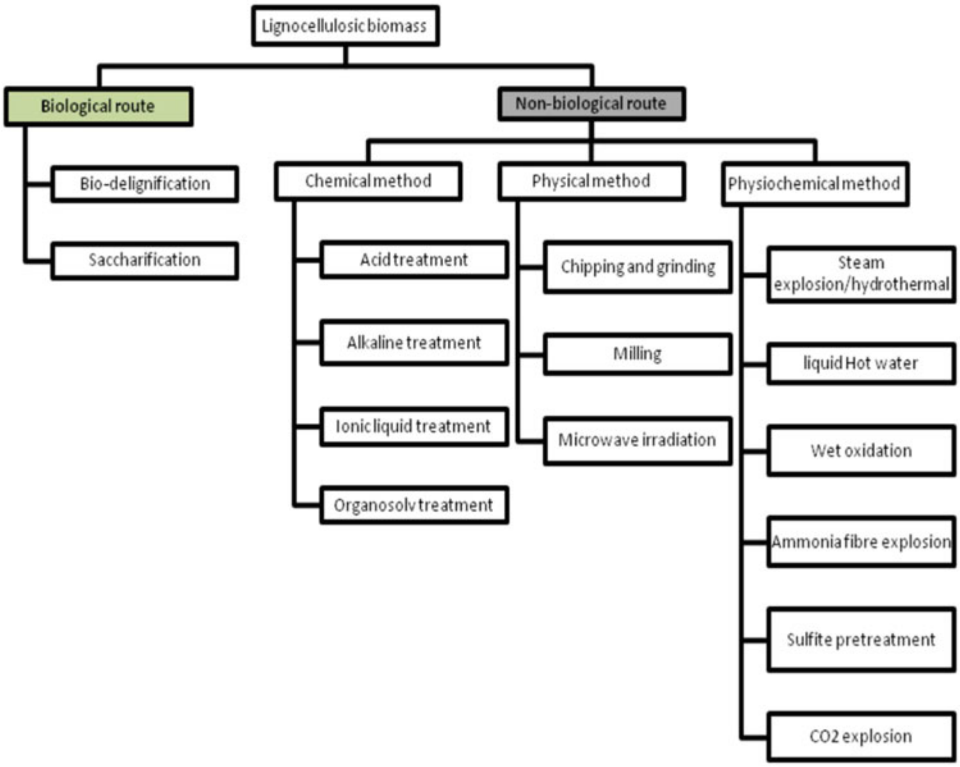


Fig. 2 Effect of pretreatment on structural components of lignocellulosic biomass

3.1 Acid Hydrolysis

This involves the use of acid in the pretreatment process of lignocellulosic biomass. This is the most commonly used method that has gained industrial application despite their high formation of inhibitors (such as furfurals, furan, phenolic acids and aldehydes) (Kanchanalai et al. 2016) and their harmful and corrosive nature. Figure 4 shows the

Fig. 3 Pretreatment techniques for lignocellulosic biomass

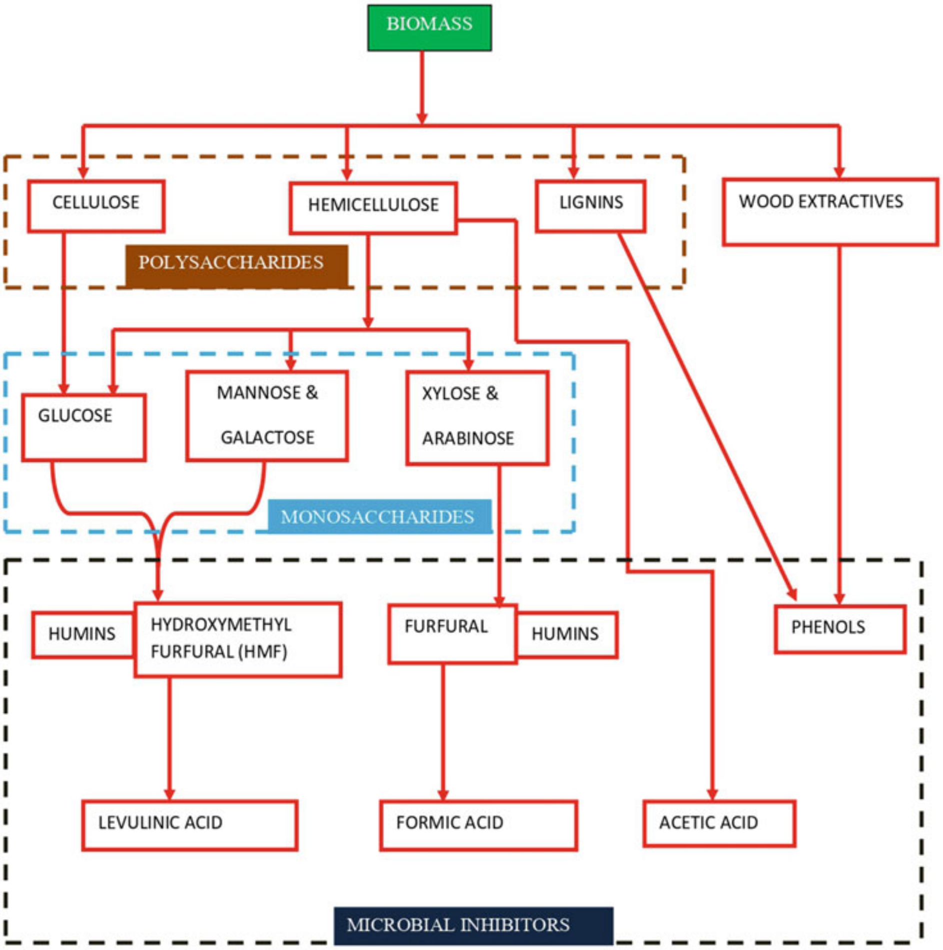


various inhibitors formed during acid hydrolysis and their source. Hydroxylmethylfurfural originates from degradation of glucose, mannose and galactose while furfural originates from degradation of xylose and arabinose. These inhibitors that are formed need to be detoxified to increase easy fermentation of hydrolysates (Laopaiboon et al. 2010; Chandel et al. 2011; Canilha et al. 2013). It is a proven process for treating wood chips, rice straw, sugar beet pulp and wheat straw (Silva 1995; Chamy et al. 1994; Pessoa et al. 1997). Concentrated acid and dilute acid have been used in this method. Research shows that acid hydrolysis of hemicellulose from sugarcane bagasse using sulfuric acid resulted in 83.3% of xylose obtained using semi-pilot reactor (Pessoa et al. 1997). Under concentrated acid usage, which occurs at 70% acid content, low temperature (100%) and pressure follow two steps to achieve sugar production. The first step involves decrystallization at about 70 wt% H_2SO_4 at temperature below 60 °C and the second step consists of hydrolysis at approximate 20–30 wt% H_2SO_4 at temperature range of 80–100 °C (Kanchanalai et al. 2016). It has high cellulose recovery and conversion rate when compared with dilute acid hydrolysis. During this process cellulose and hemicellulose are removed leaving behind a lignin-rich product. Soluble phase is attained under different levels of acid concentration. Acids utilized in this process are sulfuric, phosphoric, hydrochloric, nitric, oxalic (Carvalho et al. 2004) and trifluoracetic acid but sulfuric acid is usually used even though hydrochloric and trifluoracetic are easy to recover. This process can be carried out under low/medium pressure and temperature resulting in a small amount of degradation products. However, it has faced drawbacks like equipment corrosion issues and high operational cost (Hamelinck et al. 2005; Ogier et al. 1999; Carvalheiro et al. 2008). Increasing the temperature and acid concentration increases the hydrolysis and sugar decomposition rates as documented by Kanchanalai et al. (2016). Increasing the temperatures and decreasing the pretreatment times usually improve the recovery of xylose and enhance the accessibility of enzymes to hydrolyze cellulose (Balat et al. 2008). The utilization of concentrated acid hydrolysis is scanty in the literature. Several studies have documented the effective use of acid hydrolysis in pretreatment of lignocellulosic biomass (Świątek et al. 2020).

3.2 Alkaline Treatment

This method is more concerned with solubilization and removal of hemicellulose and lignin from biomass unlike acid treatment that aims at cellulose and hemicellulose removal. This treatment results in cell wall swelling and hydrogen bond disruption between cellulose and hemicellulose. It also breaks ester linkages between hydroxycinnamic acid and hemicellulose (Flórez-Pardo et al. 2018).

Fig. 4 Inhibitors formed during acid hydrolysis and their source



Alkaline used for this process include sodium hydroxides, potassium hydroxides, ammonia and lime. Treatment using hydroxides incurs more cost and has less recovery due to the formation of salts. Utilization of lime seems more promising as it has low cost, assures safety and easy recovery. The commonest used alkaline is sodium hydroxide even though ammonia is considered most effective because it seems possible to recover up to 90% from the process and the leftover ammonia also serves as a source of nitrogen for the fermentation process. Crude xylan extracted with sodium hydroxide showed a compositional analysis of 79% xylose, 5.3% arabinose, 1.7% glucose, 5.6% lignin and ash (Wei et al. 2018). This technique can be an effective process for hemicellulose removal and it has been employed in many studies for extracting hemicellulose from different biomass (Lawther et al. 1996; Vena et al. 2013).

3.3 Hydrothermal Pretreatment

This involves the removal of hemicellulose and some part of lignin from lignocellulosic biomass using water under high temperature and pressure. This process does not require chemicals, hence no need for corrosion-resistant reactors. It includes liquid hot water pretreatment, steam pretreatment and steam explosion pretreatment. Steam explosion yields high solubility of the hemicellulose (generating mainly oligosaccharide) with low lignin solubility (Seidl and Goulart 2016). Combining steam explosion process with enzymatic saccharification is a promising route to enhance the quantity of fermentable sugars (Canilha et al. 2012). Autohydrolysis is a form of hydrothermal treatment that involves breaking down of hemicellulose links permitting the solubilization of reducing sugar and uronic acids. This process also releases the acetyl groups, which results in ethanoic acid formation which amounts to decrease in the pH of the reaction medium, thereby increasing depolymerization rate (Baêta et al. 2016).

3.4 Wet Oxidation

This involves oxidizing suspended or dissolved material in water with dissolved oxygen using high temperature (Tungler et al. 2015). Its disadvantage is that of producing inhibitors that inhibit microbial growth. It can be overcome by using wet oxidation in combination with other pretreatment processes like alkaline hydrolysis to prevent the production of these inhibitors, thereby enhancing the production process of hydrogen gas. Combining wet oxidation with alkaline hydrolysis in treating wheat straw prevented the production of furfural and hydroxymethyl-furfural (Bjerre et al. 1996).

3.5 Enzyme Hydrolysis

This involves the production of monosaccharide from the polysaccharide. Hemicelluloses are usually reduced to fermentable sugars via this process using enzymes. The amount of sugar present in the hydrolysate is dependent on the raw material utilized and the pretreatment route employed before hydrolysis (Robak and Balcerek 2018; Choudhary et al. 2017). Usually, when hydrolysis occurs without pretreatment of lignocellulosic material, high doses of the enzyme are used.

4 Biohydrogen Production

Generally, hydrogen can be produced from biomass using two main routes, namely thermochemical method and biological methods (Hepbasli et al. 2009; Safari et al. 2015). Hydrogen produced via biological routes through the actions of microorganisms on biomass in an eco-friendly manner is known as biohydrogen. Biological methods include fermentation and photolysis. The productivity of each of the production process is measured by the following parameters as given by Eq. 1–5 (Sen et al. 2008):

$$\text{Hydrogen yield} = \frac{\text{Amount of hydrogen produced (mol)}}{\text{Amount of substrate consumed (mol)}} \tag{1}$$

$$\text{Volumetric production rate} = \frac{\text{total amount of hydrogen produced}}{\text{total volume of culture X time duration}} \tag{2}$$

Its unit is given as ml/l/h or mol/l/h

$$\text{Specific hydrogen production} = \frac{\text{amount of hydrogen produced}}{\text{mass of substrate used X time duration}} \tag{3}$$

Its unit is given as ml/g substrate/h or mol/g substrate/h

$$\text{conversion efficiency} = \frac{\text{Amount of substrate utilised}}{\text{Total amount of substrate supplied}} \text{X } 100(\%) \tag{4}$$

where this formula applies to dark and photo fermentation process.

$$\text{conversion efficiency} = \frac{\text{Hydrogen production rate X energy content of hydrogen}}{\text{Absorption rate of light energy}} \text{X } 100\% \tag{5}$$

where the formula applies to light-induced processes (photolysis) and energy content of hydrogen = 241.9 kJ/mol.

4.1 Dark Fermentation

This is an anaerobic conversion of carbohydrates or glycerol into carbon dioxide, carboxylic acid and hydrogen (Sołowski et al. 2019). It involves the degradation of organic compounds by microbes to produce energy and carbon. Hydrogen is produced from carbohydrate-rich substrate or protein and lipid-rich substrate but carbohydrate substrates are more preferred because of their high oil yield (Levin et al. 2004). This method is eco-friendly, needs less energy and can use various types of biomass ranging from first-generation fuel crops to second-generation biomass (Das and Veziroglu 2008). Also, it is faced with the challenge of industrial scale-up because of its low hydrogen yield. However, this can be overcome by optimizing the design and operation of dark fermentation bioreactors, use of cheap renewable biomass and use of inoculums enrichment methods and coupling of dark fermentation with photo fermentation or bio-electrochemical systems (Show et al. 2011; Kapdan and Kargi 2006; Ren et al. 2011; De Gioannis et al. 2013; Li and Fang 2007; Ntaikou et al. 2010; Show et al. 2012; Wong et al. 2014; Ariunbaatar et al. 2014; Monlau et al. 2013; Motte et al. 2014; Rai et al. 2014; Redwood et al. 2008; Chookaew et al. 2014; Guwy et al. 2011; Moreno et al. 2015). It has been proposed to use xylose, the main fraction of hemicellulose, to produce biohydrogen via dark fermentation. Studies have shown that hydrogen gas can be produced via anaerobic fermentation of xylose after pretreatment (Silva et al. 2019). Simple sugars are usually used in this method as feedstock but cellulose or starch can also be used when hydrolyzed into simple sugars (Karolina et al. 2019; Argun et al. 2009; Chi et al. 2013).

4.2 Photo Fermentation

This is a biological method of hydrogen production that involves the use of sunlight energy in converting residual organic acids to hydrogen gas as shown in Eq. (6) (Levin et al. 2004). This method is anaerobic in nature as the purple non-sulfur photosynthetic bacteria produces hydrogen gas via anaerobic photosynthesis using light energy (Eroglu and Melis 2011). Also, these bacteria capture solar energy to convert organic acids into hydrogen using nitrogenase in the absence of NH_4^+. Nevertheless, this enzyme has its limitations such as low catalytic activity, inhibition of their expression by ammonia and reduced photochemical efficiency (Kuppam et al. 2015). This process is light dependent. Some of the bacteria usually used are Rhodobacter sphaeroides, Rhodopseudomonas capsulate, R. palustris, Rhodospirillum rubrum. Substrates used are commonly organic acids and alcohols which are chief make-up of industrial waste and effluent of dark fermentation process (Sen et al. 2008). The benefit of this approach is that oxygen does not inhibit the process (Das and Veziroglu 2008).

$$C_6H_{12}O_6 + 12H_2O = 12H + 6CO_2 \qquad (6)$$

4.3 Direct Biophotolysis

This involves the production of hydrogen gas from water in the presence of light energy using photoautotropic organisms as shown in Eq. (7) (Levin et al. 2004; Robak and Balcerek 2018)

$$2H_2O + \text{Light energy} = 2H_2 + O_2 \qquad (7)$$

Some of the microorganisms utilized for this process include Chlamydomonas reinhardtii, Scenedesmus obliquus and Chlorella fusca. This comprises two-stage photosynthesis system, the first where CO_2 is reduced and in the second stage water is splitted to evolve oxygen. This evolved oxygen tends to inhibit the hydrogenase enzymes that produce hydrogen gas.

4.4 Indirect Biophotolysis

This process involves the production of hydrogen gas using cynobacteria in a two-step process. Cyanobacteria possess key enzymes (nitrogenase and hydrogenase) that perform metabolic activities so as to achieve hydrogen production (Gürtekin 2014; Lindberg et al. 2012). The first step begins with photosynthesis and sugar formation and the second step is light-induced process where hydrogen gas and carbon-dioxide are formed from sugar and water as shown in Eqs. (8–9)

$$\text{First step: } 6H_2O + 6CO_2 + \text{Light} = (C_6H_{12}O_6)_n + 6O_2 \qquad (8)$$

$$\text{Second step: } (C_6H_{12}O_6)_n + 12H_2O + \text{LIGHT} = 12H_2 + 6CO_2 \qquad (9)$$

The cyanobacteria has the ability to carry-out oxygenic photosynthesis where they change sunlight energy to chemical energy and store it in carbohydrates and under specific parameters it can as well generate molecular hydrogen (Allahverdiyeva et al. 2008). Several forms of cyanobacteria that have been utilized are Anabaena, oscillatona, calothrix and gloeocapsa (Sen et al. 2008; Pinto et al. 2002).

5 Bioconversion of Hemicelluloses to Biohydrogen

Hemicellulose is one of the constituents of lignocellulosic materials among cellulose, lignin and other extractives. The major substrate used for hydrogen production using biological fermentative process is carbohydrate, either as oligosaccharide or as its polymeric form (cellulose, hemicellulose and starch) (Saratale et al. 2008). The major steps involved in bioconversion of hemicellulose to hydrogen gas are pretreatment, enzymatic hydrolysis and fermentation. Effective pretreatment helps in extraction of hemicellulose, lignin removal, reduction in cellulose crystallinity and increment in its surface area (Baêta et al. 2016). For instance, the application of acid especially in its dilute form for treating hardwood recovers hemicellulose as dissolved sugar with high degradation of hemicellulose monomers resulting in the formation of microbial inhibitors (Nguyen et al. 2000) which affect the conversion of sugar into other product of choice. Usually these inhibitors are removed using the process of detoxification (Anish and Rao 2009; Mussatto and Roberto 2001; Canilha et al. 2004, 2008; Nilvebrant 2001; Hahn-Hagerdal 2000; Canilha et al. ; Wilson et al. 1989; Cantarella et al. 2004; 2012; Hou-Rui et al. 2009; Yang and Wyman 2008). Research has shown that *Clostridium beijerinckii* is a promising microorganism for generating hydrogen gas from lignocellulosic hydrolysate as it is a better resistant strain to these inhibitors (Quemeneur et al. 2012).

Ionic liquid has also been used to recover up to 90% hemicellulose from sugar bagasse with less degradation of monomers. This technique has successfully been used to separate hemicellulose and cellulose from birch wood pulp (Froschauer et al. 2013). Alkaline pretreatment has been employed in recovering hemicellulose from lignocellulosic biomass by removing lignin. This method seems to be mostly used and efficient treatment for hemicellulose (Hamelinck and Hooijdonk 2005). Autohydrolysis is another pretreatment method that recovers up to 90% hemicellulose in oligometric form using water at increased temperature (Carvalheiro et al. 2008; Nabarlatz et al. 2007; Moure et al. 2006).

Hydrolysis and fermentation processes can be employed in hydrogen gas recovery. These two processes can be carried out separately or simultaneously giving rise to separate hydrolysis and fermentation (SHF) and simultaneous saccharification fermentation (SSF), respectively. Hydrolysis and fermentation are carried out in their respective chambers separately. This will incur more cost for reactor design. The fermentable sugars produced from the hydrolysis are not usually utilized immediately, thereby leading to their accumulation resulting in end-product inhibition. Simultaneous saccharification fermentation integrates the hydrolysis process with the fermentation process to produce hydrogen gas. The fermentable sugars produced from the hydrolysis process are immediately utilized by the hydrogen-producing bacteria. This process is carried out in the same reactor hence; it requires simple reactor design with lesser cost when compared to separate hydrolysis and fermentation process.

The complexity of hemicelluloses needs a combined effort of endo-enzymes (which cleaves internally the major chain), exo-enzymes (which releases monomeric sugars) and supplementary enzymes (which cleaves the lateral chains of the polymers or associated oligosaccharides), which results in the release of various mono- and disaccharides depending on hemicellulose type (Wagner 2013). Hemicellulase is the general name for the group of enzymes that helps in conversion of hemicelluloses to its constituent sugars (such as D-xylose, D-mannose, L-arabinose) by breaking the polymeric chains within its structure. Examples of such enzymes include endo-1, 4-xylanase, xylan 1,4-ß-xylosidase. Hydrolysis of lignocellulosic biomass generates products like hexoses (such as glucose) and pentose (such as xylose) sugars. Xylose is the chief pentose sugar gotten from hydrolysis of hemicellulose representing about 80% of total sugar (Canilha et al. 2013); this sugar undergoes the fermentation process to produce hydrogen gas. Theoretically, fermenting xylose sugar results in 3.33 mol of hydrogen per mole of xylose if acetate is generated or it can yield 1.66 mol of hydrogen gas per mole of xylose when butyrate is generated (Reginatto and Antônio 2015). Hydrogen can be produced via the action of anaerobic microorganism on xylose in the fermentation process as shown in Fig. 5. Figure 5 describes the summarized metabolic pathway involved in hydrogen production from hemicellulose component obtained from the hydrolysis of lignocellulosic materials. The enzyme for each step is XI = xylose isomerase, XK = xylulokinase, Hyd = hydrogenase, AK = acetate kinase, Fd(ox) = oxidizing ferredoxin, Fd(red) = reduced ferredoxin, PDC = pyruvate dehydrogenase complex.

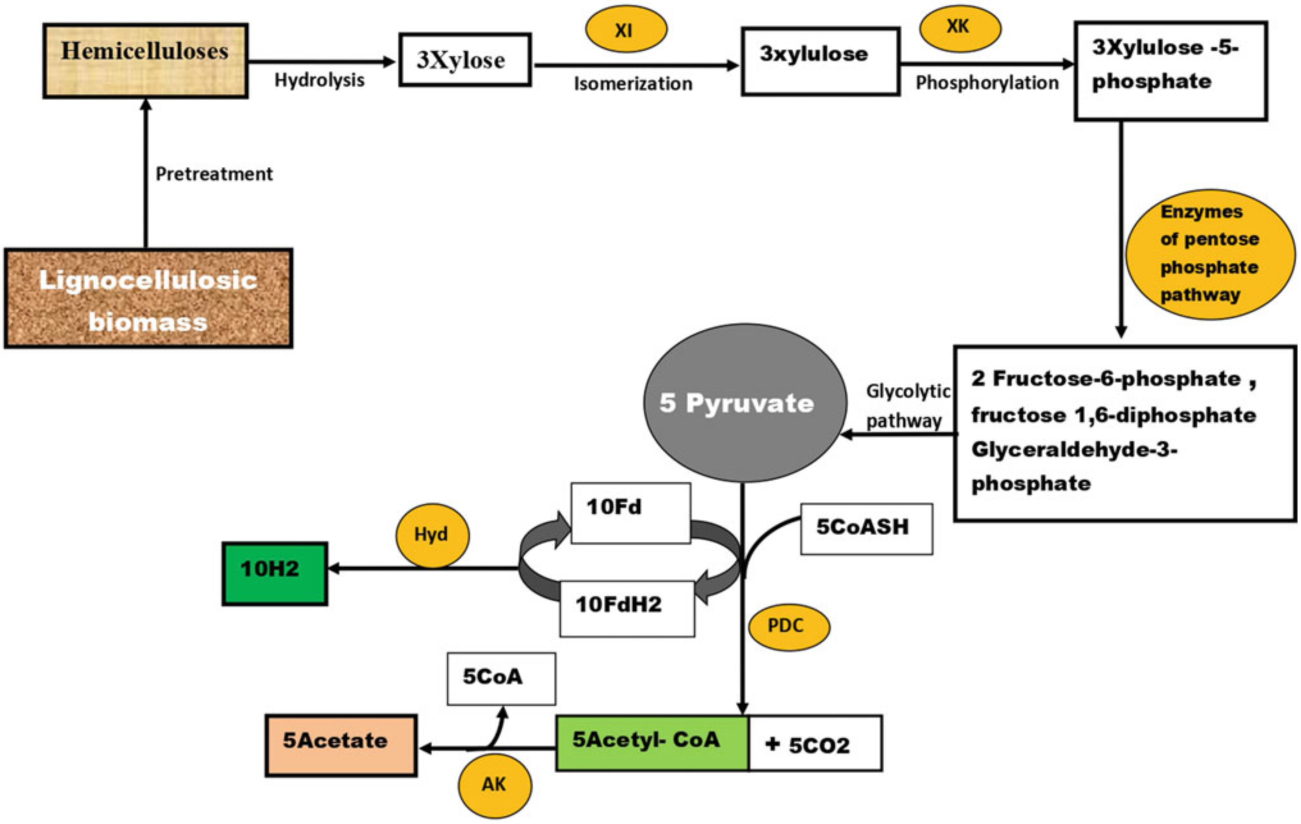


Fig. 5 Metabolic pathway for hydrogen production from hemicellulose

6 Conclusion

The production of biohydrogen from lignocellulosic waste would become a major and attractive future source of energy (Saratale et al. 2008) even though it is still undergoing a development. Hydrogen produced from this class of waste is faced with several limitations, especially the associated low yield. Nevertheless, this process holds promising benefits for the energy of the global world but better strategies must be sought to improve the process to optimize hydrogen yield from it. Research in the area of production of hydrogen from hemicelluloses is still fragmentary. Presently, hydrogen produced from bioconversion of renewable materials like hemicelluloses cannot compete with hydrogen produced from non-renewable sources despite the fact that the latter causes lots of harm to the environment. However, more research should focus on steps to be taken to increase hydrogen yield from lignocellulosic materials by developing innovative ways to overcome challenges leading to the low yield. The complex nature of hemicellulose which is created by the linkages of different monomers that need to be broken down into simpler separated monomers for it to be utilized in hydrogen production have actually made research development in this regard problematic. This area is open to novel research ideas that will help tackle this problem, thereby optimizing hydrogen yield from it at low cost and energy.

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Applications of Ionic Liquids in Plastic and Lignin Waste Recycling

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Abstract

This paper aptly reviews the advances in the application of ionic liquids in the recycling of single-use plastic and lignin. It explores the predominant use of this green solvent in recycling these wastes. Waste remediation processes often prove laborious employing traditional methods. The use of ionic liquids reveals bespoke advantages over the use of these conventional solvents. Compared to available researches and data of other solvents, studies on ionic liquids are yet to take full shape. More researches and studies on this green solvent are still required and useful in fully maximizing the field and to further promote sustainability.

1 Introduction

Increasing waste deposits remains a subject of many conversations across platforms and continents. Particularly, the United Nations and the World Health Organization, continue to draw attention to the impending dangers of neglect. In the most recent publication by the World Bank, global attention was also drawn to the continued generation and accumulation of wastes across the globe (Kaza et al. 2018). These wastes are environmentally unfavorable and noxious to human health. Plastics are now known to be the largest contributor of wastes world over. Global plastic wastes generation is about 400 MMT/yr. (million metric tons per year). The Ellen McArthur Foundation forecasted a world of more plastics than fish in the ocean by the year 2050. Another source of waste (though relatively minimal) is from the pulp and paper industry. Lignin is the major byproduct of this industry. Recent statistics reveal a production rate of 50 MMT/yr. (Wang et al. 2013). Numerous palliatives have been provided to curb the noxious effects of wastes. Recycling is now a household name in most industries as many industry players have *and* are developing strategies around the full utilization of recycling. However, peculiar challenges abound with the recycling of waste materials. From the collection of wastes to sorting, cleaning, removal of contaminants to the purification steps, numerous constraints limit its bounds. Many of the industrial recycling processes are cost-intensive (Meszaros 1995), some others require high energy utility, and some more require laborious processes of purification and re-purification; as recycling may generate new classes of wastes (Mourshed et al. 2017).

The introduction of Green Chemistry sought to create a modus operandi for the operations of chemical processes, thereby limiting the effects of waste generation through biochemical and chemical processes (Clarke et al. 2018). Ionic liquids (ILs) are a new class of chemicals (solvents), which caters to green processes and operations. Lignin and plastics recycling has increasingly seen more applications for the use of ILs in recycling processes.

1.1 Green Chemistry

From their popular release, which now forms a deep root in the understanding of Green Chemistry, Paul Anastas and John Warner defined the subject as the "design" of chemical systems, processes, and products to lessen or eradicate the usage and generation of environmentally unsafe substances (Anastas and Eghbali 2010). Green chemistry ever since is hinged on 12 core frameworks of operation. These 12 were introduced in 1998, and are now conveniently summarized into memorable acronyms as well. The chart described shows the make-up of the basic guiding principles of any green process (Fig. 1).

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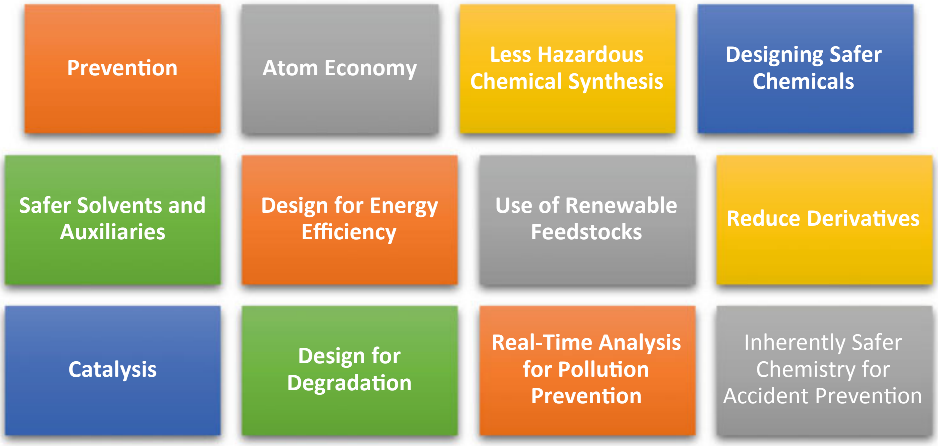

Fig. 1 A chart displaying a listicle of green chemistry's guiding principles

In this context, some of the principles are directly relevant to the application of ILs in chemical processes. These are

i. Prevention: It is better off avoiding the generation of wastes than later treating or cleaning them up. ILs do not pose a threat of waste accumulation, as they can be recycled.
ii. Less Hazardous Chemical Synthesis: As it implies, when practicable, all chemicals used and generated should either pose a minimal threat or none to the ecosystem and human health.

The toxicity level of ILs has been monitored over time, and findings indicate far less toxicity than conventional chemicals.

iii. Designing Safer Chemicals: It suggests that chemical products under this condition should still retain maximum usefulness despite curbing its hazardous effects.
iv. Design for Energy Efficiency: ILs fit in here thoroughly because with a melting point lower than water, less energy is needed, therefore drastically reducing energy usage.
v. Reduce Derivatives: Ionic molecules do not require extra reagents to clean-off after use, and if such exist, better ILs can be redesigned for the specific challenging area.
vi. Catalysis: As it implies, ILs can be useful catalysts in a wide range of operations, rather than merely acting as a solvent.
vii. Inherently Safer Chemistry for Accident Prevention: Chemical accidents are minimized since ILs have high thermal stability and negligible vapor pressure.

1.2 Ionic Liquids: Breakthrough Solvent

The term Ionic liquids (ILs) is used to describe liquid salts with an organic cation species and either an inorganic or organic anion species (Bicak 2005; Broderick et al. 2017; Cao and Mu 2014). In contrast to many other forms of salts which are crystals (e.g., normal salt, because they contain small, single-atom ions), these salts do not crystallize easily, and consequently, they remain as liquids at room temperature. ILs have irregular structures that delocalize their charges. Due to this irregular shape and low charge density, the molecules do not pack together as neatly as other salts do (Klein et al. 2011). When molecules pack very well and neatly with a strong bond affinity, they usually take on a crystal form. Essentially, to be a liquid–as with ILs–the cation should preferably be unsymmetrical, i.e., the alkyl groups should be different and bulky. ILs have a melting point that is lower than 100 °C as compared to normal salts with a melting point around 800 °C. The very fact that this class of salts exists as liquids brings a whole new world of possibilities. The earliest mention of the immense benefits of ILs happened in the twentieth century. Around this time, Walden was pretty insistent on finding a molten salt that could exist as a liquid at the operational temperatures of his equipment. He discovered ethyl ammonium nitrate. This paved way for many more because several applications of ILs are feasible.

1.3 Ionic Liquids in Green Processes

The field of ILs is fast changing, as many applications and uses are fast finding relevance both to the industry and academic locale. Green synthesis relies on one of the 12 principles of green chemistry in that the use of auxiliary substances during separation processes or any other intermediary process should eliminate unnecessary solvents use, and if necessary, should be innocuous. ILs are used both as solvents and catalysts and achieves this feat.

1.4 Unmatched Benefits of Ionic Liquids

ILs are revolutionary, in that they offer alternate usage to conventional solvents in assorted chemical activities and applications (Holbrey and Rogers 2002). These alternate advantages are visible in areas of its thermodynamics and kinetics. ILs have been (since its discovery) put to several applications. ILs have no measurable vapor pressure, and therefore cannot evolve Volatile Organic Compounds (VOCs) (Nelson 2002). ILs exist as ions and as a result are unlike other molecular liquids. Its intrinsic and extrinsic properties: polarity, viscosity, conductivity, and thermal stability can be adjusted by combining the exact pairs of cation species with a co-anion species (Tan and Macfarlane 2009). An in-depth examination and study of ILs reveal a wide range of applications for chemical processes. Some of these processes include: Friedel Crafts reaction, Diels-Alder reactions, RefÔrmatsky, Stille, Claisen rearrangement, and Heck reaction. Other applications of ILs include nanoparticle synthesis and catalytic oxidation. An increasing number of researches are finding more relevance for the use of ILs because they are practical and straightforward, compared with similar reactions in traditional organic solvents such as dipolar aprotic solvents. Conventional solvents are eco-unfriendly, particularly chlorinated hydrocarbons. Interestingly, ILs have been found to exhibit a property like no other: tenability—the ability of the solvent to be designed and redesigned to suit specific processes. Freemantle described ILs as "designer solvents," of which properties can be customized for a particular process. This can be done by (i) changing the structure of the cation, (ii) changing the structure of the anion, or (iii) changing both the structure of the anion and cation complementarily. This, in turn, changes properties such as viscosity, density, solubility, and refractive index. A common example of a green solvent is 1-butyl-2,3-dimethyl imidazolium ionic liquid (Fig. 2).

Studies on ILs are still on the rise. As of this writing, CAS revealed over 27, 000 publications on ILs. Since ILs do not give off VOCs, solvent extraction and product separations are very essential processes that rely on the ability of ILs to be adjusted in favor of a particular separation.

ILs can take the form of *switchable ionic liquids* (SWILs). A *Royal Society of Chemistry* publication in 2017 was the first to reveal and confirm distinct ionic and non-ionic regions by in situ chemical imaging mass spectrometry, which they titled *switchable ionic liquids*. These kinds can exist separately or co-exist as an ionic liquid and non-ionic liquid. This brings further possibility of ILs. It has many similar applications in catalysis, water-purification, nanomaterial synthesis, and interestingly, CO_2 capture. Partly due to the organized solvent structure of ILs, they can induce structural directionality during chemical synthesis. However, the molecular structure remains a hard nut to crack as it is unclear if the ions will be distributed evenly or attempt to retain a localized cluster of ion formation. The ability of SWILs to alter gradient with CO_2 loading. These green solvents will see many useful applications soon as well as in plastics recycling.

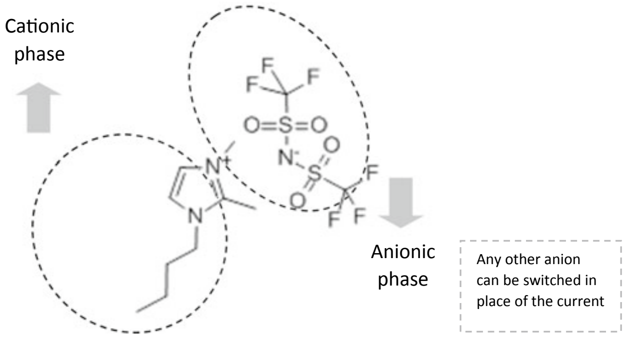

Fig. 2 2D structure of (1-butyl-2,3-dimethylimidazolium) ionic liquid (National Center for Biotechnology Information 2021)

1.5 Waste Recycling

Waste recycling is increasingly finding relevance since a bulk of them litter the environment (Ren 2003). Single-use plastics most times clog waterways. When combined, this inquiry forms a very strong footing in Green Chemistry. In plastic recycling, one of the challenges faced during chemical recycling to monomer (CRM) is the issue of contaminants. Remarkable progress has been made on the suitable ILs that effectively drives holistic green depolymerization process. For example, a recycling process was carried out on Nylon-6. The work thoroughly studied the role and exact application ionic liquids play in the depolymerization of Nylon-6. The monomer yield of caprolactam was between 43–55%. This emerged area of waste recycling is promising for researchers and the chemical industries. Selected ILs are shown in Table 1, describing the essential physico-chemical properties. These properties are essential in the determination of the unique area of the application of ILs.

1.6 Task-Specific Ionic Liquids

Task-Specific Ionic Liquids (TSILs) refers to ionic liquids that can be made true working systems employing potential

Table 1 Some physico-chemical properties of selected ILs

Cation[1]	Anion[2]	Formula	m.w. g/mol	m.t.[3] °C	Visc[4]cP 25 °C	Density g/mL 25 °C	Dec. t.[5] °C
Mim	Cl	$C_4H_7ClN_2$	118.6	74	Solid		
	NO_3	$C_4H_7N_3O_3$	145.1	71	Solid		
Mmim	Cl	$C_5H_9ClN_2$	132.6	126	Solid	1.140	253
Emim	Cl	$C_6H_{11}ClN_2$	146.6	89	Solid	1.110	285
	SCN	$C_7H_{11}N_3S$	169.3	−6	29	1.117	450
	NO_3	$C_6H_{11}N_3O_3$	173.2	39	Solid		
	$C(CN)_3$	$C_{10}H_{11}N_5$	201.2	−9	15		
EMmim	Br	$C_7H_{13}BrN_2$	205.1	141	Solid		322
	$N(SO_2C_2F_5)_2$	$C_{11}H_{13}F_{10}N_3O_4S_2$	505.3	25	Solid		
Bmim	Cl	$C_8H_{15}ClN_2$	174.5	41	Solid	1.080	154
	SCN	$C_9H_{15}N_3S$	197.3	−6	51	1.070	216
	Acetate	$C_{10}H_{18}N_2O_2$	198.3	−1	430	1.055	
Hmim	$N(CN)_2$	$C_{12}H_{19}N_5$	233.3	1	50	1.295	1.295
	PF_6	$C_{10}H_{19}F_6N_2P$	312.2	−61	480		
C7mim	PF_6	$C_{11}H_{21}F_6N_2P$	326.3	15	570		1.263
	NTf_2	$C_{13}H_{21}F_6N_3O_4S_2$	461.4	7	104		
Omim	Cl	$C_{12}H_{23}ClN_2$	230.8	8	13300	1.010	243
	$N(CN)_2$	$C_{14}H_{23}N_5$	261.4	−5	700	1.239	276
	Alaninate	$C_{15}H_{29}N_3O_2$	283.4	15	732	1.321	325
	PF_6	$C_{12}H_{23}F_6N_2P$	340.3	−40	93		
	NTf_2	$C_{14}H_{23}F_6N_3O_4S_2$	475.5	−23.5			

[1] Cation code: mim: methylimidazolium; Mmim: 1-methyl-3-mim; Emim: 1-ethyl-3-mim; EMmim: 1-ethyl-2-methyl-3-mim; Bmim: 1-butyl-3-mim; Hmim: 1-hexyl-3-mim; C7mim: heptane mim; Omim

[2] Anion code: alaninate: $CH_3–CH(NH_2)–COO^-$; NTf_2: bis(trifluoromethylsulfonyl)imide

[3] m.t: the NSIT database lists of 'melting temperature'

[4] Visc.: liquid viscosity at 25 °C in cP or mPa s at atmospheric pressure (101 kPa); density at 25 °C, unless otherwise indicated, and at atmospheric pressure

[5] Decomposition temperatures

Source Berthod et al. 2018 & NSIT database

"design" capacity. The idea of TSILs can eradicate densely the presence of species that are unnecessary to a particular operation. TSILs are simply ILs with a displaced halide by a parent species (e.g., imidazole) and in the process, replacing the organic halide with a desired functional group.

2 Applications of Ionic Liquids

2.1 Sample Pretreatment

ILs form a vital part of many processes involving pretreatment and sample preparation. In the analyses of complex matrices of biological and environmental samples, ionic liquids are very important in the sample pretreatment stages. Sample pretreatment is a separation process that relies on the isolation of interfering species in a sample through the enrichment of targets. In analyzing complex samples, it is important to improve its sensitivity, selectivity, repeatability, and precision. Extraction is enhanced by the numerous advantages ionic liquids possess, which are high thermal stability, good solubility, hydrophobic or hydrophilic properties, negligible vapor pressure, and environmental sustainability. Through designing the structure of the anion and the cation species, the exact conditions for the sample pretreatment can be effectively considered. This in turn gives better sensitivity during extraction (Fig. 3).

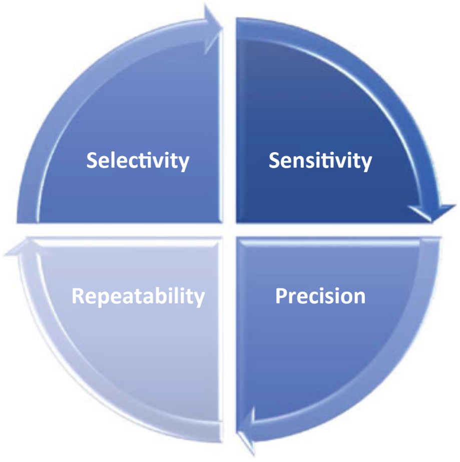

Fig. 3 A chart showing the vital components of any complex sample analysis

2.2 Catalysis

2.2.1 Catalytic Cracking of Polyethylene

The cracking process of polyethylene in the recycling process is one of the most important phases. The use of chloroaluminate (III) in the cracking of polyethylene gives rise to classes of compounds that differ from those of conventional methods (Adams et al. 2000). The cracking process reveals that ILs are a good substitute for conventional ones. ILs are used as co-catalysts with an inorganic acid. When a low-density polyethylene (LDPE) is suspended in an ionic liquid (IL), it gives rise to a distribution of products that are not dependent on the nature of the ILs.

3 Ionic Liquids in Plastics Recycling

3.1 Plastic Recycling

Recycling processes are the best way to cater to the waste reduction we currently are plagued with. Researchers, for long now, have been trying to ensure cost-effective strategies and procedures to sustain the laudable ideas on recycling plastic waste. Most virgin hydrocarbons where plastics' monomer units are sourced are readily available and cheap. For recycled monomers to do well, they must be cleared of all contaminants and relatively cheap. In recycling plastics, contaminants are classified into: (i) input contaminants (they are also known as plastics additives) (ii) chemicals used for the recycling process (detergents or solvents), and (iii) products that arise from degradation during processing (mainly stabilizers).

A difficulty arises in the absolute classification of these contaminants, and the development of an effective method for treating these plastic wastes. Chemical companies may overtime customize various use of additives for their unique purposes; this poses more difficulty in general recycling. Also, reuse of plastics (mainly bottles) for other unauthorized purposes—by end-users—may further lead to complication of processing. With these complications, it may be sometimes difficult to proffer accurate solutions to the varying degrees of the state of plastics. However, some general tendencies and materials must be employed. For example, most plastics additives are not chemically bonded to the basic polymer chain, the application of ILs in separating these contaminants are becoming useful. More research in the specific separation processes may reveal useful information on the removal of contaminants such as lubricants, release agents, fillers and reinforcement, antifoaming agents, antioxidants, plasticizers, and stabilizers. As of 2007, the most efficient and effective recycling method was chemical recycling (Woidasky 2018).

3.2 Chemical Recycling

Chemical recycling involves the transformation of polymer chains—under recycling processes—into monomer units suitable for re-polymerization reactions that reform recycled plastics (Kamimura and Yamamoto 2007). Generally, there are several types of recycling of plastics. A few—and by chance *commonest*—include energy recycling, material recycling, and monomer recycling (Al-sabagh et al. 2015). Many studies on recycling processes revealed monomer recycling as the best option in terms of optimum utilization of carbon resources. This is because, in comparison to the other recycling forms, there is higher conservation of the non-renewable carbon resource (Kamimura et al. 2011). The most critical part of the recycling process is the depolymerization phase, which is the leading process of recycling. The conventional route has always involved thermolysis or the use of supercritical fluids, which will require high temperature and increased working pressure. Organic solvents have run their course due to the challenges like emissions of VOCs, a requirement of apparatus that can withstand extreme conditions. ILs, so far, have evaded all these challenges. The stability of ILs at high temperatures and their non-volatility makes them suitable for chemical recycling. More importantly, the possibility of achieving a near-zero emission process makes ILs a great option.

3.3 Chemical Depolymerization

Depolymerization involves the transformation of polymer chains into monomer units. It is one of the most promising techniques (Hong et al. 2017). For an efficient depolymerization process, the extraction of the IL out of the reaction must be straightforward, i.e., it must not result in a complicated side reaction. The type of IL used plays a very important role as a total hydrophobic mixture will make it difficult to extract the IL. To eradicate this challenge, a hydrophilic IL can be used. The IL can be recovered easily by a liquid–liquid extraction (Iannone et al. 2017). The solubility of the IL can always be achieved through design and redesign. A study carried out in 2017 revealed the use of several ionic solvents for depolymerization of 6-nylon. The conclusion drawn was simple: 300 °C is an optimum temperature for the depolymerization reaction of polyamides. The decomposition of the IL, however, takes place at a temperature of 330 °C and higher. Over a decade now, many insights reveal effective depolymerization of polyamide to its monomeric unit: caprolactam.

3.3.1 Depolymerization of Plastics

Depolymerization of Polyamides in ILs

ILs are effectively used in the depolymerization processes of polyamides. *Kaimimura* et al. reported the first successful research on the use of ILs in the depolymerization of polyamides. Nylon-6 (a common form of Polyamide) is added to a solution of DMAP in [emim][BF_4] at a temperature of 300 °C. After 5 h of vigorous mixing, and cooling afterward, the homogenous mixture gave a caprolactam yield of 43%. Higher polarity gave an increased percentage yield of 86% when [emim][BF_4] was replaced by [PP13][NTf_2]. This process can go up to five times in reuse before the liquid degrades. The depolymerization of polyamides in an IL medium occurs as a result of a nucleophilic attack resulting in an addition–elimination cleavage. The polarity of ILs greatly affects the reaction rate of the system. Higher polar ILs like [TMPA][NTf_2] can greatly accelerate the rate of depolymerization.

3.3.2 Depolymerization of Natural Rubber

This process relies on a reported ruthenium-metathetic degradation of the polymer (NR; Natural Rubber). This process relies on several interactions between the propagating center and the allylic chain transfer agent (CTA) which results in a decrease in the mass of the polymer as well as functionalization of the polyisoprene oligomer. Mouawia reported the first practical use of IL media for a ring-opening metathesis reaction. A hydrophobic IL such as a phosphobic-based is used to prevent swell and ensure the stability of the various components.

Table 2 shows the various IL-aided depolymerization of selected plastics.

4 Ionic Liquids in Lignin Recycling

Biomass is a non-fossil organic material biologically made from water and CO_2 through a process popularly known as photosynthesis. This process takes place in the presence of sunlight. Wood consists mainly of lignin, cellulose, and hemicellulose (Kamimura et al. 2019). The quantities depend totally on the plant's origin. Lignin is the only major source of aromatic substances and as such, it needs to be preserved (Stark et al. 2010; Tolesa et al. 2017). ILs are employed in recycling lignin, and this produces the most abundant source of aromatic compounds in nature. Lignin

Table 2 Ionic liquid-assisted depolymerization

Plastic	Ionic liquids	Temp. (° C)	Major product	Yield	References
Nylon-6	[emim][BF_4] [PP13] [TFSI] [TMPA] [TFSI] [PP13] [NTf_2] [TMPA] [NTf_2]	300 330 300 300 300 270 330 350 300 270 330 350	Caprolactam	43 55 86 79 86[a] 7 [a] 55[a] 6[a] 79[a] 82[a] 77[a] 61[a]	Kamimura and Yamamoto (2007)
FRP[c]	[PP13] [NTf_2] [TMPA] [NTf_2] [Bmim] [NTf_2]	300 340 300 320 340 360 340 340	Phthalic anhydride	9[b] 30[b] 82 83 80 38 57 57	Kamimura et al. (2011)
Nylon-12	[PP13][NTf_2]	300	Laurolactam	7	Kamimura et al. (2019)

[a] In presence of DMAP catalyst (wt.5%)
[b] Using a sand-bath rather than a microwave
[c] Fiber-reinforced plastic

has a complicated structure (Tolesa et al. 2019; Dai et al. 2007), and sometimes relying on the conventional methods may not yield much improved results (Chio et al. 2019). The use of ILs, however, has proven to be a better alternative to the foregoing (Wang and Qian 2020; Zhang et al. 2015).

4.1 Ionic Liquids in Lignin Depolymerization

ILs are being used to solve varieties of challenges associated with the treatment and deconstruction of lignin to mono-cyclic aromatic such as sugars, polyols, organic acids, furans, and phenolics (Singh et al. 2017; Yang et al. 2018; Thierry et al. 2017). ILs have shown greater advantages over the thermal approach which requires metal supports such as Cu, Ni, Rh, and Pd,. as catalysts that employ high temperatures beyond 200 °C and heightened pressure. Employing a versatile catalyst like methyltrioxorhenium (MTO) may be efficient for catalyzing the C–O bond cleavage of the β-O-4 model compounds in lignin (Szalaty et al. 2018; Scott et al. 2015; Gregorio et al. 2006); however, the heterogeneous nature of the lignin still limits its application.

The main purpose of lignin depolymerization is to convert the complex lignin into renewable fuels and chemicals (Wang et al. 2017; Prado et al. 2015). Other methods have altogether yielded low due to the lack of effective conversion methods. Lignin conversion into value-added (aromatic) products is a laborious task. The depolymerization of lignin in ILs has been studied under oxidative and reductive conditions. The use of ionic liquids in lignin depolymerization helps to optimize the process hence, minimizing waste generation and resource underutilization.

Wang et al. revealed various sources of lignin that is produced in varying proportions. Organosolv beech, one of the commonest forms of lignin was reacted in 1-ethyl-3-methylimidazolium-trifluoromethane sulfonate ([emim][CF_3SO_3]) ionic liquid which in turn produced 2,6-Dimethoxy-1,4- benzoquinone at an 11.5 wt% yield. Eugenol when subjected to a temperature of 200 °C produced a 7.9% Guaiacol.

4.1.1 Protic ILs on Lignin

Protic ILs (PILs) can greatly reduce reaction pathways and minimize cost. However, due to the—interaction in lignin-derived molecules, the further application of ILs may be limited. Three PILs with different cations were utilized to demonstrate the extraction of lignin in a study by *Achinivu* et al., pyridinium $[Py]^+$, 1-methylimidazolium $[Mim]^+$ and pyrrolidinium $[Pyrr]^+$.

They showed that [Py][Ac] and [Mim][Ac] can dissolve large amounts of lignin components except for Xylan, which dissolved only in [Pyrr][Ac]. The ability that $[Py]^+$ and $[Mim]^+$ presence is selective is an advantage since it is a necessary measure in selective extraction (partitioning).

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Bioconversion of Poultry Waste into Added-Value Products

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Abstract

Larger amount of poultry waste is generated in tonnes round the whole globe due to high-level demand for poultry meat. Therefore, there is a higher challenge involved in the management of agro-industrial wastes, especially poultry waste. There are numerous applications where feather could be utilized that entails feedstock, decorative applications, bedding materials, medical devices, dusters, and fertilizers. The conventional techniques such as landfilling and burning are not eco-friendly because it involves the discharges of several threat and hazards to the environment and to humans. Therefore, there is a need to search for an eco-friendly and sustainable techniques that can convert poultry waste into added-value products using biological means. Therefore, this chapter intends to provide a detailed information on the application of beneficial microorganism as one of the environmental and sustainable approaches that could be used for effective conversion of these poultry wastes, such as feathers, into value-added products like animal feeds, biofertilizers, and many more. The modes of action thorough which the poultry waste could be degraded were also highlighted.

Keywords

Poultry waste • Feather • Enzymes • Eco-friendly • Environment • Sustainability

1 Introduction

Feathers have been identified as a significant by-product in poultry industry because they constitute almost 5–7% of the whole biomass from the chicken. It is projected that roughly numerous million tonnes of by-products are derived from feather that is produced yearly, especially from the industry worldwide (Verma et al. 2017). Feathers are normally obtained and deposited at different areas before handling because there might be presence of grease, meat, and blood around the feathers. The storage conditions which entail temperature and the period need to be prudently taken into consideration and effectively managed. Most feathers can be discarded through the process of incineration, which has been established as a sustainable technique that could be utilized to destroy any available infection agents. Moreover, it has been reported that most feathers could be disposed through controlled landfilling and burial while special management is a necessity to prevent them from water flowing on the ground (Tesfaye et al. 2017).

There are numerous applications that feather could be utilized for which entails feedstock, decorative applications, bedding materials, medical devices, dusters, fertilizer (Papadopoulos 1989). It has been observed that most of the traditional approaches utilized for the treatment of feathers and processing techniques, such as stem pressure cooking and chemical treatment, could be applied for effective transformation of feather into essential value-added products. Moreover, it has been observed that the process requires enormous amount of energy and some amino acids, but large quantity of amino acids are destroyed during the process of applying treatment (Wang and Parsons 1997).

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The utilization of feathers as a material has been identified in various fields, but several quantity of feathers are still liberated into the environment without the application of necessary treatment. Feathers have been recognized as one of the main sources of contaminant which might be linked to their recalcitrant attributes (Shanmugasundaram et al. 2018). Moreover, most of the feathers on which treatment has not been applied could harbor numerous pathogenic microorganisms and liberate numerous contaminants such as ammonia, hydrogen sulfide, nitrous oxide which have been identified as a potential hazard to people's health and environment (Tamreihao et al. 2019). Hence, the transfiguration of these poultry feathers into value-added products using economics techniques has drawn the attention of numerous researchers (Kang et al. 2018). The application of beneficial microorganism has been identified as one of the environmental and sustainable approaches that could be used for effective alteration of these feathers into value-added products such as animal feeds and biofertilizers. Hence, this chapter intends to provide a detailed information on the recent advances in technology involved in the biological transformation of poultry waste into useful products.

2 Microbial Degradation of Feathers

It has been observed that the nature of keratin-rich wastes, which include feathers, has several resistance, especially through the action of some enzymes such as proteases, which showed that keratin is not build up in nature. This indicated that microorganisms are responsible for the process of biodegradation of keratin-containing substances (Williams and Shih 1989). It has been validated that numerous microorganisms possess the capability to degrade numerous wastes that secrete proteolytic enzymes and keratinolytic, which all constitute keratinases enzymes (Tamreihao et al. 2019; Williams and Shih 1989). Typical examples of these microorganisms include fungi, bacteria, and actinomycetes (Bohacz and Korniłłowicz-Kowalska 2019). Several microorganisms have been identified to be domicile from many environs that are rich in keratin which have been utilized for biodegradation of wastes that possess keratin especially from various sources (Chaturvedi et al. 2014).

3 Modes of Action Involved in the Biological Degradation of Microorganisms

Structural investigations which have utilized keratinases for the biological degradation of feathers when carried out indicated that keratinases might not have sufficient action to disintegrate the disulfide bonds. Numerous modes of action have been proposed and identified to entail two major steps which include keratinolytic procedure, such as proteolysis, and sulfitolysis (Bohacz and Korniłłowicz-Kowalska 2019). Sulfitolysis is the stage where the disulfide bonds are separated and the process of proteolysis is required to split the protein (Lange et al. 2016). The reduction of the disulfide bonds majorly by the enzymes includes reducing agents and sulfide reductases that entail sulfites are required for conformational alteration of keratinase and ensures that the sites are presented for the breaking down of keratinase (Yamamura et al. 2002). It has been established that the application of crude enzymes shows a greater keratin degradation when compared to the purified enzymes. Moreover, it has been affirmed that the presence of two enzymes is required for the breaking down of keratin (Lange et al. 2016).

One of them is required for the generation of keratin, especially that are found in the decreased form so as to break the sites that are shown to the protease. The following steps are involved during the keratin degradation: proteolysis, deamination and sulfitolysis (Yu et al. 1968). Moreover, it has been observed that fungi and bacteria possess different modes of action for the breaking down of keratin while the presence of their keratinase could break the polyproteins. Furthermore, proteolysis, mechanical destruction and sulfitolysis perform significant function during keratinase biodegradation especially by the fungi (Bohacz and Korniłłowicz-Kowalska 2019).

4 Bioconversion of Poultry into Useful Products

There are several products produced through the application of biological degradation of waste into biostimulants, biofertilizer, bioherbicides, biopesticides, animal feeds, enzymes and biocatalyst. The list of these useful products was provided in Fig. 1.

5 Bioconversion of Poultry Waste into Biostimulants and Biofertilizer

Ertani et al. (2013) revealed that utilization of biostimulants in different industrial sectors has recently gained significant attention among players of the industries across the globe. The authors further described biostimulants as a bioactive material or microorganisms with immense potential when used in minute quantity with the ability to stimulate nutrients uptake, protect against internal and external oxidative damage plus promoting plant growth and development. Biostimulants have the capacity to activate enzymes activity, stimulate hormone production, and regulate various diverse physiological processes in plant.

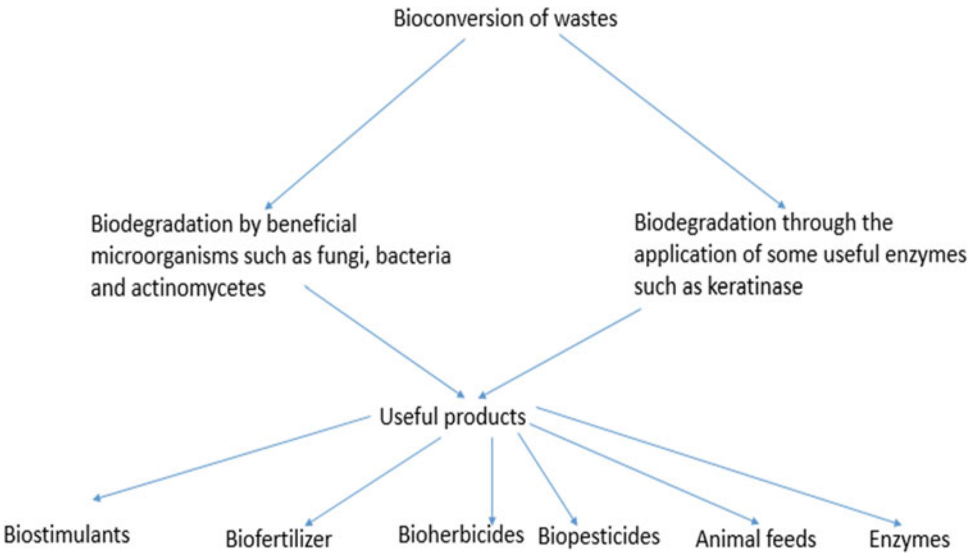

Fig. 1 Several products that are derived from the bioconversion of wastes

Ojha et al. (2020) revealed that there has been a significant progress in the expansion of waste development in poultry industry into commercial valuable products. The amount of waste product generated from poultry meat management like offal, quills, blood, visceral organs, dead winged animals and litter is very huge, thereby creating an opportunity to apply various technologies such as anaerobic treatment, microbial enzymes, incineration or burning, thermal decomposition, recycling, and vermicomposting in the bioconversion and utilization. Consequently, hydrolysates have displayed an immense potential as a bioactive substance with tremendous physiological impact. Hence, we will outline various microbes and microbial proteins like proteases, lipases, keratinases plus consolidated catalyst arrangements that have been utilized in the bioconversion of poultry waste into various biostimulants. Studies have shown that poultry waste is rich in fat, dry matter, ash content, and protein (Tesfaye et al. 2017).

Verma et al. (2017) described how organic waste can be recycled into useful and valuable products such as biostimulants with positive impact on the environment. The authors went further to recycle bovine manure and poultry litter waste into humic acid, evaluating its biological effects on corn plants with or without chemical biostimulants. The experiment lasted for 30 days and various parameters were measured. They revealed that the corn plant treated with the combination showed more increase in yield and development. They, therefore, suggested that the combination of biostimulants from organics poultry farm could be complementary effort in agricultural sector with huge economic benefits.

Barik et al. (1991) suggested that increase in the output of poultry waste could generate serious environmental concerns. The bioconversion of these waste into valuable products is becoming possible due to advances in technology. The authors revealed that large form of methane gas, propionic acids plus acetic acid could be generated via microbial inoculation. Also, studies have revealed that greater amount of poultry waste could be bioconverted into nitrogen-rich biostimulants with potential soil health benefits. The poultry industries can generate huge commercial value from waste if proper investment and market are in place to utilize the large-scale production of products generated. In the past, poultry waste is largely used as fertilizer due to small size but today large volume of poultry waste generation can induce small, environmental outbreak of infection and pathogenic attack on crops if left untreated basically because of huge ammonia content.

Jones and Ogden (1984) studied the energy potential present in poultry and livestock waste in the United States for future generation. They discovered that through anaerobic metabolism, laying hen manures, dairy cow, and hog have the potential to generate about 16.9 billion cubic feet of methane gas, and the entire farm value was estimated to be about $458 million in 1990 of biomass energy. Zhenghou et al. (1987) investigated the biogas energy generated from the North Carolina State University poultry waste through in situ utilization method. They discovered that the efficiency and production value increased tremendously with the capacity to be used as fertilizers or biostimulants. In addition, reduction in the cost of natural gas in raising young chicks could be considerably reduced when the biogas produced from the poultry waste is significantly harnessed.

Forgács et al. (2011) showed that anaerobic metabolism of poultry waste is the most proficient and sustainable eco-friendly way of reducing dependency on fossil fuel energy. The authors investigated the metabolism and energy generation of chicken feather and citrus wastes, and discovered that 15–25 million tonnes of citrus wastes were generated each year from juice industry alone and a huge amount from poultry waste. They further explained that feathers have very strong keratin compound with resistible proteins capable of generating biogas under different biological and enzymatic conditions. *Bacillus megaterium* strain was shown to possess high keratinase activity capable of degrading keratin in feather to generate methane through anaerobic digestion.

Abu et al. (2012) revealed that in Palestine farmers have lamented over the hardship posed by generation of waste close to their farm site and reduction in supply of energy. Studies have shown that energy in the form of biogas can be generated from poultry manure. In their study, increase in biogas generation was estimated to about 88%, hence economic benefits can be expected if proper investment is channeled to it due to adequate supply of raw materials. Khoufi et al. (2015) revealed that energy shortage and climate change seem to be the world's agenda recently. This has generated a lot of concerns from relevant stakeholders, making them to think of alternative solutions. The generation of biogas from poultry waste is now accepted as a novel source of renewable energy with little or no effect on the environment, cheap and readily available. Every part of chicken is now being utilized for various valued produce. The authors described the anaerobic fermentation procedures commonly utilized for the bioconversion of chicken waste into different organic acids and biogas. In addition, the slurry part again offers rich supplements for soil as biofertilizers (Joardar and Rahman 2018).

Nurdiawati et al. (2019) revealed that the gross output of poultry waste in Palestine is enormously huge contributing a major concern, hence the need to deploy effective management protocols. Khoiyangbam et al. (2004) revealed that feather, a poultry waste, is known to be a very good source of amino acids and proteins such as protein hydrolysates, and hence has become attractive to scientific communities in recent times. Studies have shown that massive amount of bioproducts can be generated with utility as plant growth or biofertilizers. The authors revealed that feathers can be converted into liquid feather-derived protein hydrolysate via hydrothermal treatment which when applied to plant can boost yield and increase quantity. Gurav and Jadhav (2013) suggested that the combination of liquid feather-derived protein hydrolysate plus inorganic fertilizer on beans increased yield and crop productivity. Li (2019) suggested that the amino acid content of feather makes them a good source of animal feeds and biofertilizers. Many microorganisms have the ability to metabolize chicken feather by enzyme called keratinases.

Xu and Geelen (2018) showed that efficient agricultural products must be eco-friendly and cost-effective, otherwise there will be negative impact on the economy. Thus, attention is beginning to shift away from fossil fuel products with high burden of environmental and health issues to waste recycling and bioresources. Many poultry-derived waste biostimulants have been revealed to possess huge agricultural benefits. However, studies have revealed that caution must be taken when consuming some of the animal by-products recycled due to potential risk for outbreaks of diseases.

6 Bioconversion of Poultry Waste into Bioherbicides and Biopesticides

Characterization of poultry feathers was examined for their chemical makeup which is mainly protein, called keratins. Keratins are the main fundamental peptides of amino acids which showed great resistance to organic decomposition (Ramnani et al. 2005). Before now, researchers have stated that *Bacillus licheniformis* can make use of degraded keratin in poultry waste by manufacturing keratin decomposing enzyme in producing animal food and manure (Riffel and Brandelli 2002; Wang et al. 2005). These proteins are majorly made up of two subunits which comprised numerous amino bonds (Takahashi et al. 2004). Research on degradation by *B. thuringiensis serovar israelensis* and *Bacillus sphaericus* of chicken feather that contain keratin served as pesticide in the eradication of mosquito larva (Takahashi et al. 2004; Ramnani and Gupta 2004).

Findings have revealed that there is a disposal of larger number of feather waste by farmers that keep poultry as waste product and also as ecological hazard. Various techniques have been developed to do off with the bulky feather as waste products, that used in filling deep, manufacturing of fossil fuel, pesticides and manure (Balint et al. 2005; Bertsch and Coello 2005; Zerdani et al. 2004). They performed this study in order to make use of the whole of the feather of the chicken, as a substratum that is cost-efficient in the production of biopesticides. Their highlighted objective was grounded on the biological means of degrading the fundamental proteins of feather from chicken using *Bacillus thuringiensis serovar israelensis* and *Bacillus subtilis* bacterial strains. The classification of waste of the feather reveals the compound arrangement which comprised peptides of amino acids (81%), fats (1.2%), ash content (1.3%), and other dehydrated matter. Since this medium is stable and there is no need for extra nutrient to culture the decomposing bacteria, this breakdown technique helps to maximize the usage of the feather by preventing any form of subsequent residual loss, leading to an enhanced creation of biopesticides production (Poopathi et al. 2016).

Researchers discovered that the utilization of feather waste as biopesticides was cost-effective. One-liter chicken feather waste together with one-liter water was not expensive since it is a waste from the poultry. From their findings they concluded that chicken feather waste in powder had great benefit similar to the whole degradation. It helps eliminate ecological adulteration and leads to improve self-lifespan, easy to conserve, cheap, and useful. The method is very cheap, so it requires little funding for its crude materials for the production of the culture media showing great efficiency on growth of bacterial and in toxicity on mosquito vectors (Zerdani et al. 2004; Poopathi et al. 2016).

7 Bioconversion of Poultry Waste into Animal Feeds

Energy is the capacity to get a work done. This is crucial in the sustainability of lifetime events comprising cell rate, development, and physiological activities. The potentials in a feed providing the needed energy are of great significance in determining the nutritive value of the feed to animals. Animal feed helps in providing maximum energy in their diet. When there is excess energy in their diet, it might lead to great deposition of fats and a diet which has lower content of energy may lead to loss of weight in the animals (Boothe and Arnold 2002; NRC 1984).

Feeding of ruminants is attributed to the utilization of poultry waste due to its high nitrogen content which serves as source of energy to the animals (Snow and Ghaly 2007; Selle and Ravindran 2007). During research, it was discovered that poultry manure in its original state is made up of 70% water and 3.5% nitrogen (Berry and Miller 2005). Extended storage time leads to increased ammonium level. The result of their findings reveals the digestibility level of dried poultry manure. Feeding fattening bulls with poultry manure revealed that dehydrated manure could be utilized as fattening feed minus changing the normal gain, feed conversion, quality of the animal carcasses, or even altering the anthropogenic importance (Flachowsky 1997; Thomas et al. 1972).

Researchers fed cattle with poultry manure and this did not affect the quality of the content present in the produced milk (Berry and Miller 2005). Okeudo and Adegbola (Okeudo and Adegbola 1993) experimented the significance of replacing local protein constituents, groundnut with offal dried manure from the poultry at 0, 13, 25, 35 and 45% for 104 days (El-Deek et al. 2009). They detected that there were no practical crucial differences in the rate of growth and then drew a conclusion that the dried poultry manure contains protein which serves effective as local protein supplement (El-Deek et al. 2009; Gradel et al. 2003; Cowieson et al. 2004).

Researchers estimated the outcome of adding poultry litter (broiler manure) to the feed of Awassi sheep at varying concentrations for 70 days (Dikinya and Mufwanzala 2010). It was then discovered that there was no net transformation in the gained weight, and also the meat quality significantly increased owing to the direct reduction of the subcutaneous and entire fat by adding poultry litter of broiler to the diets of the lambs (Obeidat et al. 2011; Axtell 1999). There was an increase in the white color of the red beef of those lamb that were fed with the litter from broiler chicken. This resulted in constant pH value, shave force, the rate at which the meat can retain water and there was no cooking loss within the three diets (Dikinya and Mufwanzala 2010). There was great reduction in the population of the microorganisms present in the litter when 60 °C heat was applied but a reverse at lower temperature (Bernhart and Fasina 2009; Alam et al. 2008; Amon et al. 2006; AOAC 2011; Cutter 2002; Elving 2009; Fares et al. 2005).

Studies showed that dried poultry waste is known to have 181.0 MJ/kg that is up to the standard of energy for the animal nutrition. This dehydrated poultry compost also contains starch of 330 g/kg and digestible roughage of 65 g/kg. The protein present in the dehydrated poultry compost is 422 g/kg being higher than regulated protein intake. The presence of protein in the diet helped in the provision of amino acids that are essential and non-essential amino acid synthesized by nitrogen (Kim et al. 2012). The presence of fatty acids in the diet also helped them in animal growth, in the production of milk, especially for lactating animals (Flachowsky 1997). The fatty acid gotten from the poultry litter is far greater (63 g/kg) than that produced by forage crops. Calcium is known to be important for bone and cartilage development. It helps to stimulate contraction of the muscle, also checking the way in which nerve impulses are being transmitted. It also does cell membrane penetrability regulation and adsorption of key nutrients such as vitamin B_{12} found in the gastrointestinal tract. This calcium is 0.042 g/kg in dehydrated poultry compost while absence of this essential component in their feed can lead to rickets (Jobling 2001).

Research was conducted by feeding poultry litter to gestating and breastfeeding sheep. Poultry litter was then substituted for the conventional protein sources. There were 200 g weight gains in their protein meals, poultry litter of 22% ration were fed to gestating sheep (Ghaly and MacDonald 2012). There was 130 g/day weight gain, while those sheep that were given soybeans meal only gained 110 g/day. In an experiment with 6 months old lambs, the result showed that the lambs fed with 235 g dehydrated poultry compost and 190 g wheat meal worked just like those lambs that were served 365 g wheat meal daily (Zhang and Lau 2007; Obasa et al. 2009). Brugem et al. (1967) discovered that sheep fed with poultry litter of 50% ration and 50% barley. The obtained result gave a stunning output than those sheep that were fed with barley and 20% sawdust.

They found out that lambs fed on 38, 58, and 68% poultry manure and rice hulls gave similar results compared with those fed on all hay rations. The cost-effective features of using poultry manure to feed wethers at high level between 50 and 70% in the form of cubes were observed by Bishop et al. (1971) in South Africa. From their findings they discovered that feeding wethers with poultry litter had profit which was two times saving compared to those of conventional feed. The setup of an experiment to investigate feeding of ewes with poultry litter at 25 and 50% showed no substantial differences in any of the experimental parameters, but there was copper toxicity in feeding the ewes with broiler litters. Sheep was found to be more sensitive to the upsurge in the content of copper in their diet compared to cattle and mono-gastric animals.

Intensive studies conducted by Goerring and Smith (1977) showed that poultry manure and liquid squeezed by screw-press from the manure of a cattle were really greater than bases of protein in soybean and urea. The result revealed that the original protein level was marginally different from the calculated value. The maximum lactic acid level observed was from liquid squeezed by screw-press from the cattle manure. There was also increased lamb growth on daily bases, compared to the other diet without urea (Nocek et al. 2006). The outcome designated a daily weight gain with lambs fed with manure-based silage and this shows an outstanding trend of lambs to utilize poultry dungs proteins than from urea or soybean (Zinn et al. 1996). Arvat et al. (1978) from their research of feeding poultry waste to sheep concluded that feeding poultry litter to sheep is of great economic importance, most importantly during the winter period. Compared to when lesser quantities are fortified with substitute for forage and feed. Combination of poultry waste into the ration of lambs that are growing up to 70% and when to be used as fattener 50% is alright (Nicholson et al. 1996). Considerable success depends on the quality of the litter, the complement forage, and feed constituents. When poultry waste is administered at 35% it usually covers up for the total protein needed by the sheep and it attributes significantly to the total energy needed. A total of 70–74% of biological materials and 80% basic proteins present in poultry litter are digestible. Appropriate mixture of poultry waste, forage, and other roughages is most significant in managing and utilizing poultry waste and also reducing health hazard in sheep. The flaw in this method of feeding is the copper toxicity. There is a need to confirm the copper content inherent in the poultry waste before administration to the sheep and also know the level of tolerance of the animal to copper (Nicholson et al. 1996).

The beneficial importance of poultry waste to pigs varies significantly. Reduced level (4–7%) of new poultry waste deprived of bedding are very tolerable and leads to stimulated growth and appetite in pigs. Fresh manure directly consumed has greater protein-bound protein level and reduced level of ammonia containing protein that decreases within hours. This validates the use of fresh litter than already decomposed litter. Normal decomposition of poultry litter does not take long time because of the presence of proteolytic activity of the microbial population of the present in the litter. Therefore, an incorporated method in hen/pig/fish is being used by some farmers in Southeast Asia. They are known to construct battery cages for layers which is 1.5 m above pig pen, thereby saving the cost of pig houses. Excreta from these layers drop directly into the pen, where the pigs consume it directly within seconds of production by the hens. Mostly three to seven (Papadopoulos 1989; Wang and Parsons 1997; Shanmugasundaram et al. 2018; Tamreihao et al. 2019; Kang et al. 2018) birds serve one pig and pig get 6.3–14.6% of layer direct manure in their diet. The flaw in this system is that pigs that are younger consume more than pigs that are older. Dry nutrient intake of laying hen manure by pig is about 10% of their total feed. This method is imperious to produce pig meal carefully so as to avoid fluctuations in their calcium and phosphorus intake. They observed that recently after long years of administration of this system to various farm scales, there was no negative record on production or health of the pig rather than good reports. Then they indicated that this system when accompanied with fish signifies a total zero-pollution cycle (Dikinya and Mufwanzala 2010; Fares et al. 2005).

During the United Nations Development Program/Food Agriculture Organization (UNDP/FAO) research in Singapore (Muller 1974) litters of broiler hens were used in feeding smaller sows in order to investigate the adequacy of portions depending on various types of litter. Seven various types of broiler dungs were combined at 35% in the food for young pigs. Each portion was stabled with other feed constituents to attain a closely related nutritional value in all meals. This was done by comparing their meals with the commercial sow gestation portion of the same nutritional value (Zhang and Lau 2009). In the absence of lucerne in their meal, all other diet were readily putative and yielded results closely related to or even better than that of the commercial portion. The introduction of poultry litter into meals lessen feed cost considerably, and there is likelihood of substituting an important part of the pig rations by poultry waste that is really financially encouraging and achievable in fixed farming. A cohesive layer/pig/fish cycle seems to be of supreme innovative and effective sound reprocessing method which has zero-pollution release. This system is effectively functional by farmers on both small and large scale. They made inferences on re-feeding of poultry manure, to be strictly feasible with very less difficulty. The single benefit seems to be from calcium and phosphorus, and the reason being that only little proportion of protein in poultry litter is efficiently used by layers. Storage of undigested matter is a serious problem and in countries where there is usually warm climate condition, it could result in great reduction in the amount of feed consumed (Lopez-Mosquera et al. 2008).

Feeding poultry manure to other kinds of birds has been stated by few researchers. Wehunt et al. (1960) advocated that hydrolyzed broiler dung could be utilized in the portions of other chicks that seem to be lacking protein. Quisenbery and Bradley (1968) discovered that the performance of layers depending on meals rich in 10–20% of crude litter and manure was mostly preferable when compared to the controls that were given portions with balanced protein and energy. They concluded that feeding poultry waste to other kind of poultry is practically possible. The cost of drying the litter seems to be the major factor limiting economic importance of this method. The cogent reason for this method is the administration of calcium and phosphorous. This method could be used where these nutrients (calcium and phosphorous) are lacking or where they are too expensive. Places with warm climates could pose a serious threat on the well-being of animals for proper digestion of feed; the introduction of this method would be very difficult to practice. This system could be possible with birds within 8–22 weeks, where their litter could be interchanged for by-products from mining (Olivera-Castillo et al. 2011).

Advanced methods indicated that minimizing the rate of inflow of constituents from poultry waste achieving maximum result is possible for the exponential growth in fishes that are found in warm areas. Tilapia fishes are found to be common in this area and have great capability of using up poultry waste (Olivera-Castillo et al. 2011). Durham et al. (1966) experimented by feeding catfish in densely overstocked fish ponds, and they replaced 50% of conventional fish feed with feedlot manure. Ponds stocked with 60,000 fishes per ha gave 8.25 tonnes of fish biomass yearly. So, they concluded that there was no variation within yields from conventional fed ponds and those fed with litter portions. Findings also revealed that poultry cages could be constructed or pig pens on a wooden stand above fish and, where fish consumes the manure. This system is time and energy saving because there is no need of washing or cleaning the poultry and pig house often, owing to the fact that the poultry of pigs are situated above the fish ponds. There is usually great air transmission which has a great cooling importance on layers, predominately sensitive to stress caused by heat and in pig also. This system increases the management of waste of livestock, improves the income gotten from fish, and completely removes problem of environmental pollution (Vezey and Dobbing 1975). It was discovered that a layer hen will generate enough energy to produce up to 6–8 kg of fish biomass yearly. This is more effective in areas where fish pond could be used for cropping at the end of every second year; this is a common practice in Asia. Engaging in this kind of practice provides great production of fishes that are free from diseases and greater yields in farm produce.

Poultry dung maybe singly used or mixed using other food supplement, and was discovered to have great value when administered to both cows and sea life such as fishes. Ruminant animals have the ability to use up the uric present in poultry compost (Smith and Fries 1973). Nevertheless, presence of alien matters like glass and plastic may disrupt the digesting potentials of the poultry dung and could hamper the health of the animals; hence, there is a need for renewal of this method before application as feed to animals. There is also need to reduce the ash content of the feed. It is therefore suggested that poultry manure with great ash content greater than 28% should not be given to animals. This ash content is said to be increased when there is removal of inherent soil from the dung (Williams et al. 1999). Unprocessed poultry dung contains pathogenic microbial population like Enterobacter spp., Clostridium, and Salmonella. Therefore, appropriate handling helps to decrease the quantity of the microbes or makes poultry litter pathogen-free (Mccaskey and Anthony 1979; Kawata et al. 2006; Watcharasukarn et al. 2009). Some fungal species that are known to inhabit the excreta of birds can produce toxins, also known as mycotoxins. These pathogenic microbes could therefore be eliminated by fermentation through chemical method, ensilation, or application of heat (McCaskey and Martin jr 1988; Cook et al. 2008).

There was no case of disease situation reported via feeding poultry litters to animals while following the standard methods, only copper toxicity has been found to be great issue, usually in sheep. When there is excess administration of copper in the diet of birds as growth improving agent, the birds excrete the copper in greater concentration in their litter owing to the fact that they hardly digest copper in their system. And sheep are less tolerant to diets with increased copper content when fed with the dung from broiler hens (Fontenot et al. 1975; Sharma et al. 2005). The use of poultry litter has been in use for over four decades now in United States. The litter containing great percentage of peptides of amino acids, fiber that are digestible, and essential minerals were purposefully incorporated in the diet of ruminant. Usually this poultry waste is mostly utilized by farmers that can produce beef and milk as winter supplement for weaned calves and cattle. Although the method of re-feeding animals with poultry waste appears to be absurd, this practice is very non-toxic and meets with the stipulations of Association of American Feed Control Officials (AAFCO) (FDA 2009). Thermally dehydrated poultry litter should have a moisture content of not more than 15% and lesser concentration of 18% unprocessed protein, less than 15% raw fiber, 30% content of ash, and feathers of 1%. Processed animal unwanted products consist mainly of excreta from large-scale poultry that have been processed to eliminate some of the corresponding unfinished protein and uric acids.

The AAFCO stipulations necessitate that crucial waste products that have been processed should not contain inessential matters like nails glass and other dangerous materials. The manure must be pathogen-free, and deposits from pesticides and medicine residue could pose harmful effect on the animal health (Nahm 2002). AAFCO used sufficiently treated poultry litter in the food of animals which might not look appealing, but was found harmless, has nourishing validity, and eco-friendly properties. Studies have shown that utilization of poultry litter as feedstuff for livestock has produce profit when applied as fertilizer; this practice is less commonly utilized by farmers. This method is effective due to a crucial process of recycling of poultry waste. Successful feed effectiveness and health of animals that reduce the outbreaks of diseases are very crucial in contemplating a thorough, limited production method in animals (Rahman et al. 2009). Utilization of growth booster in the diet of animals does not only improve the chance of saving but it also provides a primary source of removing viable contaminants like nitrogen and phosphorous in poultry litter (Vuori and Nasi 1977). Nevertheless, since several growth boosters have some metals in them, this method may seem to upsurge the concentration of elements inherent in the poultry. Exact preparation and feeding of foods to meet up to the constituent of waste management policies and not to surpass the nutritive necessities would be possibly achievable. Excretion of nutrient in poultry litter is mostly caused by the issue of ability to digest the minerals in the ration and ineffective metabolism (Rahman et al. 2009). There should be an addition of feed enhancement and adjusting feeding platform in order to advance nutrient effectiveness which could lead to substantial reduction in the nitrogen, phosphorous and air pollution that the poultry manure could have caused (Rahman et al. 2009; Sistani et al. 2001).

Some of the models of these practices are: introduction of artificial amino acid and low protein materials, which have led to reduced manure nitrogen content by 10–27% in the poultry usually broiler hens, supplementation of enzymes has reduced 12–15% dry weight of the manure of broilers, supplementation of phytase has also led to phosphorous reduction from 25 to 60% in poultry litter, preparation of diet corresponding to the standard requirements which has lowered the nitrogen level in compost from 10 to 15%, stage feeding system lowered nitrogen than phosphorous by 10–33% in the manure; utilization of raw material that are readily digestible in feed lowered the excretion of the excretion of nitrogen and phosphorous by 5% in the manure; some feed production methods could expressively escalate dry matter digestive potentials, resulting in lessened production of manure, utilizing substituents/other coccidiostats, like ‘ionophores’ could cause severe reduction in the level of arsenic poultry manure and the use of growth enhancers that are non-metal and help to lower the concentration of metals like copper and zinc in poultry manure (Martens and Bohm 2009; Silversides and Hruby 2009).

8 Bioconversion of Poultry Waste into Enzymes and Biocatalyst

Utilization of feather-based direct protein supplement is limited in use. The feather waste could be cooked via steaming by application of chemical to make it digestible, but this method is usually costly. Studies showed that microorganisms play alternate role in order to elevate bio-value of the poultry waste. Literature has shown that enzymes from feathers usually synthesized by *Bacillus licheniformis* stains of PWD-1 which comprised nutritive importance in animal feedstuff are closely related to protein from soybeans. Despite that the keratinolytic protease from the bacteria revealed a possibility for transformation of feather enhancement, the activities of enzyme and great yield are expected to make this practice a suitable industrial method (Kim et al. 2001). Bacteria that are known to degrade feather are isolated from poultry waste. Some of them are *Bacillus pumilus, Bacillus cereus*, and *Bacillus subtilis*; they have the potential of degrading poultry feathers, thereby producing varying units of keratin.

9 Conclusion and Future Recommendation to Knowledge

The chapter has provided a detailed information on the recent advances in technology involved in the biological transformation of poultry waste into useful products. Special highlights were also provided on the significant microorganisms that are responsible for the process of biodegradation of keratin-containing substances. Typical examples of microorganisms that possess the capability to degrade numerous wastes through the use of keratinases enzymes were also highlighted. Moreover, relevant information on the modes of action involved in the biological degradation of microorganisms were also discussed. Interestingly, the process involved in the bioconversion of poultry waste into biostimulants, biofertilizer, bioherbicides, biopesticides, animal feeds, enzymes and biocatalyst (Adetunji and Oloke 2013; Adetunji et al. 2017a, b; Adetunji et al. 2018a, b; Adetunji et al. 2019; Adetunji et al. 2020). There is a need for government and relevant stakeholder support that will enhance the adequate transformation of waste to wealth. This will also go a long way for effective management of ecological and economical challenges encountered during the management of these various wastes.

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Bioconversion of Agro-Industrial Waste into Value-Added Compounds

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Abstract

In the wake of increasing environmental apprehension and inevitable depleting petroleum resources, scientific interest has intensified to utilize agro-industrial wastes as a potential raw material for the production of platform chemicals to upsurge the bio-based economy. A broad-spectrum of different biomass waste materials, which are underutilized, bio-renewable, and biodegradable, is produced across the globe in enormous quantities. All these kinds of biomass wastes comprise various chemical constituents that might serve as promising starting feedstocks to manufacture an array of high-value commodities, and intermediates through different transformation routes. This chapter spotlights the biotransformation of lignocelluloses' agro-industrial wastes into a variety of high-value compounds. Besides, the explanation of various kinds and sources of lignocellulosic biomass, a number of various biomass bioconversion technologies are vetted in detail. Furthermore, the valorization of various biomass wastes for the production of platform chemicals and bio-based materials are also discussed.

Keywords

Agro-industrial wastes • Lignocellulose • Bioconversion • Pretreatment methods • High-value chemicals

1 Introduction

The food and agriculture sector is emerging at a rapid rate. The rapid population growth, coupled with accelerating economic development, has engrossed important investment in the food and agricultural industry, amounting to 75 billion dollars in 2017. With the growth of the agribusiness industry, emerging waste generation represents an important environmental problem. Five million tons of waste are produced yearly from the agricultural sector (Ravindran et al. 2018). Lignocellulose and starch are the main content of these wastes including timber and agricultural industry, home, and garden waste. Around half-plant material is made up of lignocellulose, which is the most important renewable source of soil. It also contains cellulose (35–50%), hemicellulose (20–35%), and lignin (15–25%) strongly linked by various combinations of covalent and non-covalent bonding (Bharathiraja 2017; Kohli et al. 2019). In addition to the key nutrients, lignocellulose contains other organic substances in minute quantity including fats, proteins, dietary fibers, vitamins, or inorganic compounds such as water, carbon, sulfates, nitrates, and silicates, which are not actively involved in the development of lignocellulosic-based substance (Jedrzejczyk 2019; Kumar 2019; Vassilev et al. 2015). Usually, in lignocellulosic materials, the main source of cellulose is glucose composed of homopolysaccharide linked by β (1-4) glycosidic bonds. The crystalline structure and fibril junction of cellulose remain stable due to the inter- and intramolecular linkage of hydrogen bonding. The cellulose unit is often referred to as that elemental fibril combining the formation of microfibrils (Gollakota et al. 2018; Kannam et al. 2017; Zabed et al. 2017). The hemicellulose is heterogeneous in nature having different

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sugars including (D-glucose, D-galactose, D-xylose, D-mannose, L-arabinose) and some organic acids. In hemicellulose, the arabinose to xylose ratio regulates the rate of branching. An increased rate of polymerization and shorter polymer chain is due to the low ratio and vice versa. Hydrogen bonding is parent bonding in these polymers; however, covalent bonding is also noted among hemicellulose and lignin structures that provide strength and stamina to these substances (Kumar 2019; Dhyani and Bhaskar 2018). Lignin is considered to be the most complex, abundant aromatic, and amorphous triple dimensional phenyl biopolymer. Lignin biosynthesis forms from a combination of three different monolignols: *p*-coumaryl, sinapyl, and coniferyl alcohol responsible for solid structure formation. Different monolignols interact to form lignin namely guaiacyl (G), *p*-hydroxyphenyl (H), and syringyl (S) (Abu Yazid et al. 2017; Paul and Dutta 2018; Bilal et al. 2017) acts as a cross-linking resin that assists in the binding of fibrous cellulose and hemicellulose constituents. It is found on the exterior portion of microfibrils and attached covalently with hemicellulose and provides cell wall rigidity (Kumar 2019). The lignocellulosic composition of different wastes is presented in Table 1.

Agro and agro-industrial waste contain complex substances such as bagasse, grass stems, cobs, fruit and husk crabs, skin, bones, fat, or any portion of processed food source (plant and animal) that can be used in the main process (Abu Yazid et al. 2017; Obi et al. 2016). Now a days, global trend shifts toward waste material utilization for useful product production to boost the economic profit in numerous industries. Lignocellulosic waste is used as a substrate and is most vital feed as a renewable and natural resource that is crucial for the operation of the modern industrial sector (Mehmood et al. 2019; Nadeem 2019). According to a study done domestically and internationally, it has shown that all types of agricultural waste products, especially poultry, animal feces, and agricultural grasses have great potential for food and have the ability to expand the soil for productive production capabilities. Therefore, effective modification of the recycling of agricultural waste and use has been crucial in controlling environmental pollution. Besides, dealing with a problem can also fix a major energy problem (Maitan-Alfenas et al. 2015; Wang et al. 2016). In this era, it remains extremely important to turn these wastes efficiently and economically into important industrial and profitable products and decrease the harmful effect of these pollutants on earth (Carota et al. 2018; Murtaza et al. 2017; Naveed 2020).

1.1 Types of Lignocellulosic Biomass

The lignocellulosic biomass is categorized into three divisions: first (softwood), second (hardwood), and third (grasses). Several differences are depending on the chemical composition and composition that affect their ability to rearrange or become disorganized (Zabed et al. 2016). The hardwood is explained by the occurrence of large fluids that drive vessels or pores that can remain separated through their shape, size of plates formed, and structure of cell wall. Generally, this second class of wood is identified in extensive leaves, parts of forests including moderate and tropical. There is an important difference between hardwood and softwood depending on the complexity and their biochemical confirmation. The hardwoods are commonly weightier than softwoods and grow slowly in landscape. The maximum prominent geographies that distinguish hardwood from softwood are the deficiency of pores. Northern hemisphere region is a prominent source of this kind of wood. The softwoods are well-packed with hemicellulose and lignin that enable them to withstand the environment and need strong durability conditions (Brandt et al. 2013).

Grasses are totally different from woods in terms of their pores structure. Both perennial and annual grasses are measured as widely used feed ingredients for biofuel production. Xylose is the main source of hemicellulose that exists in the meadow and is easily breakable. Perennial grasses have a high production rate but more environmentally friendly by comparison with annual grasses such as corn stalks, rice, wheat straw, and sugarcane bagasse, e.g., the less content of lignin present in grasses makes good desirable feedstock for biorefineries (Hassan et al. 2018). Table 2 represents diverse types and sources of lignocellulosic material used for energy.

2 Biomass Conversion Methods

2.1 Pretreatment

The lignocellulosic biomass for trash often requires some modification to its properties and structure before its usage in some transformation process. Thus, biomass pretreatment is a crucial parameter to break down multilayered molecular structures into a simpler layer to obtain an effective result that is followed by the conversion process. The main purpose of pretreatment is to improve the surface area, provide easy access to enzymes, amend and solubilize the lignin in the situation of biological methods and to reduce total operating costs (Kan et al. 2016). Pretreatment methodology requires lignocellulosic biomass to be categorized into different categories: Physical method of pretreatment requires raising pressure and temperature causes modification in the lignocellulosic structure that further causes a reduction in biomass resistance. Chemical method of pretreatment uses organic and inorganic substances, which causes interaction between the intra- and inter-polymer bonding of cellulose,

Table 1 Lignocellulosic composition of the different waste (adopted with modification from Bilal et al. 2017 with premission from Elsevier. Copyright © 2017 Elsevier B.V)

Lignocellulosic waste	Cellulose %	Hemicellulose %	Lignin %	References
Corn cob	45	35	50	Prasad et al. (2007)
Rice husk	28.7–35.6	12.0–29.3	15.4–20.0	Allen et al. (2001), Abbas and Ansumali (2010)
Rice straw	32.1	24	18	Prasad et al. (2007)
Wheat straw	29–35	26–32	16–21	McKendry (2002)
Coffee pulp	33.7–36.9	44.2–47.5	15.6–19.1	Sanchez (2009)
Sugarcane bagasse	42	25	20	Kim and Day (2011)
Cattle solid manure	1.6–4.7	1.4–3.3	2.7–5.7	Singh et al. (2011)
Wheat bran	10.5–14.8	35.5–39.2	8.3–12.5	Miron et al. (2001)
Barley straw	36–43	24–33	6.3–9.8	Rowell et al. (1992)
Oat straw	31–35	20–26	10–15	Rowell et al. (1992)
Cotton seed hairs	85–95	5–20	0	Singh et al. (2011)
Soft wood	45–50	25–35	25–35	Malherbe and Cloete (2002)
Hard wood	40–55	24–40	18–25	Malherbe and Cloete (2002)
Nut shells	25–30	25–30	30–40	Abbasi and Abbasi (2010)
Grasses	25–40	25–50	10–30	Malherbe and Cloete (2002)
Leaves	15–20	80–85	0	Singh et al. (2011)
Tamarind kernel	10–15	55–65	NA	Menon et al. (2010)
Pine	42–49	13–25	23–29	Pereira (2007)
Winter rye	29–30	22–26	16.1	Petersson et al. (2007)
Eucalyptus	45–51	11–18	29	Pereira (2007)
News paper	40–55	25–40	18–30	Howard et al. (2003)
Agricultural residues	37–50	25–50	5–15	Limayem and Ricke (2012)
Douglas fir	35–48	20–22	15–21	Schell et al. (1999)
Bamboo	49–50	18–20	23	Alves et al. (2010)
Jute fibers	45–53	18–21	21–26	Mosihuzzaman et al. (1989)
Sweet sorghum	45	27	21	Kim and Day (2011)
Cotton straw	42.6	21.3	8.2	Saha and Cotta (2006)
Sorted refuse	60	20	20	Singh et al. (2011)
Corn stover	38	26	19	Zhu et al. (2005)
Poplar	45–51	25–28	10–21	Torget and Teh-An (1994)
Barley hull	34	36	19	Kim et al. (2008)
Banana	13.2	14.8	14	Monsalve et al. (2006)
Sugar beet	5	5.5	NA	Murphy and McCarthy (2005)
Swine waste	6	28	NA	Sun and Cheng (2002)
Sponge ground fibers	66.59	17.44	15.46	Guimarães et al. (2009)
Olive tree biomass	25.2	15.8	19.1	Cara et al. (2008)
Pulp and paper sludge	23.4	8.6	16	Lin et al. (2012)
Bagasse	54.87	16.52	23.33	Guimarães et al. (2009)
Oil seed rape	27.3	20.5	14.2	Petersson et al. (2007)
Winter hyacinth	18.4	49.2	3.55	Singh et al. (2011)
Horticultural waste	34.5	28.6	36	Geng et al. (2012)

Table 2 Types and sources of lignocellulosic biomass

Types	Forest	Agricultural	Industrial lignin	Wood	Industrial residues
Sources	Treetops Peat moss Bark waste Limbs Wood chips Saw dust Slashes Pruning residues	Cashew nutshells Bagasse Corn bran	Lignosulfonate Organosolvent Lignin Lignin obtained after steam explosion of birch	Ground softwood Sawdust woodchips Softwood bark Mixed hardwoods Hardwoods Pine	Paper waste Birch wood waste Black pulping liquor Wood industry residues Lignin from newsprint Creosote treated waste

hemicellulose and lignin cause lignocellulosic biomass structure disruption. Both physical and chemical methods are used separately but when they are used in combination, it boosts the biomass digestibility and increases the desired end product yields (Kumar and Sharma 2017; Pattanaik 2019). Figure 1 represents the pretreatment methods for lignocellulosic biomass.

2.1.1 Physical Conversion Technologies

The physical process of pretreatment causes changes in a particular surface area, size of particles, crystalline index, or polymerization amount of biomass. This treatment eludes chemical usage, causes a reduction in the waste generation, and shortcuts for the following reactions. Pretreatment methods: microwave, mechanical, and ultrasound are commonly designed to advance the efficacy of key processes in biomass treatment. In these processes, the hard structure of lignocellulosic material is dislocated and its cellulose portion is exposed. Lignocellulosic substances pretreatment is carried to overcome the resistance that faces through the combination of structural and chemical changes in the carbohydrates and lignin (Amin et al. 2017; Onumaegbu et al. 2018). Table 3 enlists the benefits and drawbacks of different conversion technologies.

Mechanical

Mechanical pretreatment methods can be performed using a variety of procedures; however, the most abundant are grinding, milling, extrusion, or chipping. Ball milling pretreatment yielded significantly lower particle size compared to chipping or mashing but showed results in lower efficiency of hydrolysis (Yang et al. 2018). It was reported that extrusion is an effective action to reduce particle size including boiling, stirring, and trimming processes leading to alterations in the behavioral and compositional properties of biomass (Jedrzejczyk 2019). One of the benefits of using this method is the lack of the chemicals needed during this process, which lessens the quantity of post-processed garbage. The biggest drawback of mechanical pretreatment is the utilization of high power, which has an impact on the high cost of processing lignocellulosic materials. Therefore, information about equipment is necessary for the correct choice of material required for the processing of biomass, which must ensure the right balance among the cost and effectiveness of the process (Gu et al. 2018; Naimi and Sokhansanj 2018).

Microwave

Microwave is non-ionizing electromagnetic radiation having frequency among radio and ultraviolet waves. Microwave radiation exposure on the matter has the proper capacity to excite the vibration of molecules; however, its power is too squat for breakage of chemical bonds. The microwave electric field system transferences its energy to particles, leading to the production of thermal energy. Some benefits of microwave heating as compared to conventional process for heating are low power utilization, short times for a reaction, and avoidance of contact with feedstock. On the other way, longer microwave exposure surges the degradation of the polysaccharides (Bhutto et al. 2017; Kostas et al. 2017).

Ultrasound

The ultrasound usage in green technology imparts high-quality production of value-added compounds and biofuels by active decay of lignocellulosic waste. The key benefits of ultrasonic fabrication are the short duration required for processing, low operating temperature, and the endless volume of chemicals utilized during the additional process of valorization. In addition, it has the power of integration with further technologies (Chatel 2018; Subhedar and Gogate 2016).

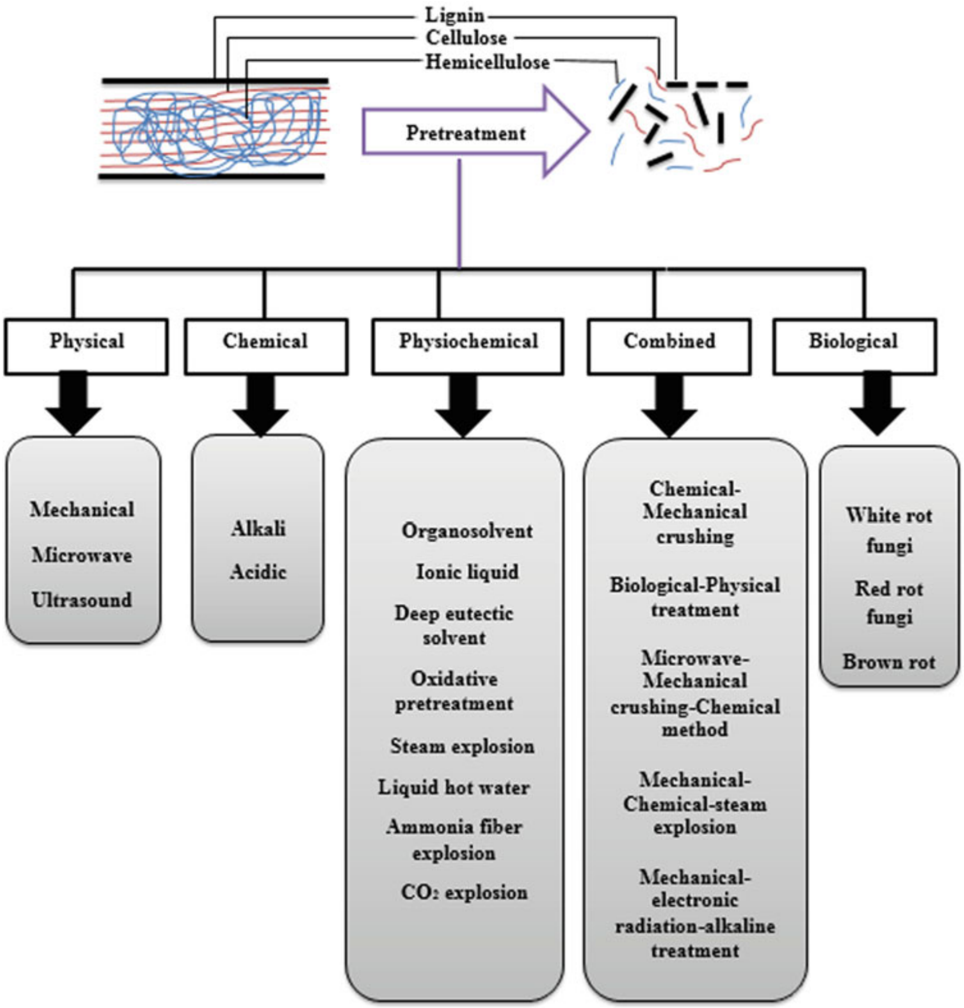

Fig. 1 Pretreatment method for lignocellulosic biomass

2.1.2 Chemical Conversion Technologies

Chemical pretreatment is utilized to attain the chemical destruction of organic lignocellulosic waste by using organic solvents, alkalis, strong acids, and ionic liquids. The chemical pretreatment effectiveness varies with the category of technique used and the nature of the substances. This degeneration viability for lightweight precursor or dietary supplements with high carbohydrate content because their rate of degradation increased and they accumulate as volatile acids leading to methanogenesis failure although it enhances the biodegradation of lignocellulosic substrates having more lignin amount (Paudel et al. 2017).

Alkaline

Alkaline pretreatment comprises adding alkali bases like calcium hydroxide (CaOH), potassium hydroxide (KOH), sodium hydroxide (NaOH), ammonium hydroxide (NH_4OH), aqueous ammonia, and hydrogen peroxide (H_2O_2) to lignocellulosic biomass, leading to increase inner surface area via swelling, reduction in the degree of polymerization, and its crystalline structure and causes breakage of linkage among lignin and its polymers. This method works better when biomass has low lignin content but with increased lignin content this method becomes less efficient. So, the efficiency of this treatment depends upon the lignin quantity of biomass. This method is useful in such a way it causes partially lignocellulosic biomasses hydrolysis. Up till now, sodium hydroxide and potassium hydroxide are efficient alkaline treatments to improve waste digestibility (Amin et al. 2017; Paudel et al. 2017).

Acidic

Acidic pretreatment of lignocellulosic biomass involves the usage of inorganic and organic acids like hydrochloric acid, phosphoric acid, nitrous acid, nitric acid, sulfuric acid, CH_3COOH, formic acid HCOOH, for hydrolysis of enzymes, and lignocellulosic biomass (Niphadkar et al. 2018). Acidic pretreatment was carried out with acid in

Table 3 Benefits and drawbacks of different conversion technologies

Methods	Types	Benefits	Drawbacks	References
Physical conversion technologies	Mechanical	Decrease the size of particles and cellulose crystals Enhance fluidity in digester	Consume high energy, not remove hemicellulose and lignin	Chen et al. (2017)
	Microwave	Operated simply, requires short time, effective energy, enhance end product yield	Requires more cost	Onumaegbu et al. (2018)
	Ultrasound	Improve cellulose reactivity and accessibility	Negative to enzyme hydrolysis, consume more energy	Das (2020)
	High temperature	Degrade cellulose quickly	Consume more energy, low end product	Ayeni (2020)
	High pressure	Decrease degree of cellulose polymerization	Requires more cost	Onumaegbu et al. (2018)
Chemical conversion technologies	Alkaline pretreatment	Perform at room temperature, breaks the lignin	Causes less breakdown of sugar	Shimizu et al. (2018)
	Dilute acid	Fast and do not require acid recycling	Requires high pressure and temperature, inhibitors formation	Wyman et al. (2005)
	Concentrated acid	Sugar conversion rate is high	Toxic and highly corrosive, highly costly	Shimizu et al. (2018)
Physiochemical conversion technologies	Organosolvent	Attain pure cellulose, lignin, and hemicellulose	Requires high cost, having an impact on fermentation and environment	de la Torre et al. (2013)
	Steam explosion	Transformation of lignin, solubilization of hemicellulose	Requires high pressure and temperature	Kumar and Sharma (2017)
	Liquid hot water	Not use chemicals, having low temperature	Large amount of products release with low concentration due to water dilution	Bhutto et al. (2017)
	Ammonia fiber explosion	Causes biomass swelling and increase surface area	Less efficient due to their corrosive nature	Kumar et al. (2009)
	Oxidative	Eco-friendly, efficiently remove lignin	Costly	Uzuner et al. (2018)
	Ionic liquid	Eco-friendly, large range of temperature, novel formation of products, decrease friction	Costly	Lopes (2017)
	CO_2 explosion	Inexpensive, enhance cellulose surface area, no formation of inhibitors	Requires high cost, not good for raw lignin material	Ayeni (2020)
	Electrical catalysis	Inexpensive, enhance surface area, efficiently remove lignin, hygienic	Requires more pressure, having low efficiency, do not affect hemicellulose and lignin	Chen et al. (2017)
	Deep eutectic solvent	Less volatility, wide range of liquid, less toxic in nature, easily biodegradability	Requires more chemicals	Loow et al. (2018)
Biological conversion	Usage of microbial enzymes	Low energy cost Break hemicellulose and lignin High yield of end products Not release toxic chemicals	Less hydrolysis rate	Behera et al. (2014)

dilute concentration 0.1% and the temperature high like 230 °C or acid in high concentration 30–70% along with lower temperature 40 °C. The concentrated form of acidic treatment causes more effective cellulose hydrolysis but it is corrosive and toxic and requires very expensive reactors for construction (Behera et al. 2014; Niphadkar et al. 2018; Kumari and Singh 2018).

2.1.3 Physicochemical Bioconversion Technologies

A combination of physical and chemical pretreatment methods can enhance the cellulose accessibility for enzymatic hydrolysis via solubilizing the hemicelluloses and abolishing the structure of lignin (Behera et al. 2014). It was reported that to increase and enhance the efficiency of lignin removal, physical factors like pressure were included in chemical methods such as alkaline pretreatment. Several physicochemical bioconversion technologies like a steam explosion, ionic liquid, oxidation, CO_2 explosion, aqueous ammonia pretreatment, organosolvent, and liquid hot water pretreatment have been carried out by topical researchers. The cellulose solvent-based fractionation and ionic liquids and of lignocellulose have been recommended recently. These physiochemical bioconversion technologies depend upon conditions for processing and usage of solvents, which affect the physiochemical possessions of lignocellulosic biomass (Rabemanolontsoa and Saka 2016).

Organosolvent

Organosolvent pretreatment of biomass uses many organic or aqueous organic solvent combinations for solubilization of hemicellulose and extraction of lignin. Organic solvents like acetone, ethanol, ethylene glycol, methanol, tetrahydrofurfuryl alcohol, tri-ethylene glycol are utilized commonly in this method, although organic acids include acetylsalicylic, oxalic, and salicylic are used as a catalyst in organosolvent method (Kumar et al. 2009). The organosolvent lignocellulosic pretreatment via alcohol usage leads to internal bonds hydrolysis of hemicellulose and lignin, as well as hydrolysis of ester and ether inter-polymer bonds among them. These outcomes come in the form of lignin removal and nearly whole hemicellulose solubilization. In organosolvent method, the existence of organic acids results in the formation of hydrogen ions that facilitate biomass delignification and lignin dissolution. The optimum temperature 100 °C–250 °C required for this process but depends on biomass nature although catalyst usage permits the procedure to efficiently run at low temperatures. In reaction mixture when inorganic acid is added, it causes hemicellulose hydrolysis that significantly enhances cellulose availability (Jedrzejczyk 2019).

Ionic Liquid

The ionic liquid method is a new comparative technology, which provides the lignocellulosic deconstruction with salts having low melting points. Ionic liquid usage as waste processing solvents began with the forming of cellulose that dissolves ionic liquid and then followed by usage of already known ionic liquid as an alternative solvent for synthetic cellulose fibers rotation, i.e., ion cell-F method. Two different strategies for the ionic liquid pretreatment of lignocellulosic biomass are being developed: The first tactic is a breakdown of the lignocellulose structure including crystalline cellulose (dissolution pretreatment), which came directly from the dissolution of cellulose via ionic liquid. The second, more current tactic uses ionic liquid to replace lignocellulose by dissolving hemicellulose and lignin but leaving the cellulose residue as a filterable solid. This method is analogous to organosolvent treating but takes place at atmospheric pressure (Lopes 2017; Elgharbawy et al. 2016).

Deep Eutectic Solvent

Deep eutectic solvent (DES) is a mixture of two or more than two components in which act as a hydrogen bond acceptor (HBA) and the other acts as a hydrogen bond donor (HBD). It comprises those compounds having a low melting point as compared to distinct components. Deep eutectic solvent (DES) application for biomass pretreatment is an alternative to conventional ionic liquids, because of their lesser charges. As compared to ionic liquids, the deep eutectic solvent biosynthesis is easy and it can be obtained from broadly accessible and low-priced components (i.e., quaternary salt of ammonium and metallic chloride) (Loow et al. 2018). Three kinds of deep eutectic solvents differ in hydrogen bond donors. The choline chloride urea, choline chloride citric acid, and choline chloride glycerol were produced and utilized for the sago waste pretreatment from enzyme hydrolysis into simple sugars (Wan and Mun 2018).

Oxidative Pretreatment

Oxidative pretreatment utilized oxidizing agents like oxygen, ozone, air, or hydrogen peroxide for lignocellulose biomass treatment. These methods involve lignin removal from the structure of biomass and enhance cellulose accessibility. Unluckily, oxidation of biomass is not a careful process. The lignin removal is often done with the loss of cellulose and hemicellulose. The process of delignification shows its efficiency by aromatic rings oxidation existing oxidizing agents into carboxylic acids. Time and oxidizing agent concentration can be affected by the oxidation method (Uzuner et al. 2018; Ayeni and Daramola 2017).

Steam Explosion

Steam explosion is a physicochemical method of lignocelluloses biomass pretreatment using high-pressure steam (saturated) which is quickly dropped causing volatile decompression. The conditions required while performing steam explosion method are 160 °C–240 °C temperature and 0.7–4.8 MPa pressure (Agbor et al. 2011). Steam explosion aims to improve the cellulose accessibility and solubilization of hemicellulose by evading the formation of the inhibitor for enzymatic processing. The steam explosion method causes hemicellulose partial hydrolysis with the release of acetic acid. To a small extent, lignin is also removed but again melting repolymerization and depolymerization cause its reorganization on the exterior of fiber (Kumar and Sharma 2017; Kumar et al. 2009).

Liquid Hot Water

Liquid hot water is also called compressed hot water and shows similarity with the steam explosion method although its name shows; it consumes water at high temperature, i.e., 170 °C–230 °C and uses pressure up to 5 MPa as compared to steam (Agbor et al. 2011). This causes hemicellulose hydrolysis and lignin removal to produce more accessible cellulose, which inhibits the formation of inhibitors at the highest temperature. It can be based on the direction of water flow and biomass into the reactor performed in three different ways. Cocurrent pretreatment: In this method, both water and biomass slurry heated at the required temperature with controlled pretreatment conditions before cooling. Current counter pretreatment: In this procedure, hot water is propelled in controlling conditions against biomass. In the third procedure, biomass behaves like a stationary phase and hot water acts like a mobile phase and flows through it, and fractions undergo hydrolysis passed out from the reactor (Kumar and Sharma 2017).

Ammonia Fiber Explosion

Ammonia fiber explosion pretreatment takes place at a higher temperature. Aqueous ammonia is a type of ammonia fiber explosion that treats biomass with ammonia in the aqueous form at 30 °C–60 °C in a batch reactor. In an ammonia fiber explosion, lignocellulosic biomass through liquid ammonia is heated in a closed vessel at 60 °C–90 °C temperature and 3 MPa pressure for 30–60 min. After holding the vessel at the required temperature for 5 min then the vessel valve is opened for release of pressure and ammonia evaporation with a drop in temperature of the system. This methodology shows similarity with the steam explosion but utilizes ammonia in the place of steam. Other methods that used ammonia for pretreatment are soaking aqueous ammonia and ammonia fiber explosion (Ayeni 2020; Rabemanolontsoa and Saka 2016).

CO_2 Explosion

CO_2 explosion done lignocellulosic biomass pretreatment uses CO_2 gas which behaves like a solvent. CO_2 gas is passed through a vessel with high pressure enclosing the biomass. At mandatory temperature, this vessel is heated and placed for a few minutes. CO_2 gas with high pressure enters into biomass and generates carbonic acid that hydrolyzes hemicellulose. This gas with high pressure when released upsets the lignocelluloses structure that increases the surface area. This method is not good for that biomass with less moisture percentage. Greater the moisture content greater hydrolytic yield (Ayeni 2020).

2.1.4 Combined Bioconversion Technologies

In the combined method strategy, the experimental procedure involved more than two pretreatment methods. The combination involves chemical or mechanical crushing, biological or physical treatment, microwave-machine-driven crushing-chemical process, machine-driven-chemical-steam explosion, mechanical-electronic radiation-alkaline action methods. Only one pretreatment methodology does not show more efficient results due to its restricted specific mode of functioning and some disadvantages. But these methodologies face many technologic trials, generate pollution, consume a lot of energy, slow procedure, and are destructive for apparatus. But they also have several benefits over single methods like enhanced hydrolysis efficiency, decreasing pretreatment harshness, increased methane (CH_4) production, and agreeing more complete biomass utilization. However, these methods increased the pretreatment cost, so economic analysis must be carried out for collective lignocellulosic biomass pretreatment methodology (Chen et al. 2017; Ummalyma 2019; Zheng et al. 2014).

2.1.5 Biological Bioconversion Technologies

Biological pretreatment is closely linked to the action of microbes like white, brown, and soft tissue molds that are able to produce degrading enzymes for hemicelluloses and lignin (Sindhu et al. 2016). The breakage of lignin assemblies on cell walls using microbial enzymes as biocatalysts is often referred to as the first hydrolysis step in the pretreatment process (Tanjore and Richard 2015). The usage of cellulases to convert cellulose into oligo and monomers is called enzymatic saccharification and happens in the second hydrolysis stage. These natural processes keeping separate is perfectly reasonable, but it should be considered that most of the relevant microorganisms simultaneously cause hydrolysis of lignin and cellulose to gain carbon and biomass energy. To remove physical barriers required for hydrolysis, several biological pretreatments required that involved chemical and enzyme intermediaries to deal with such as the mixing of enzymes can work harmoniously by enlarging small pores and increasing contact by the opening of the cell wall matrix (Laca et al. 2019). But, biological pretreatment of lignocellulosic biomass has to be environmentally favorable so with the expansion of technology, knowledge, and advancement in genetic manufacturing, microbes will perform an imperative role in the above procedure that brands the appliance of biological pretreatment approach more remarkable (Chen et al. 2017).

3 High-Value Compounds from Agro-Industrial Waste

Nowadays, agro-industrial wastes get much attention due to the presence of high potential compounds to recover for the development of value-added products to endorse the bio-based economy. The worthy sources of these natural products have diverse functions ranging from living systems to industrial level. If we can't reuse the large amount of these agro-industrial wastes, resulting in a serious threat for the environment. This risk can be reduced by the utilization of bio-wastes for extraction of large amounts of useful products and proper management of pollution. If we cannot use these wastes, we have no viable alternatives and consequently discarded them straightway into the surrounding environment. Apart from a substantial and gradual decline of valuable materials, the large amount of different agro-wastes generated through agro-industries causes serious management problems, both from environmental and economic points of view (Mirabella et al. 2014). The viable and sustainable applications of the waste by-products include production of animal feeds, organic fertilizers, essential oils, ethanol, enzymes, and additives in various biotechnological processes (Ferrari et al. 2004; Kobori and Jorge 2005; Alexandrino et al. 2007; Rodrigues 2009; Liu et al. 2012).

There has been an explosion of scientific interest to use agro-industrial wastes as potential raw materials for the development of value-added products to promote the bio-based economy. There are a number of different advantages associated with bioenergy production including local energy safety, a decrease in energy cost, extenuating global climate change, getting better carbon balances, and the utilization of local technologies ultimately leading toward improved economic growth (Maes and Van Passel 2014). Despite the well-known potentialities of economic and environmental transformation, the generation of organic energy is not as easy as it seems and has several different challenges as a possible tool for sustainable development (Yuan et al. 2008). Factors that influence the sustainability of organic matter for energy generation systems include land, soil, water, biodiversity, and overall productivity (Pollesch and Dale 2016). The number of different industrial applications of biomass and bioenergy has been discussed in the later sections.

3.1 Bioactive Compounds Recovery from Plant Wastes Are Valuable for Antibacterial and Antioxidant

Bioactives are defined as ingredients with biological activity and are able to moderate metabolic processes substantially in the promotion of healthier health conditions. The benefits revealed by these compounds comprise antioxidant activity, inhibition or induction of enzymes, inhibition of receptor activities, induction, and inhibition of gene expression (Correia et al. 2012). The agro-wastes including waste of grains, vegetables, and fruits are potential sources of bioactive, which comprise a diverse class of compounds largely polyphenolic, tocopherols, phytosterols, organosulfur, carotenoids, etc. the important bioactives that generally present in agro-wastes are shown in Fig. 2 (Carbonell-Capella et al. 2014; Serrano-León et al. 2018).

The secondary metabolites that are extracted from agro-wastes have good potential to inhibit the growth of microbes. The most effective group of compounds with antimicrobial activity is a flavonoid, phenolic, anthocyanins, terpenes, aldehydes, aliphatic alcohols, ketones, and acids (Spanos and Wrolstad 1992; Burt 2004; Arshad and Batool 2017). The primary action of phenolic is associated with the plant defense against abiotic and biotic stresses, pests, and pathogens (Atanasova-Penichon et al. 2016; Zhang and Tsao 2016; De Camargo et al. 2018). The maximum activities are exhibited by the class of flavanols, particularly the

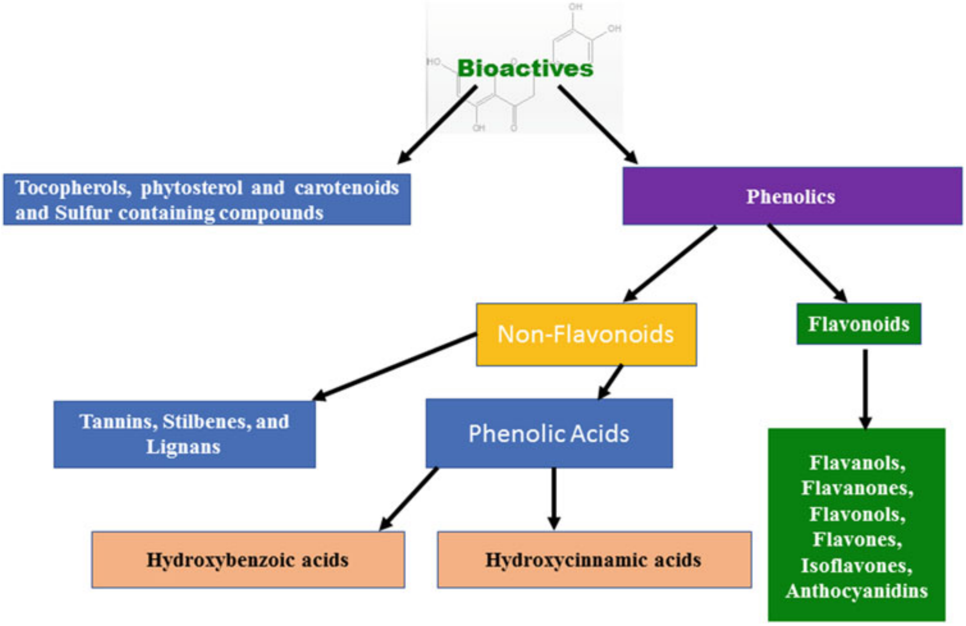

Fig. 2 Bioactives and their classification

procyanidin group and catechins, epicatechins, and their esterified derivatives. The profile of phenolic acids revealed many activities including, antimicrobial, antioxidant, anticarcinogenic, antimutagenic, and some other biological properties (Xu 2008). Substituted derivatives of hydroxybenzoic and hydroxycinnamic acids are the predominant phenolic acids. The most common hydroxycinnamic acids are caffeic, p-coumaric, and ferulic acids, which frequently occur in food as simple esters with quinic acid or glucose (Shahidi and Ambigaipalan 2015) while the most common benzoic acid is gallic acid, occurring in red fruits, onions, and black radish (Xu et al. 2017).

Plants are the core bases of natural antimicrobials, i.e., compounds accomplished to inhibit the microorganism's growth. These compounds are used along with older antibiotics to intensify the potency to evade the development of microbial resistance. The plant compounds that are broadly employed for antimicrobial purposes contain terpenoids, alkaloids, phenolics, and sulfur-containing compound (Khameneh et al. 2019). Therefore, more than 30,000 antimicrobial ingredients are extracted from different plants with effective antimicrobial potential (Tajkarimi et al. 2010). Plants are a large stake as bases of natural antimicrobials agents, and in this sense, the use of plant parts is usually thrown as wastes, and this agro-waste is a useful, sustainable and safe selection in the search of new antimicrobial compounds.

3.2 Bioactive Compounds Recovery from Agro-Industrial Wastes Useful Fermentation and Food Industry

The agro-industrial products generate a large number of fruits and vegetable peel, which create problems related to municipal landfills and safe management of these wastes. These wastes highly biodegradable and leachate produce methane, which creates problems for the environment (Misi and Forster 2002). These agro-industrial wastes mostly consist of seeds, bark, peels, pulp, etc., it can be used to extract high-value bioactives including enzymes, essential oils proteins, and some other compounds with potential biological activity that can be recovered and used for different useful purposes (Schieber et al. 2001). Figure 3 represents the usage of agro-industrial wastes as a natural source in fermentation and food industries for bioactive compounds production.

3.3 Bio-Surfactants Production

Surfactants are chemical substances, known for their potential to minimize surface tension and ultimately leading to the proper dissolution of immiscible solvents. Chemical synthesis is generally a common synthesis strategy for these surface-active compounds that cause severe side effects and impact in environmental hazards. The bio-surfactants are bioactive macromolecules generated by a variety of different microorganisms having hydrophobic and hydrophilic characteristics. They are the best alternative of chemical-based surfactants in terms of biodegradability, low toxic profile environmentally close to nature, and production via low-cost agro-industrial raw materials as beneficial part of "green technology" (Mukherjee et al. 2006). Bio-surfactants consist of long-listed chemical constituents; lipopeptides, phospholipids, glycolipids, lipoproteins, and lipid-polysaccharide derivatives. They present various applications as emulsifiers, conditioners, cosmetics, and food industries (Singh et al. 2007) and are also found effective in tackling environmental pollution through bioremediation (Banat and Thavasi 2019).

Despite having several commercially viable and environmentally friendly properties, the generation of industrial-scale bio-surfactants is still in its initial stages because of the utilization of expensive substrates with low production yield. The selection of a suitable substrate is an important step, as the substrate accounts for about 50% of the overall bioprocess cost of bio-surfactant development (Rodrigues et al. 2006; Asgher et al. 2019). Therefore, reducing the cost of the fermentation substrate could significantly reduce the overall cost of the bio-surfactant generation. A huge amount of renewable agro-industrial byproducts is generally disposed of in the environment including sugarcane bagasse, coconut husk, wheat straw, rice straw, and vegetables and fruits waste among others (Bilal et al. 2017; Arevalo-Gallegos et al. 2017). The utilization of such organic byproducts as raw substances for the development of value-added substances like bio-surfactants would not only reduce the overall bioprocess cost but also minimize the risk of environmental pollution. The generation of industrial-scale bio-surfactant requires in-depth studies to formulate and optimize nutritionally balanced growth media and certain substrates, which give the best bio-surfactant yield.

The agriculture processing industry generates a considerable amount of organic waste and byproducts. The processing of corn, barley grains, rice, and wheat release a huge amount of organic waste rich in carbohydrates. Therefore, various researches have been conducted to explore the potentialities of low-cost agro-industrial byproducts including starchy substances, oil wastes, plant oils, and distillery wastes for cost effect bio-surfactants generation presented in Table 4. Microbes, due to their metabolic variety, could use a variety of nutrients for their growth and can produce different kinds of bio-surfactants. However, researchers are required to study the induction of a desired biochemical pathway to improve the generation of a specific type of

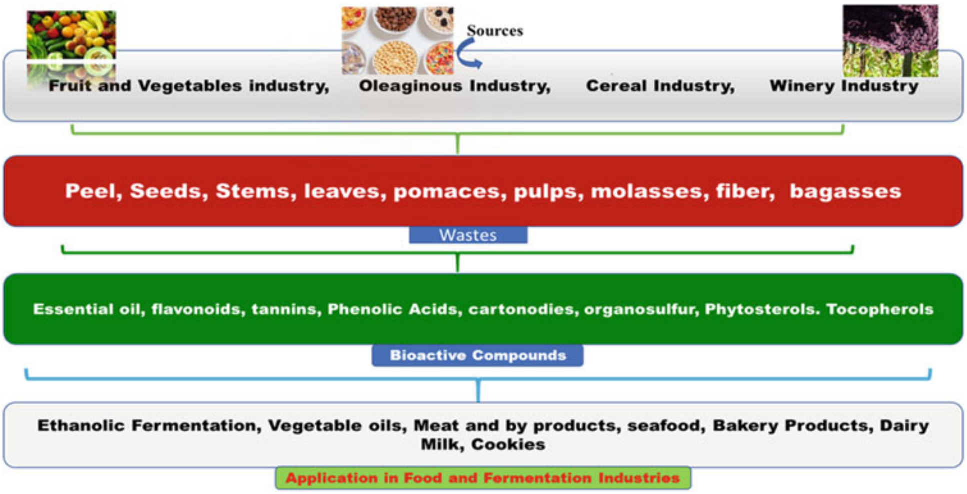

Fig. 3 Agro-industrial wastes as a natural source in fermentation and food industries for bioactive compounds production

bio-surfactant at the industrial scale. The optimization of metabolic pathways can be attained using statistical-based, response surface methodology (RSM) approach, which can help to study individual factors affecting the overall bio-surfactant production.

3.4 Fine Chemicals

The agriculture processing industry generates a huge number of organic wastes/byproducts in the form of kernels, pulp, and peels. Their disposal in municipal bins or an open environment enhances ecological pollution (Anwar et al. 2014). Therefore, the extraction of phytochemicals and/or other bioactive compounds from organic wastes, which could be used in cosmetics, pharmaceutics, and food processing industries, could be the best option (Anwar et al. 2014). This could, on one hand, provide a sustainable solution toward the environmental pollution problem, while being economically viable on the other hand. However, the utilization of agro-industrial waste in bio-refineries lacks advanced research explaining the economic feasibility of these biomaterials. Cristobal et al. (2018) concluded that not all organic wastes possess similar potential as a raw substrate in bio-refinery processes. The best economic replacements are those letting the capitalization of economies of scale and the

Table 4 Different types of bio-surfactants obtained using various agro-industrial raw materials/by-products as substrates

Agro-industrial waste (substrate)		Bio-surfactant class	Total yield (g/L)	References
Starchy byproducts	Potato peels	Rhamnolipids	1.160	Das and Kumar (2018)
	Rice straw	Surfactin	1.503	Zhu et al. (2013)
	Rice mill waste	Surfactin	4.170	Gurjar and Sengupta (2015)
Sugar industry wastes	Liquor industry waste	Surfactin	3.400	Zhi et al. (2017)
	Crude glycerol	Sophorolipids	12.70	Ashby and Solaiman (2010)
	Molasses wastewater	Rhamnolipids	2.600	Li (2011)
Dairy industry waste	Cheese whey waste	Sophorolipids	33.32	Daverey and Pakshirajan (2010)
	Paneer whey waste	Rhamnolipids	4.800	Patowary et al. (2016)
	Whey waste	Glycolipids	0.890	Vera et al. (2018)
Oils processing waste	Olive oil mill wastewater	Glycolipids	0.139	Meneses et al. (2017)
	Palm oil mill waste	Rhamnolipids	0.430	Radzuan et al. (2017)
	Soybean oil waste	Lipopeptide	–	Li et al. (2016)

concentration of production stages. Though, the risks also appear associated with instability problems of organic wastes, supply, and logistics. In addition, the organic waste-derived products show variable prices depending upon various factors like supply–demand, purity, and product composition. Therefore, it is difficult to determine the turnover rates and the profitability of the products (Carlini et al. 2017). The conversion of agricultural industry waste into value-added fine chemicals requires multi-step processing that comprises (i) biological, chemical, or mechanical pre-treatment; (ii) enzymatic hydrolysis; and (iii) fermentation processes (Menon and Rao 2012). The conversion of lignocellulosic biomass via biochemical and thermo-mechanical pathways into different value-added fine chemicals is shown in Fig. 4.

The valorization of agro-industrial wastes into value-added products demands the identification of the main industrial sources of each country/region. In addition, it is necessary to understand the type of chemical compounds to be extracted and how much is their value. These are some key factors to take into consideration when the industry decides to invest in a new product or process. The way to attain the above-mentioned tasks is not so easy. Few alterations are required to stabilize the agro-industrial wastes before processing. Several research groups are focusing to investigate the stabilization of agro-industrial wastes by both anaerobic and aerobic digestion methods (Fernandez-Bayo et al. 2018). Different compounds originating from agro-industrial byproducts have been described in Table 5.

Such as, if the focus is on the extraction of functional chemicals from agro-industrial biomass, the stabilization must decrease the biochemical pathways into agro-industrial wastes, adjusting the benefit of bioactive chemicals (Caballero and Soto 2019). Some researchers are focusing on technologies as freeze-drying, superficial drying, and spray drying to extract bioactive compounds (Rezende et al. 2018).

Bioconversion of agro-industrial wastes into organic acids, e.g., lactic acid, oxalic acid, citric acid, enzymes, and other products via solid-state fermentation is getting scientific attention in the modern era. Agro-industrial biomass is considered the best substrate for the development of several industrially important enzymes (Nadeem 2019; Arevalo-Gallegos et al. 2017). The occurrence of hemicellulose, cellulose, and lignin among biofibers acts as a bio-inducer, and the majority of these organic wastes are rich in sugars, which allow improved fungal growth ultimately leading to the economical production of cellulolytic and ligninolytic enzymes. Accept bioconversion, there are several other methods, used for the extraction of bioactive compounds, i.e., direct extraction of chemicals, leaving the fraction rich in bio-fibers (Sagar et al. 2018) that can be used for the generation of bioenergy.

3.5 Bioplastic/Bio-Composites Development

Composite can be defined as a material that involves more than one type of polymers/materials to induce desired characteristics (thermal properties, specific strength, biodegradability, biocompatibility, and surface properties) that cannot be achieved by using a single type of

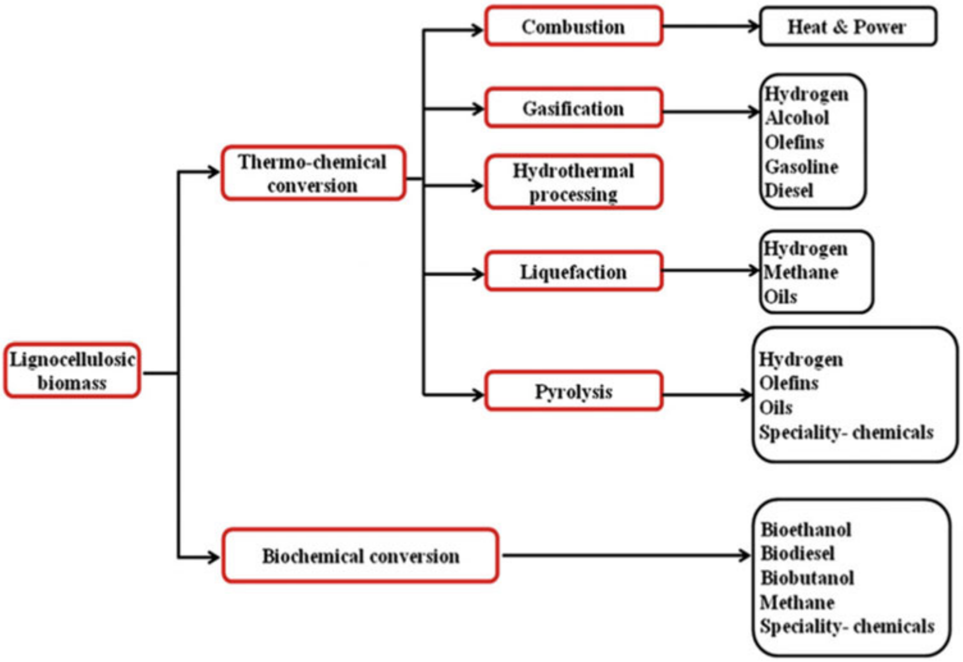

Fig. 4 Biochemical and thermo-mechanical conversion of agricultural biomass into value-added fine chemicals (adapted with permission from Menon and Rao 2012 from Elsevier. Copyright © 2012 Elsevier B.V)

Table 5 Compounds extracted from various agro-industrial byproducts and their applications in different industrial and biomedical sectors

Agro-industrial waste/byproducts	Compounds	Applications	References
Rosa damascena wastes	Polysaccharides, polyphenols	Bioactive substance	Slavov et al. (2017)
Lettuce waste	Polyphenol	Antioxidant properties	Plazzotta and Manzocco (2018)
Citrus peels	Dietary fibers, oils, flavorants	Food supplements and additives	Nafisi-Movaghar et al. (2013)
Onion solid waste	Polyphenols	–	Stefou et al. (2019)
Mango peels/seeds	Polyphenols, pectin	Preservative, gelling agent, stabilizing agent	Bouarab Chibane et al. (2019)
Pomegranate peels	Polyphenols	Treatment of prostate cancer	Ma et al. (2015)
Grape seeds extract	Polyphenols	Cancer treatment, antiaging	Kasiotis et al. (2013)
Vegetable feedstock	Succinic acid	Agriculture, food and pharmaceutical usage	Islam et al. (2018)
Tomato processing waste	Lycopene	Therapeutic, antioxidants	Kehili (2017)
Cranberry extract powder	Tannins	Antibacterial agents	Harich et al. (2017)

polymers/materials. When composite consists of at least one material derived from a biological origin, it is termed as bio-composite materials (Iqbal 2015). According to another broader definition, bio-composites are substances that are composed of bio-based or bio-derived polymers such as polylactic acid PLAs or polyhydroxyalkanoate PHAs (Iqbal 2015).

Sustainable bioplastics and bio-composites made up of biodegradable and bio-based materials are designated as “green composites” and are major research areas among environmental biotechnology (Saberi et al. 2017). Recently, bio-composites have been developed for various functional applications, e.g., biomedical, pharmaceutical, textile industry, bio-based packaging, and others using agro-industrial waste/byproducts (Lancaster et al. 2013) to overcome the rising environmental pollution caused by the high dependency on petroleum-based resources (Iqbal et al. 2013). Materials that are obtained from agro-industrial wastes, having an acceptable level of biodegradability, recyclability, environmental and commercial feasibility are termed as sustainable bio-based materials.

Possible routes for the effective exploitation of agro-industrial wastes and by-products into bio-composites development have been represented in Fig. 5. The utilization of agro-industrial wastes in bio-composites development offers several advantages, i.e., a decrease in the relative amount of non-renewable materials in bio-composites ultimately leading to the development of environmentally friendly materials. Therefore, we can enhance the component of renewable biomass, which may also reduce the overall bio-composite cost (Väisänen et al. 2016).

The environmental issues as a result of fossil-based materials have increased the researcher’s concern in bio-based and biodegradable materials development. About 90% of total thermoplastics is made up of six types of polymers, e.g., polystyrene, polyethylene, polypropylene, polyvinyl chloride, and polyethylene terephthalate (Lee et al. 2004). The exploitation of agro-industrial biomass for the development of composites materials seems rather limited. The desire for sustainable utilization of such wastes is an emerging area due to an increase in agro-waste in developed countries, possibly due to the availability of advanced facilities than developing and under-developed countries, which are rich in agro-industrial wastes. The present scientific studies are focusing on scaling up rather than optimization approaches. In conclusion, the development of agro-waste plastic composites was lagging behind in terms of commercial-scale development as compared with fossil-based materials. Table 6 summarizes recent data related to bio-composites development based on agro-industrial biomass using a variety of different techniques.

During the previous few years, the properties of composite materials have significantly been improved using various synthetic, bio-based, or nano-scale reinforcements. The market demand is increasing for natural fiber reinforced polymer composites (Vaisanen et al. 2017) to reduce the environmental damage caused by high usage of non-biodegradable, petrochemical-based materials (Bilal 2020; Asgher et al. 2020). Proper utilization of agro-industrial biomass requires a combination of global policies, financial drivers, and environmental awareness that

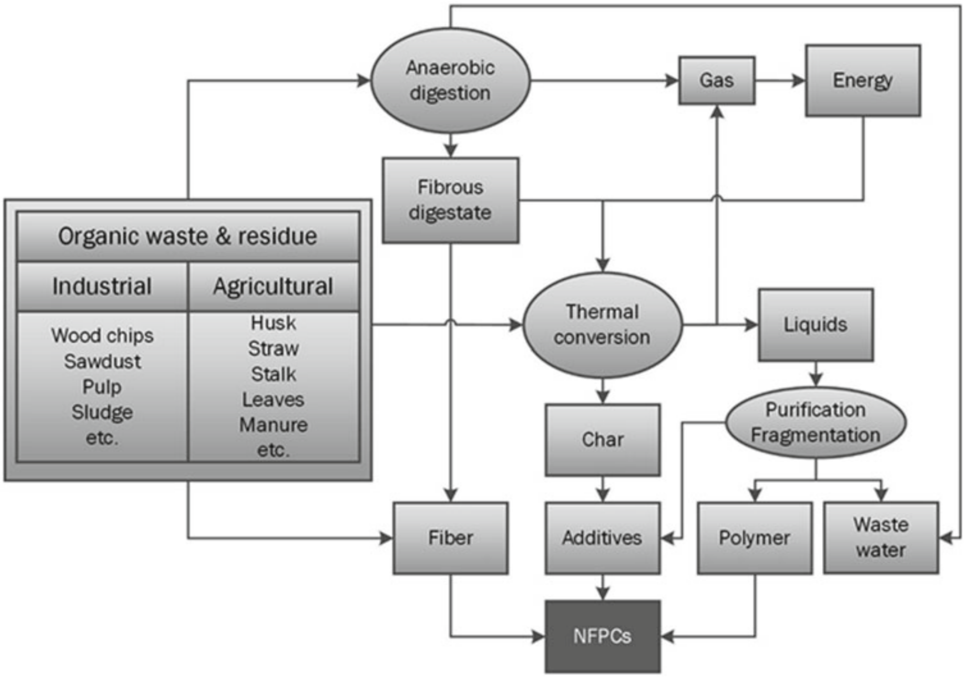

Fig. 5 Effective utilization of agro-industrial wastes/by-products into natural fiber polymer composites (NFPCs) and other value-added products (adapted with permission from Väisänen et al. 2016 with permission from Elsevier. Copyright © 2016 Elsevier B.V)

Table 6 Overview of bio-composites based on the matrix of agro-industrial biomass

Agro-industrial biomass	Co-material	Technique used	References
Nut shells	Cassava starch	Thermocompression	Engel (2020)
Rice husk	Polypropylene	Injection molding	Hidalgo-Salazar and Salinas (2019)
Wood fibers	PHBV	Extrusion and injection mould	Vandi et al. (2019)
Potato pulp	PHBV	Extrusion and injection mould	Righetti et al. (2019)
Wood fibers	Starch	Mill and injection	Grylewicz et al. (2019)
Sugar palm starch	Microcrystalline cellulose	Casting	Salit (2018)
Silk cellulose	Microcrystalline cellulose	Casting	Stanton et al. (2018)
Thai silk	Microcrystalline cellulose	Casting	DeFrates et al. (2017)
Palm cellulose	Butyl methacrylate	Casting	Zailuddin et al. (2017)
Coconut shell cellulose	Butyl methacrylate acid	Casting	Farah et al. (2016)
Cellulose	Polycaprolactone	Compression molding	Cocca et al. (2015)
Curaua fibers	PHBV	Mill and injection	Beltrami (2014)

DMAc/LiCl: dimethylacetamide/lithium chloride, PHBV: poly 3-hydroxybutyrate co 3-hydroxyvalerate

provide incentives to extract organic waste components and promote their secondary utilization in different industries. The extraction and reuse of secondary and tertiary biomass resources at industrial sectors will ensure that there is a good supply of waste organic biomass and promote the development of bio-based chemicals and products.

3.6 Bio-pulping and Paper Industries

Pulping is the conversion of wood/lignocellulose to isolated pulp fibers for papermaking. Paper and pulp can be produced after lignocellulosic waste biomass, e.g., wood residues, wastepaper, or agricultural biomass. This conversion process involves three main steps, i.e., pulping of lignocellulose, bleaching of fibers, and paper production. Major types of pulping include groundwood or mechanical pulping, chemical pulping, and the combination of both mechanical and chemical pulping (Das and Houtman 2004). Mechanical processes consume a considerable amount of energy during refining steps. However, bio-pulping involves the treatment with microbial inoculum before the refining process giving biomass soft and porous texture. These microbial-treated biomass chips are more effectively broken apart while the purification process, ultimately reducing energy consumption (Bajpai 2018). Moreover, production done from microbial treated bio-fibers exhibits improved paper properties (Akhtar 1998).

The paper industry is facing high stress due to the increasing demand for lignocellulosic pulp, which is going to enhance in the near future. A large number of paper and pulp industries are using classical procedures, i.e., chemical and/or mechanical-based pulping. These industries compete in the international market, where the material cost and energy determined profitability. Production of pulp requires plenty of chemicals and electrical energy. Moreover, bleaching processes generate a huge amount of wastewater containing toxic effluents. These hazardous chemical-based methodologies can be effectively replaced by bio-based pulping strategies (Giles et al. 2011). Bio-pulping can be successfully established in industrial sectors to save chemicals, and the use of agro-industrial waste for the extraction of bio-fibers will significantly reduce the overall production and process cost by improving fiber texture.

Bio-pulping includes (i) steam-based decontamination of lignocellulosic chips from naturally occurring microorganisms and (ii) inoculum addition of selected microbe, followed by incubation for 2 weeks in an aerated chip pile. Under specific growth conditions, i.e., optimum moisture and temperature, fungal grows on the surface of chips and penetrates the interior using hyphae. These hyphae start making ligninolytic enzymes, which help in easy breakage during subsequent refining and result in flexible and intact bio-fibers.

Chemical-based pretreatments alter the structure of pectin and hemicellulose. These modifications have been exploited in the synthesis of chemo-mechanical pulps of wood chips. This results in stronger paper products as mechanical properties are enhanced by mixing with chemical pulps. White rot fungi exhibit the ability of bio-pulping by attaching or creating oxalate esters (COOH groups) on carbohydrates present in the wood. Because of the dicarboxylic nature of oxalic acid, the insertion of one carboxylic group leaves another group as free. Configuration of the COOH group increases the absorbance of water, and hence, the wood bulges, which decreases the cost of refining. The carboxylic functional group present at the surface of fibers serves as reinforcement between fibers, which ultimately improves the mechanical properties of paper products (Scott et al. 1998).

4 Conclusion and Future Prospective

Today the world is facing environmental and energy disasters so it is forced to use or search for alternate uses for renewable and natural resources by green technologies. In this case, lignocellulosic biomass has great potential to encounter the existing need for energy for the modern world. All pretreatment methodologies for lignocellulose bioconversion have been recognized to be effective but it depends upon biomass nature, global location, and its final products. All the methods you have chosen have benefits and drawbacks but they can be overcome with advanced technology. Any method you have selected must be put toward bearing in mind the feedstock belongings, the budget of process, and final product yield. It must be considered that the processing of biomass must be handled using integrated technologies where procedures from downstream and upstream phases are in a solitary line.

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Bioconversion of Straw Biomass into Bioproducts

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Abstract

Agricultural industries produce a significant amount of lignocellulosic materials and wastes that can be converted and developed into cost-effective energy and value-added bioproducts of commercial importance. Bioconversion turns organic matter into products using biological methods or agents. Straw biomass is an important agricultural residue that can be harnessed for the production of bioethanol, high-value biochemicals, special enzymes, organic products, proteins, and biomaterials. The tough lignin layer of the lignocellulosic components necessitates the pretreatment steps including the physico-mechanical, chemical, or biological methods to allow further processes such as saccharification, fermentation, and anaerobic digestion; and to enhance accessibility to the microbes and enzymes, for bioconversion into products of interest. However, there are major economic and technological challenges that have to be taken into consideration. This chapter highlights the straw biomass and its key composition for the bioconversion into valuable bioproducts. Different biological pretreatments using lignocellulolytic enzymes for the degradation of biomass are elaborated. The challenges for industrial-scale implementation to develop bio-based commercial production using straw biomass are also addressed.

Keywords

Sustainable development • Green technology• Eco-friendly processes • Agro-wastes • Straw biomass • Lignocelluloses • Bioconversion • Biological treatments • Biofuels • Bioproducts • Biomaterials

1 Introduction

Bioconversion converts organic matter, for instance, animal, plant, or lignocellulosic wastes, into value-added extracts/products and bioenergy, by utilizing the biological methods or biological agents (microorganisms). The development of bio-refineries, as shown in Fig. 1, for the transformation of raw materials/wastes/residue into bioproducts should provide alternatives to the petrochemicals and conventional oil refineries (Ferreira 2017). The bio-refinery concept aims to utilize different potential biomass feedstocks, based on different treatments and conversion protocols, toward the production of a wide variety of products. The bioconversion processes should be eco-friendly, consume less energy, generate zero or less wastes, and be economically viable. The potential applications of lignocellulosic biomass are shown in Fig. 2 (Iqbal and Kyazze 2013). Nevertheless, the major challenge is that the agricultural wastes or straw biomass are protected by a tough lignin layer, thus inhibiting the microbes and enzymes to access and convert them into the required products. Hence, bioconversion requires precise and effective methods in which the pre-treatment step plays the most important role. There are different treatment methods for the lignocellulosic waste materials including physical, chemical, physio-chemical, and biochemical or biological treatments (Fig. 3) (Kumar and Sharma 2017). The pre-treatment of wastes is needed to modify the structure of straw wastes to isolate the cellulose, hemicellulose, and lignin, employing various methods; for instance, saccharification or enzymatic hydrolysis, to release the sugars

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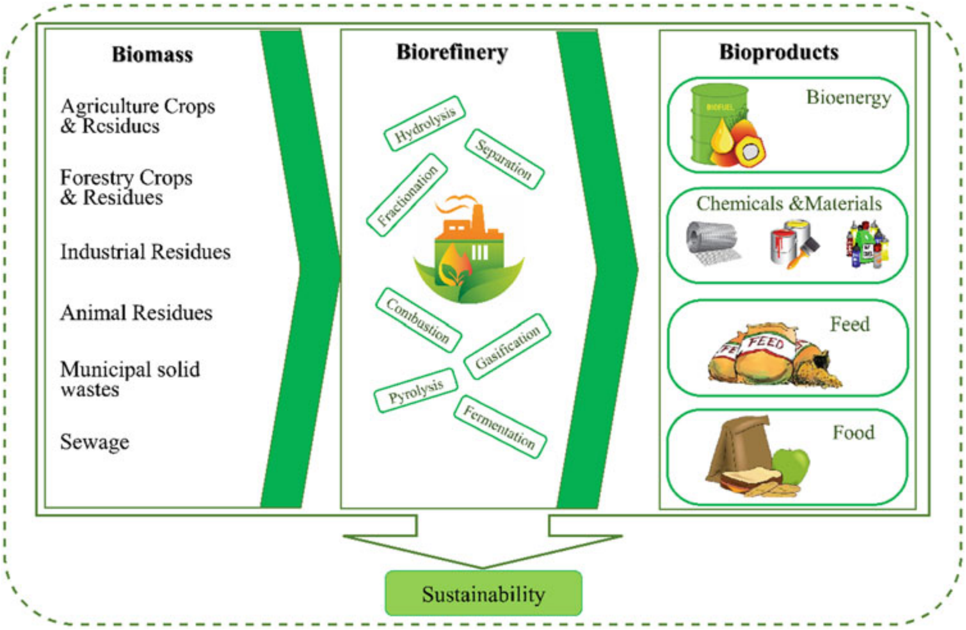

Fig. 1 A bio-refinery concept from biomass feedstock utilization to the production of wide variety of bioproducts (Modified from Ferreira 2017)

(as shown in Fig. 4) (Den and Sharma 2018), and to carry out fermentation or anaerobic digestion using microbes to obtain different products.

As shown in Fig. 5, cellulose is not easily accessible due to the presence of hemicellulose and lignin, (Tian et al. 2018), suggesting that the combined pretreatments based on mechanical, chemical, and biological means, should be practically considered to reach the reaction sites (Tian et al. 2018). Depending on the composition of the lignocellulosic materials, pretreatments may involve high energy consumption for the conversion into fuels or biochemicals. The methane production based on rice straw varies from 92–280 L/kg of volatile solids, depending upon the digestion constraints and pretreatment protocols (Mussoline et al. 2013). The synthesis of fuels, chemicals, and products of industrial interests based on the bioconversion processes is the way forward to meet the Global Sustainable Development goals (Kennes 2018). The optimization and enhancement of bioconversion routes and the bio-refineries are being implemented in combination with the existing conventional processing plants (Cho et al. 2020; Arellano-Garcia et al. 2017). The feedstock is the biomass, solid waste, sewage sludge, wastewater and biogases, agricultural waste residues/husk and straw wastes, and by-products such as glycerol from different bio-refineries (Rulkens 2008; Kirchmann et al. 2017; Pancha et al. 2019; Santos et al. 2017; Nda-Umar et al. 2019; Crosse et al. 2019). For economics reason, most bioconversion protocols are employed without pre-treating the primary feedstocks, but some require specific pretreatments before undergoing the microbial fermentation or conversion. Some feedstocks comprise complex polymeric constituents, which necessitate the first step of breaking down the polymers into smaller or monomeric molecules, to allow easy access to the microorganisms (Tian et al. 2018; Xiu et al. 2017; Ren et al. 2016). Diverse strains of microorganisms (pure or mixed cultures of anaerobic and aerobic bacteria, algae, fungi, and yeast) taken

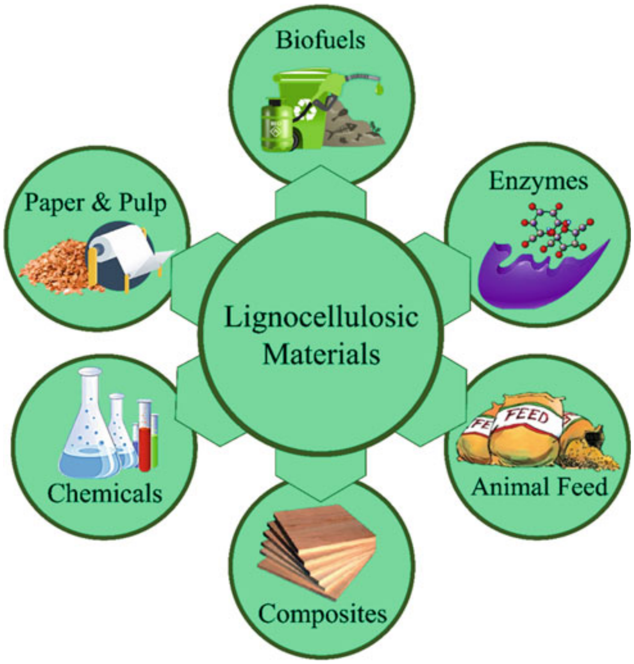

Fig. 2 Potential applications of lignocellulosic materials (Modified from Iqbal and Kyazze 2013)

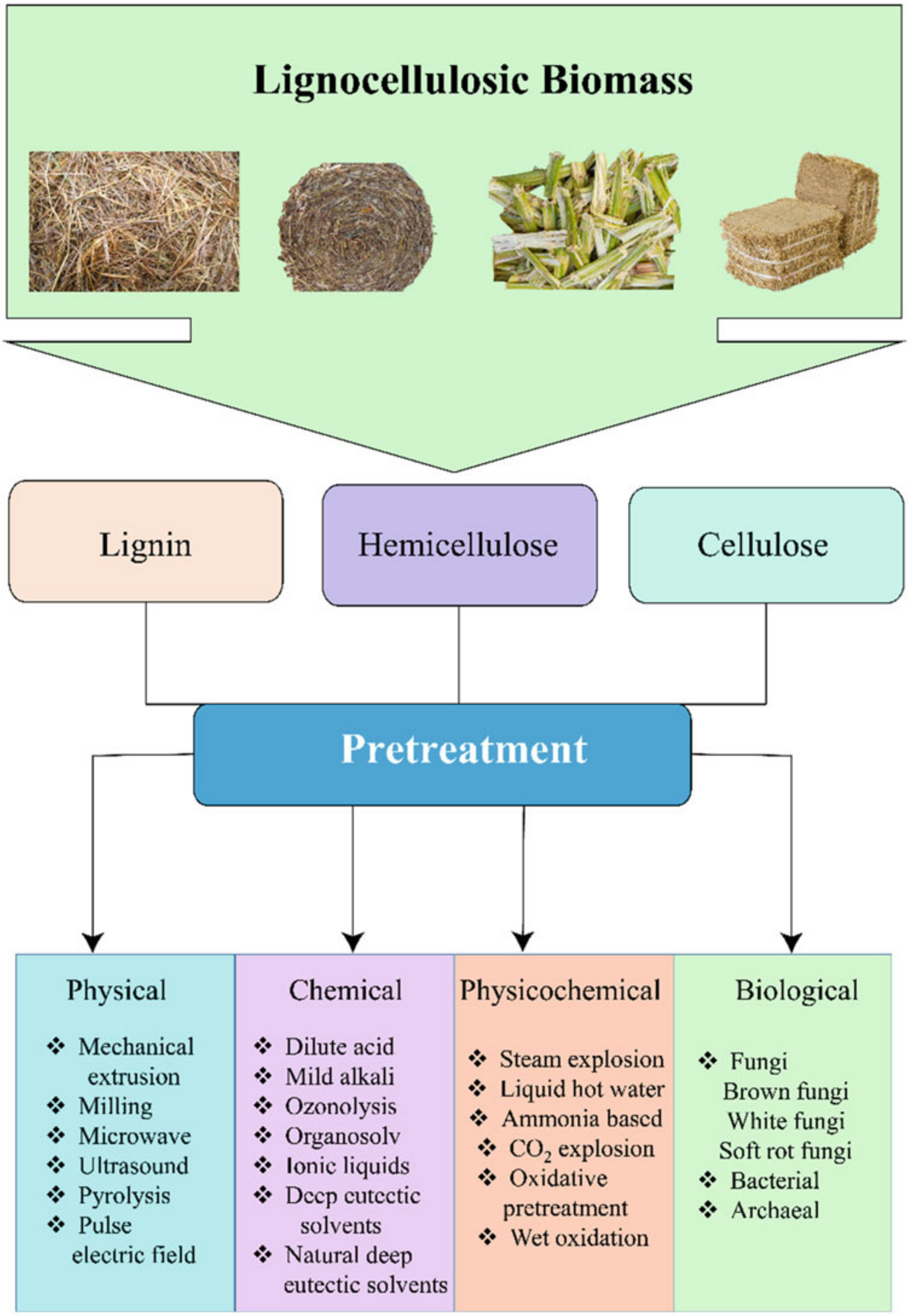

Fig. 3 Different pretreatment protocols for the treatment of lignocellulosic biomass (Modified from Kumar and Sharma 2017)

from either nature or culture have been tested and developed as biocatalysts (Dashtban et al. 2009; Yu and Jin 2019; Alahyaribeik et al. 2020; Patthawaro et al. 2020).

The aim of this chapter is to highlight the bioconversion of the straw biomass into valuable bioproducts, the use of pre-treatment methods such as the lignocellulolytic enzymes, and the challenges for industrial-scale production.

2 Waste Material Feedstocks

Bioconversion may be carried out in the bioreactors or in complete bio-refineries setup (Kennes 2018; Biernat and Grzelak 2015). The bioreactor working conditions including pH, residence time in continuous protocols, and the medium

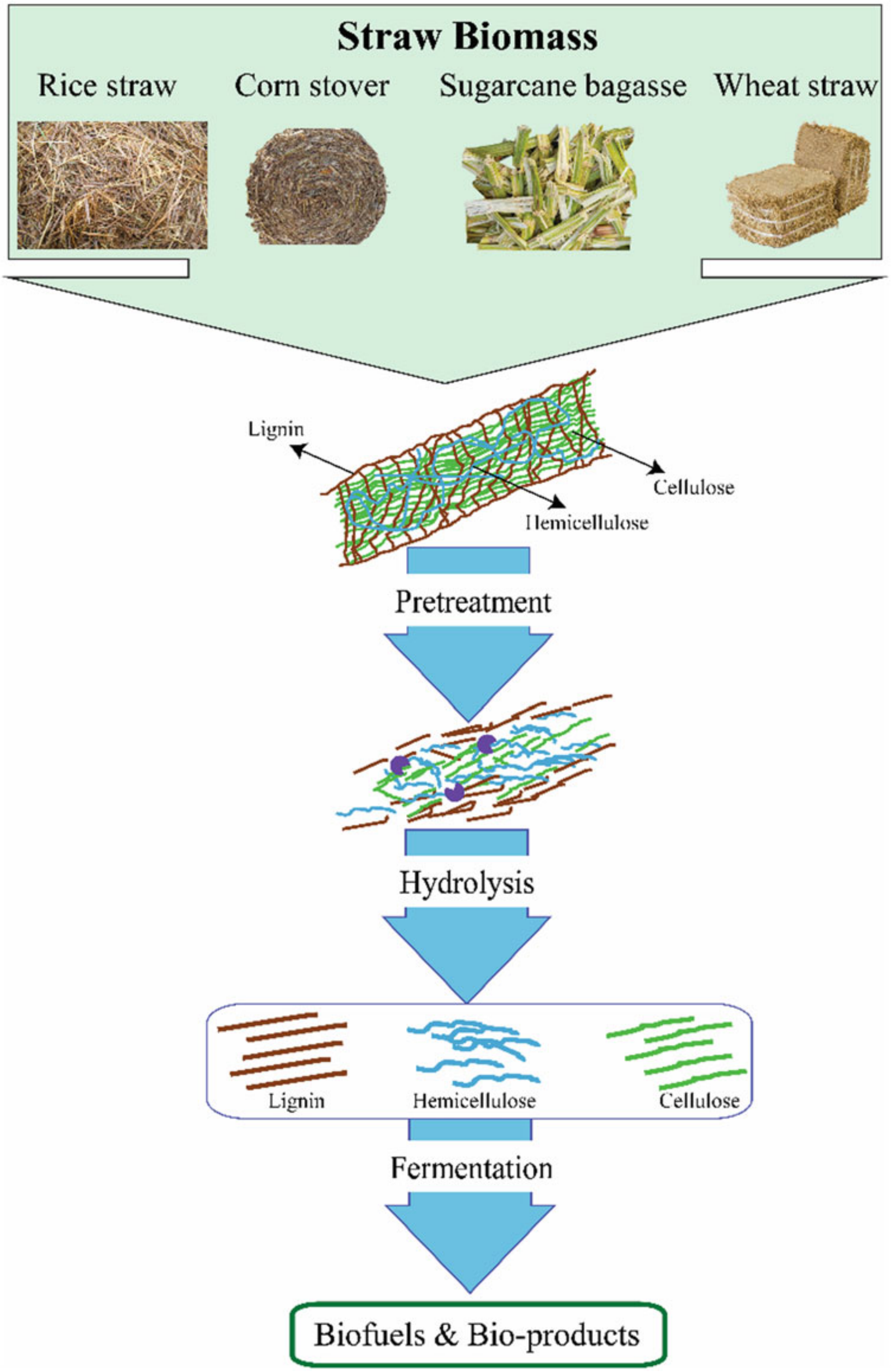

Fig. 4 Bioconversion of straw biomass involving pretreatment, saccharification or enzymatic hydrolysis, and fermentation to obtain biofuels and bioproducts (Modified from Den and Sharma 2018)

compositions are very much dependent on the feedstocks (Pino et al. 2018; Zhen et al. 2019; da Rosa et al. 2019). The solid wastes from different sources such as the domestic wastes; wastes from offices, schools, or municipalities; and wastes from industrial sectors and factories, must, therefore, be sorted out and screened (Lebersorger and Beigl 2011; Millati and Cahyono 2019). The four major types are domestic, agricultural, commercial, and industrial wastes (Pancha et al. 2019; Millati and Cahyono 2019; Hargreaves et al. 2008; Han et al. 2018). Among them, agricultural wastes from the agriculture fields may include weed and husk waste, cattle wastes (Millati and Cahyono 2019), or

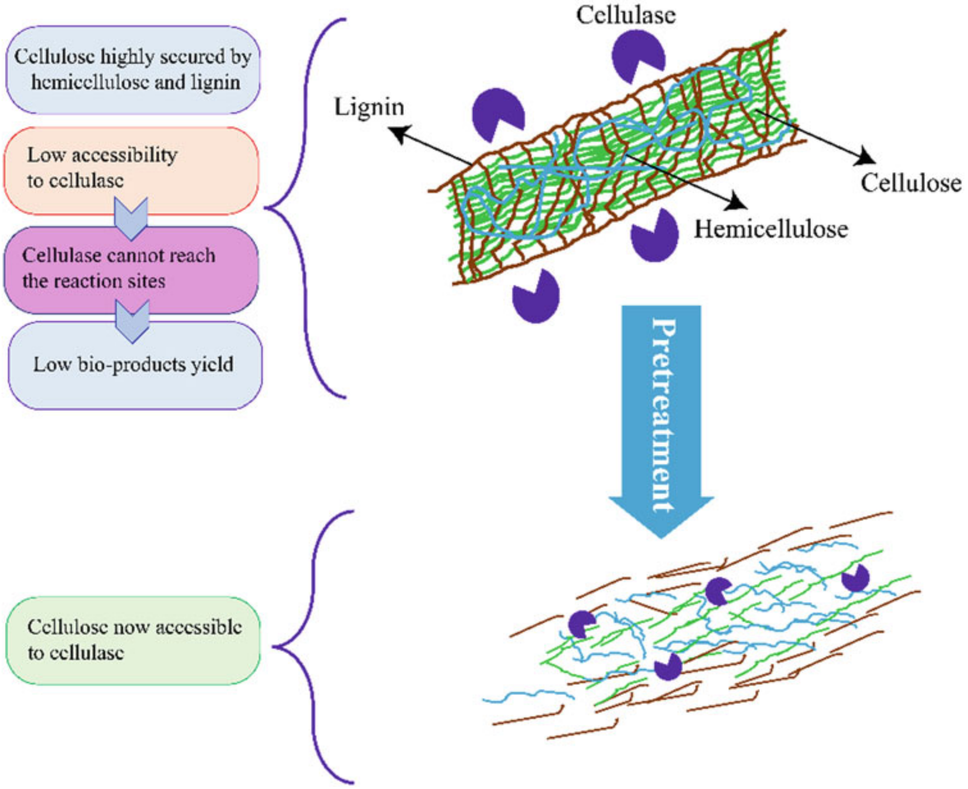

Fig. 5 Pretreatment for lignocellulosic biomass to isolate cellulose, hemicellulose, and lignin (Modified from Tian et al. 2018)

even pesticides, and agro-chemicals to promote plant growth. Depending on the objectives of the bioprocesses, these feedstocks provide important organic and inorganic compounds that can be into valuable products (Swain 2017). Furthermore, the advantage is that the bio-refinery based on waste conversion provides integrated management of wastes (Biernat and Grzelak 2015). The agricultural activities principally generate tons of waste, in the form of straw wastes or agro-effluents. The straw crops are wheat, rice, oat, barleys, rye, and grained crops, and the straw wastes include the dry stalk of cereal plants that remain after the extraction and removal of grains and chaffs, e.g., sawdust, sugarcane bagasse, corn stoves, rice hulls, rice straws, and wheat straws (Santulli 2017). The straw remains constitute almost half of the total harvested yield, making them abundantly available agricultural residues (Smil 1999). Besides, these straw wastes have found applications as fuel, livestock duvet/beddings and fodder, thatching roofs, and for making baskets. Straw biomass is considered as the major lignocellulosic material to be exploited for biofuels and bioproducts (Santulli 2017; Ghaffar et al. 2015).

The straw biomass mainly comprises lignocellulosic residues such as cellulose, hemicellulose, and lignin as core constituents of plants cell wall, which are readily accessible for biofuels and bioproducts generation (Kucharska and Rybarczyk 2018; Putro et al. 2016). The average composition and amount of these constituents in the straw biomass are summarized in Table 1. Cellulose is a polysaccharide of linear chains of β associated D-glucose units, ranging from several hundreds to many thousands. The simple structural arrangement of cellulose makes it biodegradable (Lavanya et al. 2011). Hemicellulose or polyose is a macromolecule having molecular weight less than cellulose (Saha 2003). The key difference is that cellulose is more crystalline in nature, and highly resistant to hydrolysis, while hemicellulose has a more amorphous structure, having low stability and easily hydrolysable. Hemicellulose in straw biomass generally contains xylan, while the softwood hemicellulose contains glucomannan (Pérez et al. 2002). Lignin is a cross-linked phenolic polymer, having a rigid structure that forms the main structural base in order to provide support to tissues in some algae and vascular plants (Buranov and Mazza 2008). Lignin is biodegradable and among the most durable biopolymers available. Globally, around 73.9 Teragram (dry weight %) of the crop wastes/agriculture residues could provide around 49.1 giga-liter (GL) of bioethanol per year (Kim and Dale 2004). Hence, the bioconversion of these lignocellulosic residues could lead to a more sustainable production of bioenergy and bioproducts, and could address the problems caused by climate change.

Table 1 Composition and amount of lignocellulosic residues in straw biomass

Sr. No.	Straw biomass type	Cellulose (% Dry weight)	Lignin (% Dry weight)	Hemicellulose (% Dry weight)	References
1	Corn straw	38	17	26	Li et al. (2010)
2	Wheat straw	30	17	22	Ballesteros et al. (2006)
3	Barley straw	34	14	22	Singh nee' Nigam et al. (2009)
4	Oat straw	39	18	27	Singh nee' Nigam et al. (2009)
5	Rice straw	31	13	22	Chen et al. (2011)
6	Rye straw	31	25	22	García-Cubero et al. (2009)

3 Pre-treatments of Straw Biomass

Biological pre-treatment is carried out using microbial hydrolytic enzymes to degrade the lignin structure, to allow the release of sugars (Chen et al. 2010). This is a low-energy consumption process when compared to the conventional chemical pretreatments. Hydrolysis of lignocellulosic biomass without any pretreatment may result in low productivity, with less than 20% of the total sugars (Alizadeh and Teymouri 2005). It is, therefore, important to select the most appropriate and effective bacterial strains such as the cellulase enzyme-producing bacteria or cellulolytic bacteria *Cellulomonas fimi* and *Thermobifida fusca* (Sharma et al. 2019). *Paenibacillus campinasensis*, which can withstand extreme conditions, has great potential in the pretreatment of lignocellulosic materials (Maki et al. 2009). Anaerobic *Bacteroides cellulosolvens* and *Clostridium thermocellum* have exhibited significant cellulase activity but the enzyme concentration produced is insufficient (Mathews et al. 2015), while *Zymomonas mobilis* has produced high yield of ethanol (Duff and Murray 1996). In addition, bacterial strain *Orseolia oryzae* BMP03 has shown good capacity for lignin degradation while *Bacillus* sp. BMP01 exhibits good capability for cellulose and hemicellulose degradation (Tsegaye et al. 2018). Bacterial laccases, peroxidases, and β-etherases have all been reported effective for lignin degradation (Brown and Chang 2014; de Gonzalo et al. 2016; Vasco-Correa et al. 2016).

A highly impermeable and rigid structure of lignin and the insoluble crystalline property of cellulose makes them highly resistant to enzymatic hydrolysis. Much work on lignin degradation has focused on fungi as they are widely found in nature, which causes decay to the lignocellulosic residues via the activities of cellulolytic, hemi-cellulolytic, and ligninolytic enzymes. Ascomycetes including *Aspergillus* sp., *Penicillium* sp., and *Trichoderma reesei*, white-rot and brown-rot fungi, and some anaerobic species of fungi have been reported to exhibit the lignocellulosic degradation activities (Andlar et al. 2018; Dashtban et al. 2009). A cellulase-producing mutant of *Trichoderma reesei* has been developed to produce substantial amounts of β-glucosidase and xylanases (Tangnu et al. 1981). The ligninolytic enzymes excreted by the white-rot fungi include laccases, manganese-reliant peroxidases, lignin peroxidases, and peroxidases (Daniel and Roland 2016). The fungal pretreatment of cotton stalks attains high sugar productivity (20–65%) and rapid lignin biodegradation (Shi et al. 2009). The pretreatment of cornstalk using lignin-degrading *Irpex lacteus* has produced the highest hydrolysis yield of 313.5 mg/g or 82% after 28 days, as compared to the lower 200.1 mg/g without any fungal pretreatment (Du et al. 2011). A cost-effective pretreatment of corn stover has been evaluated based on the screening of white-rot fungi, and the best sugar yields have been reported by using *Cyathus stercoreus* (394 ± 13 mg/g), *Pycnoporus sanguineus* (393 ± 17 mg/g), and *Phlebia brevispora* (383 ± 13 mg/g) (Saha et al. 2016).

Other biological pre-treatment methods including the use of insects, snails, slugs, worms, and ruminants have been evaluated in combination with different methods such as mechanical and enzyme-based gut flora. These non-microbial organisms possess feeding/pulverizing mechanisms to achieve physical breakdown and diverse enzymatic activities for cellulosic digestion. More than 20 families such as crickets, termites, wood wasps, beetle, and silverfish have been identified to degrade cellulosic biomass (Sun and Zhou 2011). Earthworms which feed in waste along with the microbial flora and enzymes, within their guts, could degrade cellulosic material, chitin, starch, and lignin (Rakkini et al. 2017; Wani and Rao 2013; Cheah and Sankaran 2020). Others that play important role in the cellulose degradation include the liquid leachate of vermicomposting, which could be an alternative to acidic pretreatment (Siti Norfariha and Siti 2013), and the micro-floral consortium of gastropods and ruminants (Pawar 2015; Sheng and Huang 2016). This has led to the isolation of intestinal microbes and flora for subsequent pre-treatment of lignocellulosic biomass (Gupta et al. 2012).

4 Bioconversion Processes

Bioconversion is optimally carried out through combined physical and chemical methods with biological treatments. The biological treatments address the issues on minimizing the environmental hazardous effects and concerns associated with the chemical pretreatments such as high chemical loadings and high energy consumption with mechanical pretreatments. The physical and chemical treatments, however, would speed up the pre-treatment steps, as the biological pretreatments could be time-consuming. Table 2 shows the lignocellulosic biomass pre-treatment approaches using different combined pretreatments. The biological and liquid hot water pretreatment could assist the enzyme-based hydrolysis of *Populus tomentos*a (Yuan et al. 2012), resulting in the hemicellulose extraction of 92.33% and a 2.66-fold increase in glucose productivity. The combination of biological pretreatment (under mild conditions) with sodium-bicarbonate salt pretreatment and autoclaving has also enhanced the enzymatic saccharification of corn stover (Huang et al. 2018). The combined fungi and diluted acid pretreatments of olive tree biomass have enhanced the sugar yields to 51% of the theoretical calculations, and the yield of enzymatic hydrolysis to 34%, in comparison to acid pretreatment alone (Martínez-Patiño et al. 2018). Mild chemical or physical pretreatment in combination with biological pretreatments of rice hull have significantly increased the lignin degradation higher than the single-step pretreatments (Yu et al. 2009).

Enzymatic hydrolysis or saccharification is the second most important step, after pretreatment step, to obtain the bioproducts from lignocellulosic residues. Saccharification involves the production of fermentable sugars through enzymatic activities (Khare et al. 2015). As shown in Table 3, different bacterial strains producing lignocellulosic degrading enzymes, e.g., cellulase and hemicellulase, have been reported. Cellulases are important to carry out cellulose hydrolysis, while xylanases are important for the hydrolysis of hemicelluloses. Furthermore, the saccharification efficiency is subjected to the amount of lignin in the pretreated biomass, and the inhibitory compounds from lignin degradation. The enzymatic hydrolysis, the activities of cellulases and hemicellulases, the pH, temperature and reaction time, and the enzyme substrate loadings (Zhao et al. 2012) must be optimized to obtain optimal results for saccharification and to produce the highest yield of fermentable sugars.

The third most important step towards the production of bioproducts from the saccharified biomass is fermentation. Different microorganisms like bacteria and fungi can convert fermentable sugars such as hexoses and pentoses into bioproducts. The two main modes of fermentation are liquid-state fermentation (LSF) and solid-state fermentation (SSF). In LSF, the substrate is suspended/solubilized as tiny particles in a sufficient quantity of water. The SSF is carried out in the absence of water, and the insoluble substrate is fermented with the necessary level of moisture. Anaerobic digestion or anaerobic fermentation plays an important role to obtain valuable bioproducts (Cui et al. 2011). During anaerobic digestion, microorganisms break down the biomass residues using oxygen-free environment (Chahal and Chahal 1998).

5 Bioproducts

5.1 Bioenergy

Straw biomass is considered as the major lignocellulosic feedstock to obtain biofuels and bioproducts in an environmentally friendly manner (Passoth and Sandgren 2019). The conversion could be via thermochemical or biological methods (Maguyon-Detras and Migo 2020). The degeneration of organic substrate by anaerobic bacteria in oxygen-free conditions leads to biogas production or biomethane, while the saccharification and fermentation of sugar produces ethanol

Table 2 Combined pretreatment methods of lignocellulosic biomass

Sr. no.	Pretreatments	Biomass	References
1	Biological pretreatment under mild condition + alkali salt pretreatment	Corn stover	Huang et al. (2018)
2	Biological pretreatment + liquid hot water pretreatment	*Populus tomentosa*	Yuan et al. (2012)
3	Fungal pretreatment + diluted acid pretreatment	Olive tree biomass	Martínez-Patiño et al. (2018)
4	Biological pretreatment + mild physical or chemical pretreatment	Rice hull	Yu et al. (2009)

Table 3 Different cellulase and hemicellulase enzymes for improved saccharification efficiency

Sr. no.	Enzymes	Pretreated biomass	Saccharification efficiency (%)	References
1	Xylanase and Novozyme	Steam-pretreated wheat straw	Increases from 40 to 50%	Olofsson et al. (2010)
2	Cellulase and hemicellulase produced by *Aspergillus tubingensis*	Sugarcane bagasse	0.161 g/L/h productivity, 77.9% fermentation efficiency	Prajapati et al. (2020)
3	*Trichoderma Reesei* cellulases	Sodium hydroxide, sulfuric acid and hydrothermally-pretreated rice straw and eucalyptus	–	Kawai et al. (2013)
4	Cellulolytic Extract from *Pycnoporus sanguineus* (white-rot fungi)	Acid-treated and alkali-treated sugarcane bagasse	60.4% sugar yield in alkali pretreatment	Falkoski et al. (2012)
5	*T. Reesei* cellulases	Microwave-pretreated sugarcane tops	90.24%	Maurya et al. (2013)
6	Cellulase enzyme by *T. Reesei*	Nile grass	74.32%	Vishwakarma et al. (2019)

(Kaltschmitt 2012). Biogas generation by anaerobic digestion (AD), which is later captured, could prevent the release of greenhouse gases to the atmosphere. The AD involves four stages: biopolymer hydrolysis, acidogenesis, acetogenesis, and methanogenesis, as shown in Fig. 6 (Mussoline et al. 2013). Methane, which is obtained from the biomass conversion, is a safe and sustainable energy source, which make up 14% of the energy consumption worldwide (Demirbaş 2006). Fermentation or gasification of rice straw or spent wheat straw could be employed for the preparation of liquid or gaseous fuels (Al-Haj Ibrahim 2018). Wheat straw from horse stall possesses greater volatile fatty acids proportion than pure wheat straws. Using solid-state anaerobic digestion, maximum methane production of 150 L/kg of volatile solids, which is 56.2% greater than the raw wheat straw, has been reported. Furthermore, the anaerobic co-digestion of horse manure has resulted in higher biogas yield (Yang et al. 2020), as similarly observed in co-digestion of corn stover with oil sludge which has resulted in increased biogas production volume (Yang et al. 2020).

Ethanol production based on sugar derived from straw biomass, utilizing *Saccharomyces cerevisiae*, has been found to be the most widely explored method (Selim and El-Ghwas 2018). However, the most recognized yeasts for industrial production of ethanol are *Brettanomyces bruxellensis* and *Zymomonas mobilis* (Blomqvist et al. 2011). Many types of yeast could ferment oat straw hydrolysate to ethanol, but some are not effective on the xyloses or pentoses present in the hemicellulose. Thus, for higher ethanol yield, the transformation of hemicellulosic sugars to ethanol using different *S. cerevisiae* strains has been reported. A commercially viable ethanol production from wheat straw has been demonstrated in a pilot-plant scale by Inbicon at 576 kg ethanol/h capacity (Larsen et al. 2012). Crescentino, in Italy, has established the world's first second-generation ethanol production plant at industrial scale, utilizing around 2,70,000 tons of rice and wheat husks as feedstocks, and producing 40,000 metric tons of ethanol annually (World's 'first' commercial second-generation bioethanol facility 'shuts down. 2017). Simultaneous saccharification and fermentation of alkali-pretreated straw, in the presence of an optimized mixture of cellulase and a novel pentose-fermenting fungus *Mucor circinelloide*, have achieved 90% conversion of fermentable sugar within 36 h, producing 30.5 g/L of ethanol from 100 g/L of treated rice straw (Takano and Hoshino 2018). The combination of acid pretreatments with ultrasound for subsequent enzymes treatment could ensure high conversion of rice straw into fermentable sugars for higher ethanol yield (Belal 2013). High carbohydrate-content feedstocks such as the barley straw are all potential resources to achieve high bioethanol production (Paschos and Louloudi 2020).

Biodiesel is the next important biofuel globally, after bioethanol. Generated from vegetable oils, such as canola seeds, palm and soy oil, the major concern has been on the impact on the environment and eco-system as a result of global warming, land-use/cover changes, and water consumption (Schmidt 2015). For this, agro-industries such as palm oil plantation has been made to obtain certification to ensure sustainable production and strict regulations enforced, to enter a more developed market such as Europe. Microbial lipids from lignocellulose residues for biodiesel

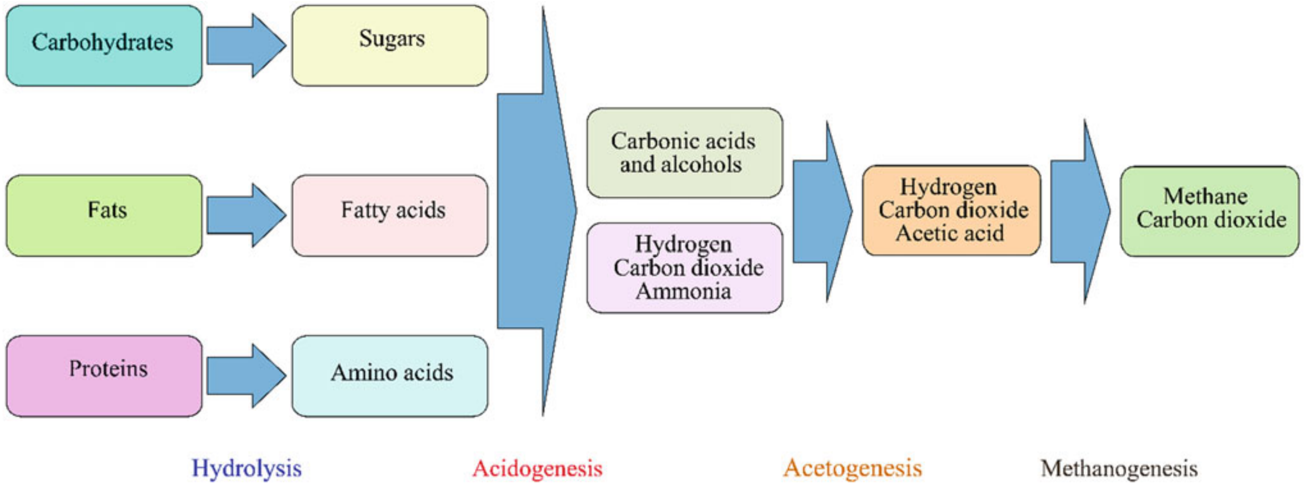

Fig. 6 Stages involved in the anaerobic digestion process for methane production (Modified from Mussoline et al. 2013)

generation could offer a viable alternative to vegetable oils (Karlsson et al. 2016). In addition, there are no issues with microbial sources in regards to the large hectare of land-use cleared for oil crops, or any controversy with regards to the "food versus fuel" debate, as faced by the vegetable oils. The drawback is that the lignocellulosic microbial biodiesel production is still not economically viable (Biddy et al. 2016). The generation of biodiesel and co-products can possibly make the production more competitive. Hydrocarbons with properties similar to the fossil-based diesel could be produced using corn stover, by employing *Rhodotorula toruloides* for fermentation, followed by catalytic hydrogenation (Sànchez i Nogué and Black 2018). *Rhodotorula* species have red color because of the formation of carotenes (primarily β-carotenes). Carotenes are extensively employed as antioxidants and colorants in foods, feeds, pharmaceuticals, and cosmetics. Co-production with lipid can enhance the economic sustainability of biodiesel (Schneider et al. 2013).

5.2 Biochemicals

Generation of biochemicals by utilizing wastes as the feedstocks has been gaining momentum as part of the effort to tackle climate change (Han et al. 2019). This is also spurred by the declining fossil fuel-based resources, and to address the carbon dioxide released from the use of non-renewable carbons. Biomass wastes are biodegradable and abundantly available, to provide a wide range of chemical components that could act as precursors for the production of a diverse range of biochemicals, and eco-friendly end-products, or intermediates. These include oligosaccharides, monosaccharides, bioactive molecules, biofuels, lignin, and nanocellulose (Cho et al. 2020). Wheat straw serves as a feedstock to produce high-value furfural compounds. Furfural is obtained via dehydration of pentoses, and could be utilized as a precursor for the generation of biofuel, fuel additives, and different chemicals. It is also a by-product obtained during the thermochemical pretreatment but it could be an inhibitor during fermentation. The furfural production technologies need further improvement to avoid damaging the cellulose, and preventing the glucose monomer from being transformed into biofuels (Machado et al. 2016). Simultaneous production of furfural, ethanol, and lipid is, however, attractive, where 1 kg of straw biomass could produce 110 g of furfural, 111 g of ethanol, and 33 g of lipid (Brandenburg et al. 2018). This may be advantageous to address the environmental concern of large-scale plantation such as palm oil production, and this could also be implemented as an integrated bio-refinery with microalgal cultivation (Abdullah and Hussein 2020).

Cellulase production has been carried out via Solid State Bioconversion (SSB), utilizing rice straw, an agricultural and lignocellulosic waste, as the substrate of *Phanerochaete chrysosporium* and *Trichoderma sp. P. chrysosporium* resulting in maximum cellulase at 2.4 IU/ml of carboxymethylcellulose activity and 1.43 IU/ml of filter paper activity. The reducing sugar and glucosamine are detected to evaluate the amount of substrate use. Maximum glucosamine of 1.60 g/L and the reducing sugar released at 2.58 g/L are attained on the fourth fermentation day with *P. chrysosporium* (Khan et al. 2007). The multispecies biofilm membrane (MBM) reactors have been utilized for the culture of anaerobic and aerobic microbes at the same time to process cellulose and produce short chain fatty acids (SCFAs). A consortium-based consolidated bioprocess (CBP) makes use of rumen microbiome, co-cultivated with aerobic fungi grown in a biofilm. The use of fungal biofilm has improved the yields and cellulolytic activities as compared to that attained by using the rumen microbiome alone. The MBM scheme with *Trichoderma reesei* biofilm has resulted in 7.3 g/L SCFAs, which is 39% greater than the simple rumen microbiome, utilizing 15 g/L of crystalline cellulose as the substrate (Xiros et al. 2019). Oil palm empty fruit bunch (EFB) is a rich source of polysaccharide and potassium, but the conversion of the EFB lignocellulosic biomass for biochemical and bioenergy is replete with challenges due to its compact structure. The hydrothermal (HT) pretreatment of the EFB in the presence or absence of a sulfonated bentonite catalyst (HT_{cat}) has been reported, for the evaluation of its impact on anaerobic digestion and enzymatic hydrolysis. The catalyst and temperature in the HT_{cat} pretreatment have been shown to improve both the production of biohydrogen and glucose up to 3.32–4.36 and 1.04–1.14-fold, respectively, as compared to the HT in the absence of the catalyst. The catalyst present also improves the lignin and hemicellulose removal from the EFB (Charnnok et al. 2019).

Polyhydroxybutyrate (PHB), a polyhydroxyalkanoate (PHA) polymers from polyester class, can be developed into biodegradable plastics, to replace the fossil fuel-based plastics. Different microorganisms have produced the PHAs as intracellular (C) carbon and energy storage compounds, but the major challenge is for the production of economically competitive PHAs. The use of inexpensive C source for the microbial synthesis of PHAs could be an effective strategy, such as the production of PHB by *Ralstonia eutropha*, utilizing an alkali-pretreated rice paddy straw (Saratale and Oh 2015). The intracellular PHB accumulation of 75.5% within 48 h of fermentation has been achieved, with the PHB yield of 11.4 g/L. Another important chemical, mainly synthesized using fossil resources, is 1,4-butanediol. It has a global production of around 2 million tons annually, for applications in plastics production and other products. The commercial-scale microbial-based production of 1,4-butandiol from carbohydrates using *Escherichia coli* has been reported achieving relatively high yield and efficiency (Burgard et al. 2016). A base-catalyzed pretreatment method with a naturally obtained *Cupriavidus* strain has been developed with the potential to degrade lignin and for PHAs biosynthesis. The use of *Cupriavidus basilensis* B-8 enhances the rice straw digestibility for the conversion of carbohydrate to achieve 984.2 mg/g of reduced sugar, in combination with alkaline pretreatment. At the same time, the PHA yield of 482.7 mg/L is attained via the conversion of the detached lignin utilizing the ligninolytic bacteria (Si et al. 2018). One of the major challenge for efficient biomass conversion is the presence of the inhibitor in the biomass hydrolysates that lowers the efficacy in the bio-refinery setup involving the microbes as the biocatalyst. Acetic acid is the main inhibitor in the bioconversion of xylose using *S. cerevisiae* strains, which limits the cell growth, xylose consumption rate, and the product yield. A new strain, XUSE, has been engineered for high tolerance of acetic acid, during the bioconversion of xylose into bioethanol. The developed XYSAE57 strain has efficiently converted xylose to obtain the highest yield of 0.43–0.50 g of ethanol/g of xylose, under the acetic acid stress of 2–5 g/L. The XUSAE57 strain not only attains twofold increase in ethanol production, but also enhances the xylose consumption rate two-times greater than the XUSE at 4 g/L acetic acid (Ko and Enkh-Amgalan 2020).

5.3 Biocomposites

The composite materials like fiber-board, plywood, particle-board, and oriented strand board, based on the use of petroleum-derived adhesives, could result in hazardous formaldehyde emission. A range of commercial oxidizing enzymes (by oxidizing the phenolic compounds) and the enzymatically pretreated lignin could be employed as adhesives for lignocellulosic materials and also for boards and laminates Enzymatic bonding techniques using peroxidase or laccase have been utilized in the lignocellulosic-based medium-density fiber-boards and particle-boards. (Widsten and Kandelbauer 2008). The particle-board treated with laccase has shown improved properties/stiffness. The addition of enzyme mediators further elevates the enzymatic oxidation of lignin (Batog et al. 2008). The adhesion property of the fiber-boards from wheat straw is attributed to the activation of fiber surface by oxidative pre-treatment during defibration process (Halvarsson et al. 2009). The characteristics of dry-formed hardboard from soybean and wheat straws biomass and from common soft wood fiber have been evaluated, along with the adhesion characteristics of a soybean-derived adhesive and the common urea-formaldehyde resin. The soybean and wheat straw exhibit water resistance and mechanical properties suitable for the manufacturing of hardboard, but with lesser water resistance as compared to the hardboard from the wood fiber. The soybean and wheat straw could be developed as co-fibers without any treatment for both water resistance and mechanical properties, comparable to the clean wood fiber (Ye et al. 2005).

The biocomposites from wheat by-products, wheat straw fibers and wheat gluten, have been fabricated utilizing the thermomechanical method. The analyses of the mechanical energy consumed during fabrication, contact angle dimensions, and the cryo-fractured surfaces prove that the adhesion at the wheat straw fiber/wheat gluten interface is improved. This is due to the wheat straw fibers hydrophobicity as a result of consecutive grinding, and the large surface area from the small fibers (Montaño-Leyva et al. 2013). The wheat straw-based biocomposites with high thermal property, mechanical strength, and stability even after water absorption have been fabricated from the solvent-free, thermoplasticization method. The superior supramolecular interactions are attributed to the hydrogen bonding, re-enforced by the interactions between the hydroxyl groups of the wheat straw with the chlorine atoms in the supramolecular inducer. The strong hydrogen bonding, however, could considerably be lowered as a result of the supramolecular interactions between the inducers and the wheat straw powders (Dong et al. 2019). The nano-TiO_2 adopted frothed wheat straw fiber/polypropylene-hierarchical (F-WSFs/PP) composites have been fabricated via hot-extrusion technique. The TiO_2-KH550 modified F-WSFs/PP composites have exhibited excellent mechanical strengths and UV-protective properties (Wang et al. 2020). The biocomposites of nanocrystalline cellulose (NCC) from the rice straw and chitosan (CS) have been developed using acid hydrolysis-ultrasonic and blending-casting technique. The NCC/CS biocomposite interfaces show the rod-like structure attained from the higher ultrasonic power at constant acid hydrolysis conditions. Larger interfacial compatibility of the NCC/CS biocomposites with excellent ductility is accomplished at 5% NCC. The optimum distribution of the NCC exerts electrostatic interactions, and strong hydrogen bonding between the NCC and the CS, resulting in higher thermal stability (Xu et al. 2018). The rice straw biomass has been utilized to separate the cellulose nanofibers with different oxidation degree. The bleached rice fibers are derived from the rice straw biomass undergoing the bleaching processes and chemical extraction. The oxidation of rice fibers is facilitated by the radical (TEMPO) 2,2,6,6-tetramethylpiperidine 1-oxyl to remove the rice cellulose nanofibers. The reinforcement capacity of the rice nanofibers is achieved by casting the nanocomposite films with poly(vinyl alcohol), to achieve the critical tensile strength of the films (Alcántara and González 2020). Green composites based on rice straw (RS) have been fabricated by utilizing benzylation techniques and soda-pulping. The RS products include the benzylated RS pulp, untreated RS, RS pulp, and pulping liquor along with the benzylated RS, which are integrated into the starch (thermoplastic) via a twin-screw extrusion procedure. The RS pulp with the cellulosic microfibers has increased the tensile strength of the plasticized starch much greater than the untreated RS. The thermoplasticization process considerably enhanced the toughness of the plasticized starch/RS biocomposites due to the improved phase miscibility (Shoja et al. 2020).

The groundnut shell (GNS) and rice husk (RH) have been utilized to make hybrid polypropylene (PP) biocomposites for green building materials. The rice husk morphology with low aspect ratio is excellent to be developed into composites having good flexural and tensile strength (maximum value of 37.6 MPa and 15.6 MPa, respectively). The thermal conductivity of the composites range from 0.156 to 0.270 W/mK and the highest sound absorption coefficient is 0.48. The flame retardation property of the composites is equivalent to the market gypsum derived ceiling tiles, but the composite water absorption is 85% less than the gypsum tiles (Guna et al. 2020). Biosilica, from the teff straw, has been blended with alginate and chitosan to produce alginate-biosilica (AlgBS) and chitosan-biosilica (ChiBS) for use as sorbents. The pyridine removal efficacy is influenced by the pyridine concentration, biocomposite dosage, pH, temperature, and contact time. The maximum removal efficiency for early pyridine concentration of 50 mg/L for ChiBS and AlgBS is 90 and 96%, respectively (Bageru and Srivastava 2019). A novel biocomposite has been produced by combining poly(vinyl alcohol), graphene oxide, and chitosan, for application in wound dressing. It also exhibits anti-inflammatory and antimicrobial properties, with the ability to promote cell proliferation (Chen et al. 2020). The biomass bioconversion into biocomposites and high-value bioproducts meet the sustainability goals of the industries on “reduce, recycle, and reuse” of wastes. However, the challenges remain for a large-scale implementation within a more economically viable integrated bio-refinery set-up (Abdullah and Hussein 2020).

6 Conclusion and Future Perspectives

Straw biomass as a lignocellulosic agricultural residue possesses tremendous potential as feedstock for bioconversion into valuable products. The bioconversion of organic matters into bioenergy or bioproducts can be achieved through eco-friendly and biological methods, in combination with light physical and chemical pretreatment methods along with technologies based on enzymatic hydrolysis, fermentation, and anaerobic digestion. However, the major challenges are to meet the goals of sustainable development for community-based, eco-friendly, and cost-effective processes. Thereby, substantial effort is needed to address the scaling-up of an integrated bio-refinery for the bioconversion of straw biomass into bioproducts especially in terms of the selection of the plant location to be close to the energy grids and the market needs. The diverse applications on the use of biomaterials and biocomposites should be explored further especially in the construction sector, infrastructure building, pharmaceutical, and biomedical segments, to attain the full potential of the bioproducts derived from the straw biomass.

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Production of Biodiesel from Organic Wastes by Bioconversion

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Abstract

Biodiesel comes in the category of renewable and biodegradable fuel. It has shown promising performances for substituting petroleum. Due to the outbreak of urbanization and population blast in recent years, there is enormous increase in the production of waste and also lack of its appropriate disposal. Municipal solid wastes, agricultural waste, industries and manufacturing processes generate large amounts of waste materials. The technologies associated with waste to energy conversion produce various types of fuel which are further utilized to meet the needs of energy. Production of synthetic fuels from organic wastes follows four important techniques like bioconversion, gasification, pyrolysis and hydrogenation. This chapter throws light on waste biomass, different categories of organic waste, utilization of organic waste for production of value-added products especially biofuels. Moreover, bioconversion of various types of organic waste into biodiesel guided by microorganisms, algae, insects, etc. are also discussed in this chapter.

Keywords

Bioconversion • Biodiesel • Organic waste • Microorganisms • Insects • Biomass

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1 Introduction

Due to different types of human activities, there is production of waste materials which causes danger in utilization of natural resources like natural scenery, soil, water and air sustainably (Basnet 1993). Waste refers to something which is unwanted and useless and in general the waste materials produced are in solid form. Fortunately, large amounts of these waste materials are reusable and hence act as a vital source for energy generation or industrial production (Hauser et al. 2001). The technology of converting waste into energy involves conversion of waste materials into diverse forms of fuels which can be utilized for meeting the energy demand (Demirbas et al. 2011; Demirbas and Balat 2010). Every year, around the world, nearly a hundred million tons of waste are processed in approximately 800 wastes to energy facilities (Michaels and 2007). More advanced waste to energy conversion technologies helps in the production of pure hydrogen, biodiesel and ethanol (liquid biofuels), hydrogen and carbon monoxide (syngas), carbon dioxide and methane (biogas) as well as electricity, which can be generated from these fuels. The techniques involved in waste to energy conversion include biological, thermal and physical methods. The organic waste, which has potential in the production of fuel, includes animal wastes, short rotation herbaceous crops, agricultural waste, short-rotation woody crops, wood and more. In this context, biomass could be identified as potentially large and one of the best options for insuring a supply of fuel and meeting these demands in the future. Both for developed countries and developing nations, biomass has been reported to be a promising source of renewable energy (Aluya 2014; Balat 2009). In developing countries, it fulfils nearly thirty-five percent of consumption of primary energy (Demirbas et al. 2009; Balat et al. 2009). Utilization of biofuels is substantially beneficial for the environment and absorbs, during its growth, carbon dioxide and releases it at the time of combustion. Hence, biomass assists in recycling of atmospheric carbon dioxide and has

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no contribution to the greenhouse effect. The consumption of carbon dioxide by biomass from the environment is in equal amounts for both combustion and growth purposes. Additionally, there is reduction in emission of carbon dioxide overall owing to the fact that biomass as fuel is neutral of carbon dioxide (Demirbaş 2005). In the year 2017, Alptekin et al. reported that production of biodiesel by triacylglycerol trans esterification causes discharge of lesser pollutants like aromatic compounds, sulphur, carbon dioxide and carbon monoxide in comparison to the diesel (Alptekin 2017). The organic wastes generally consist of inexpensive and ideal particulates necessary for production of microbial oil. Moreover, organic waste's chemical composition causes an effect on production of lipids. This chapter discusses various examples of bioconversion of organic waste into biodiesel. It also highlights microorganisms of diverse organic waste for economical production of biodiesel based on microbial lipids. Biodiesel is a renewable source of energy which meets the worldwide demands of energy for transportation (Hill et al. 2006; Ragauskas et al. 2006). For the production of biodiesel, the technology is not a hurdle rather the raw materials generally used is the limitation (Koonin 2006). The general raw materials include edible vegetable oil like sunflower, palm, soybean, rapeseed, etc. which cannot be exploited blindly for production of biodiesel as it also meets the food requirements (Tilman et al. 2009). Furthermore, the feedstock cost is an economical hurdle for the production of biodiesel (Demirbas 2011). Hence, for reducing the cost of production of biodiesel there is the requirement of cost-effective feedstock. For this purpose, certain renewable sources of feedstock for biodiesel production are required like Jatropha curcas and microalgae (Huang et al. 2010; Lu et al. 2009). For fulfilling the energy requirements, it is not wise to affect the surrounding and society, rather necessary to use alternate sources of feedstock which will be economically sound, environmental friendly and also feasible technically (Lang et al. 2001) like black soldier fly also known as Hermetia illucens which are capable of converting the organic waste into value-added products without compromising with the food sources (Craig et al. 1994). This chapter discusses biodiesel production guided by insects and microbes and various other examples of biodiesel production from organic wastes.

2 Biomass of Waste

In general, biomass consists of natural renewable resources, proteins, lignin, and hemicellulose, large amounts of cellulose, lignocellulosic materials and precious materials. Mostly, the materials of biomass exist as residues of wood which are left behind after any forest activities, food wastes and municipal solid waste (Oliveira and Franca 2009). On an average, the energy of biomass is generated from landfill gases and agricultural waste (5%), municipal solid waste (24%) and wood waste (64%) (Demirbas and Demirbas 2007; Balat 2009). Basically, biomass wood structure is composed of three types of polymers, which are lignin, hemicellulose and cellulose present in bark, foliage and trunk. The quantity of constituent existing in wood varies from species to species, and there is a unique variation between soft and hardwood. Generally, hardwood consists of nearly 2–8% extractives, hemicellulose (25–35%), lignin (16–24%) and cellulose (43–47%). Similarly, softwood consists of extractives (1–5%), hemicellulose (25–29%), lignin (25–31%) and cellulose (40–44%) (Balat and Demirbas 2009). In Table-1, there is the display of different residues and their respective wastes and percentage of composition of lignin, hemicellulose and cellulose in the biomass. Cellulose comes in the category of homopolysaccharide made up of units of β-D- glucopyranose joined by glycosidic bonding. The primary limitation was to depend on biowaste as the only source for fuel even though biomass exhibits distinct characteristics. The presence of high quantities of ash and moisture in biowaste fuels leads to combustion and ignition problems (Demirbaş 2005). Biomasses which are highly rich in moisture are suitable for processes like fermentation which involve reactions which are mediated biochemically. Similarly, biomasses which contain lesser amounts of moisture are preferred for cost-effective processes like gasification or pyrolysis, combustion (Oliveira and Franca 2009). In comparison to coal, biowaste is different in many ways including physical, inorganic, organic characteristics and energy content. Compared to coal, biowaste in general contains lesser amounts of carbon, iron, aluminium and higher amounts of potassium, silica, oxygen, and moisture, lower friability, density and heating value. Agricultural residues disposal methods cause environmental issues widely. For example, wheat and rice straw when burnt in an open field lead to pollution (Demirbas 2008). Treatment of solid waste generated due to agricultural activities anaerobically has attracted attention in recent years. Generation of methane, during organic matter digestion anaerobically, is dependent on the kind and amount of material included in the system. Agricultural leftovers like molasses, green leaves, plant stalks, seeds, fruit, fruit shells, nutshells and straws are resources of renewable energy. Rice straw is a potential source for production of approximately two hundred five billion litres of bioethanol every year which is the highest quantity produced from one feedstock of biomass. In Fig. 1, there is the illustration of the composition of waste produced globally (Karimi et al. 2006).

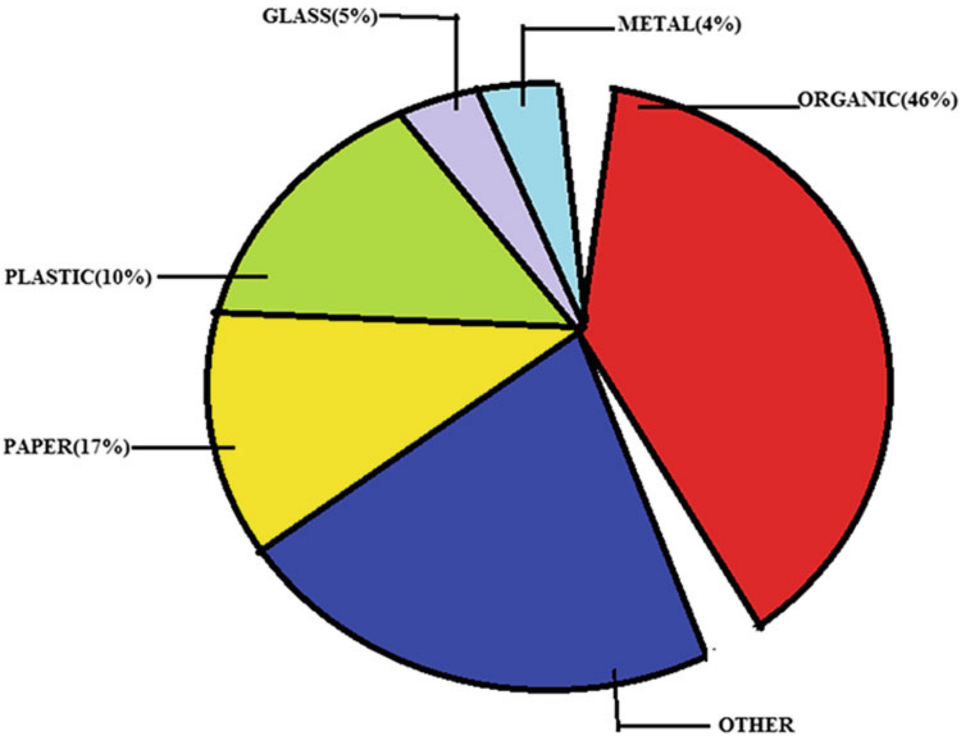

Fig. 1 Composition of waste distributed globally (Yang et al. 2015)

3 Types and Properties of Organic Wastes

Organic waste prevails in every step of development of biomass. In general, the constituents of waste are dependent on the origination of the biomass. Here, we discuss different categories of organic wastes and their characteristics (Yang et al. 2015).

3.1 Organic Waste Generated Out of Residue of Agriculture

Traditionally, organic waste originates from agricultural residue. This type of waste economically and strategically proves beneficial for producing a variety of products. Majority of forest and crop waste can be utilized as raw material which is lignocellulosic in nature. In comparison to other categories, organic waste originating from the agricultural residue possess more stability in composition. Around 2/3rd of this organic waste is converted to bioenergy. Owing to wide-scale utilization of lignocellulosic in biorefinery industries, development and improvement of the pre-treatment procedure is a topic of concern for the researcher. The primary target is to lower the cost of processing and to find a better pre-treatment procedure capable of eliminating lignin. Depending on the composition of raw material, the procedure of pre-treatment process is developed to more complex techniques from single biological, chemical and physical methods. Pre-treatment complex processes are capable of obtaining better amounts of cellulose by more removal of lignin but there is still a requirement of reducing the cost by simplifying the procedure (Kim et al. 2013a, b, c, 2011; Limayem and Ricke 2012; Kemppainen et al. 2012; Nakayama and Imai 2013; Karthika et al. 2012; Chaudhary et al. 2012; Zavrel et al. 2009; Monavari et al. 2009; Wang et al. 2013). According to some reports, protein beam or electron beam are feasibly utilized for pre-treatment of lignocellulose, which were found to be saving the time during the process (Kim et al. 2011, 2013). Due to the stable constituents of forest and crop products and advanced pre-treatment procedure this category of organic waste has got maximum attention for industrial-scale application (Kim et al. 2013a, b; Kemppainen et al. 2012; Nakayama and Imai 2013; Karthika et al. 2012; Chaudhary et al. 2012; Zavrel et al. 2009; Monavari et al. 2009; Wang et al. 2013; Dashtban et al. 2009; Brown and Chang 2014). In countries like the U. S. and South America, technologies for utilization of organic wastes coming from agricultural residue are designed already and utilized for biorefinery industries (Viikari et al. 2012). In recent decades, hydrophyte has been identified due to its extraordinary performance in both biorefineries as well as environmental bioremediation (Kim et al. 2012). In comparison to the agricultural residue, there is no need to cultivate hydrophyte and hence land is saved both for animal feed and for food production by humans. Micro and macroalgae are in the category of recent targets of research in the field of biorefinery. Bioconversion application by utilization of agricultural residue has been practised since very long.

3.2 Organic Waste Generated of Residue of Industries

With the advent of industrialization and population, waste from industrial practices has attracted researchers. In this context, waste coming from paper and food manufacturing industries are widely used in research associated with biomass. Majority of organic wastes coming from food industries which are used for this purpose includes potato chips, instant noodles and orange juice (Kim et al. 2011). The benefits of this category of organic waste are that they are easily available and their composition is stable. Moreover, it requires an easy pre-treatment procedure for obtaining a highly potential product. Additionally, it is indicated by some researchers that food industry waste is not perfect for animal feedstock due to presence of artificial additives and antiseptics. In general, this organic waste pre-treatment is easier in comparison to lignocellulosic organic wastes. This is due to the easier digestion of food, and it can also be obtained by organism and enzymes commercially (Barnard et al. 2010). Economically, industrial organic waste stability has been considered essential for consideration as feedstock during the process of bioconversion. Additionally, production of more than one product from single organic waste has emerged for the very first time in the context of food residue bioconversion application. Bioconversion products are dependent on the involved microorganisms' metabolic pathway. United Kingdom scientists in the year 2010 reported orange peel waste biorefining. During the study, it was found that orange peel waste biorefining produced a number of value-added products like single cells proteins, industrial enzymes, essential oils, methane and ethane. These results displayed that food industry organic waste consists of large quantities of nutrients which is highly beneficial for microorganisms intake for their efficient performance during conversion.

3.3 Organic Waste Generated from Urban Activities

In the last century, urbanization has developed a lot. In the path to the development of the city, the excessive growth of population has given rise to large amounts of urban residues which have disturbed the pace of development. In this context, engineers, as well as scientists, face problems in handling these urban residues. Urban residues are also a kind of organic waste which includes medical wastes, catering wastes and home scrapes. Recent biofuel conversion technologies can be applied in wide scale for utilization of urban residues. In comparison to other biomass, the composition of this category of organic waste is unstable, hence prior to utilization analysis of composition is highly essential. Owing to this instability of composition, there is the requirement of complex pre-treatment procedure prior to the hydrolysis in order to retain sugar for the process of fermentation subsequently, which needs to be solved for future applications in order to reduce the cost of overall bioconversion. Production of biofuel is the primary concern of this category of organic waste. Biofuels like biodiesel, bioethanol and biohydrogen are successfully produced since the last decades by utilization of urban residues organic waste. The major constituents of the home scraps are carbohydrates which can be used during bioconversion by extracting fermentable sugar out of it. Moreover, they also contain few quantities of lipids which act as essential inhibitors during the fermentable sugar hydrolysis. Owing to the instability of organic waste from urban residues, complete use of it is quite difficult. In order to improve this efficient pre-treatment procedure of organic waste needs to be developed.

4 Organic Waste Utilization

The development of the biomass has come into light since the mid of the previous century, and its use can be revolutionary in human history for the development of technology speedily. In the field of utilization of organic wastes, there is the requirement of accurate and fast method of analysis for producing multiple values added products out of the biomass, and this issue is a topic of concern for many researchers. Recently, organic waste has attracted researchers as a new category of biomass and can be divided into two classes, use of organic waste and bioconversion. Organic waste pre-treatment can be easier. Because of the presence of organic compounds almost all biomass can be called as organic waste. At this point, hydrophyte like microalgae, urban residues and food industry residue are preferred mostly for bioconversion processes. Metabolic and genetic engineering are present for enhancing the target product production and simultaneously for the reduction of the rate of conversion of the side products and this has been successfully achieved.

5 Biofuels Generated Out of Biowastes

Environmental problems like global warming and reduction in the reserves of fossil fuels have led to alarming need for sources of renewable energy. In this context, biomass has emerged as a neutral carbon resource and contributes primarily to production of fuels. Biomass in the advanced stage utilizes only organic waste as the renewable source of energy which after the application of diverse application process gets converted into gas, liquid and solid phase (Aristidou and Penttilä 2000; Frąc and Ziemiñski 2012; Saxena et al. 2009). Statistical data reflects that biomasses comes fourth in the list of energy sources and fulfil nearly fifteen percent of consumption of energy worldwide. Previously, organic waste can be directly utilized for combustion, and, however, it is applied for producing a number of value-added products by using modern technology. Apart from biodiesel and ethanol production, hydrogen has also attracted researchers for organic waste utilization. Initially, for using organic waste, pre-treatment procedure is necessary, then there is wide use of microorganisms for different types of bioconversion and finally, there are studies which aim at separation of desired products. Additionally, conversion efficiency can be improved by the process of optimization. Biorenewable or biofuel is defined as gaseous, liquid or solid fuels produced from biomass predominantly. Gaseous and liquid biofuels are more preferable due to their environmental friendliness. Biofuels are reliable, sustainable, accessible, locally available and non-polluting fuel. In the coming future, generation of electricity out of biofuels is considered as highly potential. Generation of electricity from biomass depends on integration of gas or gasification turbine methods which provides efficient conversion of energy (Demirbas 2009). Recently, there are many investigations on environmental and economic effects of biofuels like biohydrogen, biogas, biodiesel and bioethanol (Demirbas 2009, 2010a, b; Balat and Balat 2009; Phalan 2009). The potential of biofuel industries is a source of large new markets and income for small farmers and rural areas. In developing countries the production of biofuel is comparatively more profitable due to lower labour costs, suitable climatic factors for agriculture and large availability of land. Biofuels production on a larger scale in many developing countries provides opportunities for reduction of their oil import dependence. Biofuels can be categorized according to their technology of production, first, second third and fourth generation of biofuels. First generation of biofuels is produced from animal fats, vegetable oil starch and sugar by using suitable methods. Basically, the feedstock involved for the first generation biofuels production are grains or seeds like wheat which produces starch which are further fermented to ethanol and sunflower seeds which are pressed to convert it into vegetable oil which can be utilized in biodiesel. Third- and second-generation biofuels are known as advanced biofuels. Second-generation biofuels are produced from crop, wood, corn, wheat straw, non-food crops by applying conventional technologies. Third-generation biofuel uses oil algae or algae fuel. Fourth-generation biofuel is dependent on conversion of biodiesel and vegetable oil to biogasoline by utilization of suitable technologies (Demirbas 2009).

6 Biodiesel

This fuel is produced from grease, animal fats and vegetable oils following the process known as transesterification. It is an alternative fuel in liquid forms which is beneficial for the environment and which can be utilized in any type of diesel engine without any alteration. Early in the 1990 s, there was initiation of wide production of biodiesel and from then its generation is increased day by day (Balat and Balat 2008). Utilization of biodiesel in diesel engines causes reduction in emissions of particulate matter nitrated polycyclic aromatic hydrocarbons, sulphates, carbon monoxide and unburned hydrocarbons. These emissions can be further reduced when the blending of biodiesel with conventional diesel enhances (Ulusoy et al. 2009). There are many literatures available which report on use, analysis and production of biodiesel (Demirbas 2008, 2009, 2010; Selim 2009; Sinha et al. 2008; Huang et al. 2010). Presently, biodiesel high cost is the main hurdle in the process of product commercialization. Production of biodiesel is comparatively more costly than diesel fuel based on petroleum. Biodiesel performance economically is determined by certain factors like chemical costs, raw material prices, and process technology and plant capacity (Zhang et al. 2003). Biodiesel fuel cost is dependent on crude petroleum price, season to season variation in the crop production, geographic area and base stock (Demirbas and Karslioglu 2007). Feedstock cost is a topic of concern from an economic point of view in the context of production of biodiesel (Krawczyk 1996; Connemann and Fischer 1998). From literature survey, it is known that nearly seventy to ninety per cent of the cost of biodiesel production arises from the raw materials price. Presently, approximately, ninety-five per cent of biodiesel produced worldwide is from vegetable oil whose availability is very large from the agricultural field (Gui et al. 2008). Hence, large scale and continuous biodiesel production from vegetable oils are a matter of great concern owing to their competition with food supply. To solve these problems, substitution of the raw materials with oily food and agricultural residue which are less valuable is effective. Since the last few years, investigation has been made for biodiesel production out of various oilseed crops which are inedible (Qiul et al. 2011; Ghadge and Raheman 2005; Zullaikah et al. 2005; Wang et al. 2006; Demirbas 2009, 2010; Veljković et al. 2006; El Diwani et al. 2009; Ozkurt 2009). To name a few, some inedible oil examples are microalgae, tall oil, silk cotton tree, mahua, rubber seed, pongamia pinnata, neem, jatropha, calophyllum inophyllum, azardirachta indica, ficus elastica, madhuca indica and jatropha curcas which are both available easily and economically friendly in comparison to edible oils (Darici and Ocal 2010).

6.1 Production of Biodiesel by Using Hermitia Illucens Larva

Hermitia illucens larvae are decomposer by nature which feed on organic wastes. From literature survey, it was known that palm decanter cake coming from oil palm mill, fruit waste and sewage sludge are the three organic wastes which were investigated as feedstock for Hermitia illucens larva. Hermitia illucens larva which feed with palm decanter cake and fruit waste displayed growth rates of 0.23 ± 0.09 and 0.52 ± 0.02 g dl, respectively. There was no growth sign when the larva fed on sewage sludge. Biodiesel was produced as fatty acid methyl ester (FAME) by larva lipid transesterification by utilization of catalyst sulphuric acid in presence of methanol. From data, it's reported that fatty acid methyl ester obtained from lipid of larvae is suitable for utilization for biodiesel production. In the year 2011, Li et al. reported synthesis of biodiesel by utilizing Hermitia illucens feeding on dairy manure. Ultrasonic, Soxhlet and immersing are the three methods used for extraction of lipids from Hermitia illucens. Hermitia illucens when fed on dairy manure produces biodiesel with 0.75 g dl yield. In the year 2012, Zheng et al., reported production of biodiesel by using rice straw and restaurant food waste to feed Hermitia illucens larva and biodiesel yield was 4.38 g dl. Similarly, production of biodiesel was performed by Li et al. in the year 2012 by utilizing Chrysomya megacephala (oriental latrine fly). Moreover in the year 2013, Zheng et al. reported a similar way of production of biodiesel by using Tenebrio molitor larvae (yellow mealworm beetle) and obtained nearly thirty-five gram of biodiesel (Leong et al. 2016).

6.2 Biodiesel Formation Assisted by Black Soldier Flies Initiated Dairy Manure Bioconversion

Diaries, in general, accumulate large amounts of dairy manure which incurs harmful impact on the environment. Moreover, this manure acts as a primary resource of larva for insects like Hermitia illucens, black soldier fly, etc. Insects have the largest biomass throughout the world. They are available everywhere, every corner, mountain to sea, equator to poles. Fats of insects are considered as an essential source. Insects scavenger nature makes them break down and feed on dead animal matter and plants, thereby providing organic materials to the environment. Organic wastes are very essential for nature. Black soldier fly is generally linked with livestock and outdoor and is involved with decay of organic wastes like plant materials and animal manure. Black soldier fly larvae have high potential in consumption of decayed organic matter like manure, spoiled feed and also kitchen wastes. Recently, larva of black soldier fly has been recognized as a novel bio technique for bioconversion of dairy manure into sugar and biodiesel. This is considered as economical. Black soldier fly larvae can lead to production of grease by petroleum ether and further produces biodiesel by a two-step process. The leftover dry black soldier fly larvae after extracting grease can be utilized as feedstuff of protein. The samples which are extracted are subjected for drying at sixty degree Celsius the whole night and the efficiency of extraction was determined by sample weighing after and before the process of extraction. The grease which was extracted consisted of different types of impure substance like solid impurities, phospholipids, pectin and water. Hence, it is essential to purify them by addition of a small amount of sulphuric acid. In a water bath inside the reactor which is filled with black soldier fly larvae, grease is subjected to heating to a temperature of around 73 °C. Simultaneously sulphuric acid as catalyst and oil/methanol in the ratio 1: 8 is added to it. Later, after two hours this particular mixture is poured in a separating funnel for biodiesel separation and neutral oil. Then, the layer present at above is put back into the reactor, and transesterification is performed by adding sodium hydroxide as catalyst and methanol/oil. Further, the mixture is stirred and subjected to reaction for thirty minutes at 65 °C in a water bath. This mixture was again separated. Biodiesel was obtained by washing with distilled water, and it was washed till the washing liquid attained neutrality (Li et al. 2011).

7 Production of Microbial Lipids by Utilization of Organic Waste Which Is Less Costly

7.1 Oleaginous Yeasts

Oleaginous yeasts, microbial lipids generally contain carbon 16 to 18 fatty acids which are suitable for utilization as biodiesel. Hence, the integration of lipids and organic wastes production by oleaginous yeasts could be economical technology for substituting fossil fuels with biodiesel which is environmentally beneficial. Oleaginous yeasts like Rhodosporidium sp., Rhodotorula sp., Lipimyces sp., Cryptococcus sp., and Yarrowia sp., are applied for producing microbial lipid (Park 2018).

7.2 Oleaginous Microalgae

Utilization of wastewater or organic waste for cultivation of microalgae is a better option for reduction of cost and moreover this procedure simultaneously produces microbial oils and lowers concentration of nutrients in organic waste as reported by Cho et al. in the year 2017. Production of biodiesel by utilization of microalgae has lipid yield higher in comparison of corn and soybean oil crops as reported by Li et al. in the year 2011, Kim et al. in the year 2014, Fei et al. in the year 2015, Cho et al. in the year 2015 and Chiu et al. in the year 2015 (Park 2018).

8 Conclusion

In the production of biodiesel, cost is an important issue, hence it is vital to produce a cost-effective source for generation of biodiesel. Biodiesel is formed by utilization of insect fats which resulted from organic waste. Biodiesel produced from insect biomass does not affect food or land either in modern large-scale or small-scale production. Moreover, based on lipids of microbes, biodiesel commercialization needs to be studied for determination of contribution of every micronutrient inside organic waste. The word waste indicates something which is unwanted and useless and generally they are solid. These waste materials are reusable and can act as a source of energy.

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