Chapter 1
Biorefinery Concept

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Abstract Biomass valorization is an important issue which could be significant in the reduction of the global dependence on fossil fuels. This chapter will focus on the overview of pathways for conventional and alternative biomass valorization, including transformation to valuable materials and energy. The efficient and flexible use of biomass and the innovative technologies will be discussed as a biorefinery concept. The "raw" biomass, its transformation, and the further conversion into energy and coproducts are considered, aiming to achieve sustainable proposals and maximum valorization. The development and application of the best possible technologies for all processes (e.g., combustion, pyrolysis, gasification, fermentation), including also pretreatment are essential in a biorefinery. The biorefineries can be classified considering the feedstock or the technology: lignocellulosic and marine biorefineries, biochemical and thermochemical biorefineries and advanced biorefinery. The sustainability and the economic factor of the biorefinery are extremely important, and should be evaluated to understand the energy and environmental issues, and the associated costs of any conversion system. Therefore, several sustainability assessment tools have been developed. It is expected that this chapter will contribute to improve understanding the biorefinery concept, the intense and sustainable use of biomass.

1.1 Introduction

The concern of the society regarding environmental issues and sustainability has increased in the last decades. The growing consumption of fossil fuels, in its majority those derived from crude oil, has been questioned especially in the context of its long-term environmental, energy and material sustainability, being at the center of global climate change policies discussion worldwide, which aim to

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implement new and alternative solutions to respond to these concerns. It is fundamental to increase and develop renewable energy generation, aiming to improve energy production and use efficiency, increase the security of supply, and enhance primary energy sources diversification. New energy sources have been regarded as a potential commodity to reduce fossil fuel dependence and to mitigate the negative environmental effects (European Commission 2005).

Biomass is considered to be one of future's key renewable resources, being the most important source of energy for three quarters of the world's population living in developing countries. Globally, it already supplies around 14% of the world's primary energy consumption (Star-colibri 2011).

The use of biomass as a resource for energy and fuel production will be limited by the maximum production rates and the supply of biomass, rather than the demand for energy and fuel. Significant barriers to the use of biomass are the relatively low energy content and the seasonality and discrete geographic availability of biomass feedstocks. (Basu 2013; FitzPatrick et al. 2010) In addition, sustainable biomass production is a crucial issue, especially concerning a possible fertile land competition with food and feed industries (Cherubini 2010; Harmsen and Powell 2010).

In order to optimize and exploit all of the elements of biomass, reuse secondary products and wastes of the conversion process into valuable products, as also to produce energy which may help to power the process itself, should be developed—this should be considered within an integrated biorefinery strategy (i.e., efficient and flexible use of biomass).

Basically, the concept of an integrated biorefinery is similar to a petroleum refinery, where oil is refined into many marketable products including chemicals, energy, and fuels. Though, the main difference is that biorefineries are based on the use of renewable materials as a feedstock, namely, biomatter, while the petroleum refineries are based on the use of nonrenewable materials such as fossil fuels (Biernat and Grzelak 2015).

The term biorefinery is derived from the raw material feedstock which is renewable biomass and also from the conversion processes often applied in the treatment and processing of the raw materials. The biorefinery approach involves multistep processes in which the first step, following feedstock selection, usually involves the treatment of biomass for further processing (pretreatment). Afterwards, the biomass is subjected to biological and/or chemical treatments (Strezov and Evans 2014).

There are different definitions for the term "biorefinery," however all of them have the same propose. For the National Renewable Energy Laboratory (NREL), a simple biorefinery concept has been devised that is built on three different "platforms" to promote different product routes, biochemical, thermochemical, and microorganism platforms (King et al. 2010). A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, chemicals, and value-added products productsfrom biomass. Following the U.S. Department of Energy, the biorefinery is an overall concept of a processing plant where biomass feedstocks are converted and extracted into a spectrum of valuable products. The IEA (IEA Bioenergy Task 42 2009) has the similar definition to the biorefinery: "Biorefinery is the sustainable processing of biomass into a spectrum of marketable products," as an integrated biobased industries using a variety of technologies to make products such as chemicals, biofuels, food and feed ingredients, biomaterials, fibers, and heat and power, aiming at maximizing the added value along the three pillars of sustainability environment, Economy and society (Sonnenberg et al. 2009). In product-driven biorefineries the biomass is fractionized into a portfolio of biobased products with maximal added value and overall environmental benefits, after which the process residues are used for power and/or heat production, used internally, and/or sold to the national electrical grids. Some residues or coproducts after appropriate treatment processes may also be considered as valuable outputs. These high value-added materials have considerable importance from the industrial and economic point of view, and their appropriate exploitation is a key step in the development of an economy based on recycling and renewable resources—the biobased economy or simply bioeconomy.

A crucial factor for biomass utilization is the cost of the input materials, which today can range from "negative costs" for waste materials (credit for waste disposal), to the more expensive and specialized crops (Grigg and Read 2001). Meaning that, the spectrum of biomass resources can ensure the diversity of the raw material exploitation.

There is a competition for different biomass uses for bioenergy (heat, electricity, transportation fuelsfuels), food (vegetables, meat, among others), biomaterials (paper, construction material, chemicals, cotton, ribber, fertilizer, among others), and feed. The new way in bioeconomy is from competition to integration. Bioeconomy means the part of the economy using biological resources (biomass), or bioprocesses, for the production of value-added products, such as food, feed, materials, fuels, chemicals, biobased products and bioenergy (Sonnenberg et al. 2009). Agriculture, forestry, fisheries, and aquaculture, but also the biotechnological use and conversion of biomass, in addition to biogenic waste materials and residual materials: these are the central starting points for the bioeconomy's value chains and value adding networks, which are interlinked in a multitude of ways.

The transition to a biobased economy has multiple drivers: need to develop an environmentally and socially sustainable global economy; the anticipation that oil, gas, coal, and phosphorous will reach peak production in the not too distant future and that prices will climb; the desire of many countries to reduce an over dependency on fossil fuel imports, so the need for countries to diversify their energy sources; the global issue of climate change and the need to reduce atmospheric greenhouse gases (GHG) emissions; and the need to stimulate regional and rural development. A strategic factor of a successful biobased economy will be the development of biorefinery systems, allowing highly efficient and cost-effective processing of biological feedstock to a range of biobased products, aiming also to reduce GHG emissions and make efficient use of resources (IEA Bioenergy Task 42 report 2011).

Biorefineries should be highly energy efficient and make use of mostly zero-waste production processes, where those "waste" products are regarded as coproducts and may be reallocated for added value use or conversion processes.

Most biorefineries are closely integrated with traditional biomass processing industries. The purpose of the biorefinery is to optimize the use of resources and minimize waste, thus maximizing the benefits and profitability. Full-scale, highly efficient, integrated biorefineries allow competitive manufacturing of high value biobased products. Flexibility is the key. Flexibility has to be intended as the possibility to choose among different processes and, within a specific process, the possibility to select optimal operating conditions and proper technology in dependence on the specific characteristics of the available biomass stream. This allows the production of a broad spectrum of valuable, marketable products.

This chapter will give an overview of several types of biorefinery. Biorefineries can be classified considering the feedstock or the technology, such as: lignocellulosic biorefineries (uses nature dry raw material, such as cellulose-containing biomass and wastes), marine biorefineries (based on marine biomass), biochemical and thermochemical biorefineries (based on a mix of several technologies), and advanced biorefinery (multiple feedstocks, products, and platforms), among others (Cherubini 2010; Sonnenberg et al. 2009; Ververis et al. 2007).

Figure 1.1 shows a scheme of the overview of the biorefinery concept, in which a biorefinery that admits one of the many possible biomass inputs, is able to use several treatment and conversion processes aiming to produce a wide spectrum of products, including primary products and coproducts valorization.

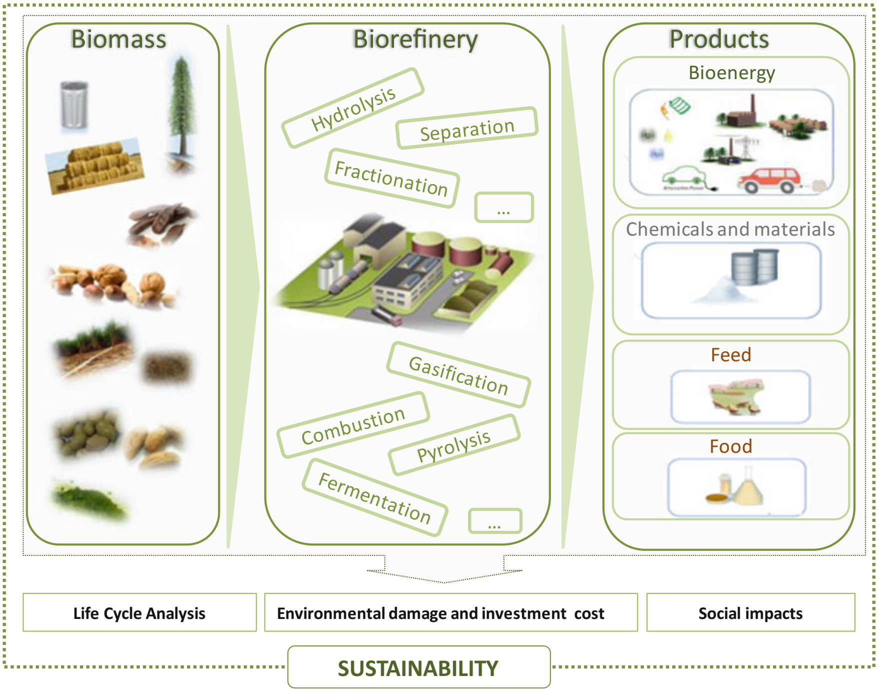

Fig. 1.1 Scheme of biorefinery concept

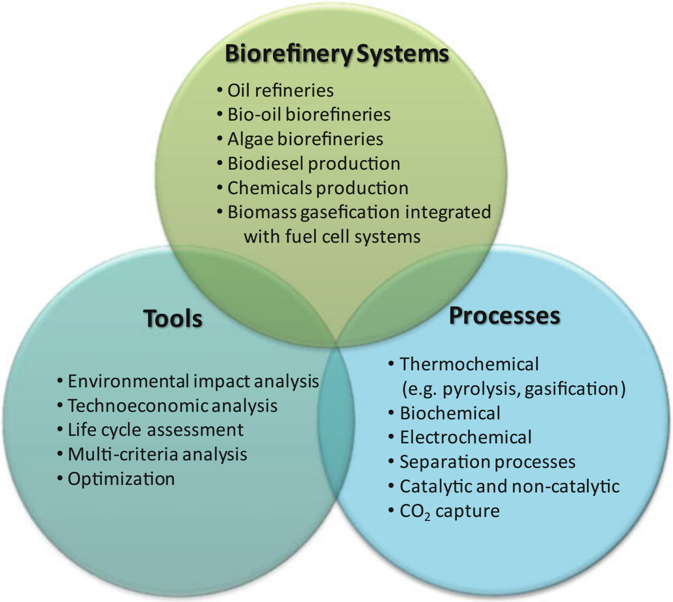

Fig. 1.2 Examples of some of the topics considered in this book

Figure 1.2 introduces some important topics treated in this book, such as some examples of biorefinery systems, the most relevant processes considered in these systems to obtain the primary products and coproducts, and some tools that are essential to evaluate the system viability and sustainability.

1.2 Biomass Feedstock Biorefinery

The choice of biomass and final products is fundamental in biorefinery design due to the large-scale production implications. Initial biomass availability, its potential use, and its characteristics need to be considered (Mabee et al. 2005). There are many options available, each with advantages and disadvantages. The biomass from forest, agriculture, aquaculture, and residues from industry and households can be used on the biorefinery, including wood, short-rotation woody crops, agricultural wastes, wood wastesWaste, bagasse, waste paper, sawdust, biosolids, grass, and organic residues (e.g., waste from food processing), aquatic plants and algae, animal wastes, among others (Demirbas 2005). Detailed and accurate characterization of biomass feedstocks, intermediates, and products is a necessity for any biomass conversion process, to understand how the individual biomass components and reaction products interact at each stage in the process. Based on biomass feedstock, the biorefineries can be classified as lignocellulosic or marine.

1.2.1 Lignocellulosic Biorefineries

Lignocellulose materials contain high amount of sugars, but in the form of polysaccharides, and can be used in the context of biorefinery (Fernando et al. 2006).

So, the lignocellulosic feedstock biorefinery consists in the refinery of the raw material into intermediate outputs (cellulose, hemicellulose and lignin) that will be processed into a range of products and bioenergy. Lignocellulosic biomass and residues such as wood, grass, and straw are abundant, nonfood raw materials for renewable fuels fueland products. These substrates are abundant, geographically widely distributed, and do not compete with food, freshwater, and fertile land (Cherubini 2010). However, biorefineries based on lignocellulosic feedstocks have to face with the problem of seasonal availability and mainly with the requirement of biobased fuel and materials/chemicals meeting specified standards independently on the biomass stream they come from (Clark et al. 2009).

Nowadays, the use of biomass is still more costly than the use of fossil resources for these applications. Therefore, the development of fundamental and applied research in this area is necessary. This means processing technologies that can deal with multiple biomass feedstock streams either within a single process or through a combination of several integrated ones. This allows the production of a broad spectrum of valuable, marketable products. A scheme of Lignocellulosic biorefineries is represented in Fig. 1.3.

Many pilot and demonstration plants have been developed based on lignocellulosic matter biorefinery, and several commercial projects are under development. A most extensive review will be shown in Chap. 7. However here are some examples of pilot plants and commercial projects.

- There are some pilot plants in Europe, Australia, Canada, and USA such as LEUNA (Germany), a 2-platform (C5 and C6 sugars, lignin) biorefinery for the production of biobased synthesized building blocks and polymers from lignocellulosic residues (wood, straw) (http://de.total.com/en-us/search/site/LEUNA);

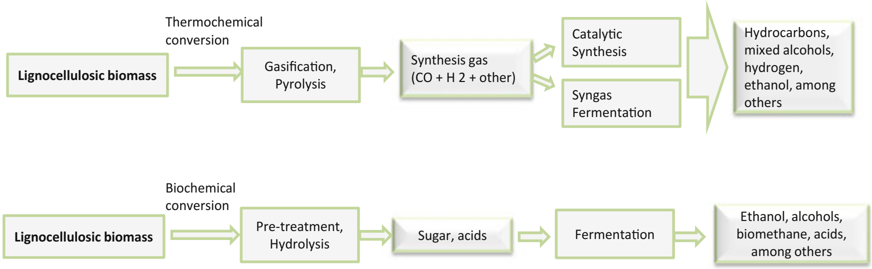

Fig. 1.3 Scheme of two types of the lignocellulosic biorefinery

- Bioprocess Pilot Facility—BPF (The Netherlands), a sugars and lignin platform biorefinery for the production of biobased products and bioenergy from lignocellulosic biomass (www.bpf.eu);
- BDI bioCRACK Pilot Plant (Austria), a one-platform (pyrolysis oil) refinery for the production of diesel fuel, pyrolysis oil, and bio-char from solid biomass (http://www.bdi-bioenergy.com/de-biomass_to_liquid-24.html);
- Microbiogen—Lignocellulosic "Fuel and Feed" Biorefinery (Sydney, Australia), a 2-platform (lignin, C5 and C6 sugars) biorefinery using wood chipschips to produce bioethanol, green coal, and yeast;
- GreenField Specialty Alcohols 2G Ethanol Pilot Plant (Ontario, Canada), a 2-platform (lignin, C5 and C6 sugars) biorefinery producing bioethanol, acetic acid and CO_2 from lignocellulosic biomass (http://www.gfsa.com/);
- Enchi Corporation (former Mascoma Corp.) (USA) Pilot plant CBP with little or no pretreatment—only mechanical disruption or hydrothermal wood chips, switchgrass, and other lignocellulosic biomass (http://www.enchicorp.com/).

Some of commercial lignocellulosic pretreatment technologies (e.g., Liberty™ Technology, POET/DSM, USA; Abengoa Bioenergy Biomass of Kansas, USA) are already available for the production of bioethanol and coproducts from a wide variety of woody material, wastes and other residues, contributing to the deployment of advanced biorefineries using raw materials other than readily available sugar and starch feedstocks. However, these advanced biorefineries are not mature yet but still under development.

Some of commercial scale are also available in Europe:

- CELLULAC (Ireland), a 3-platform (C5, C6 sugars and lignin) for the production of chemicals and fuels from lactose whey permeate and lignocellulosic biomass (http://cellulac.com/sf/);
- Matrica SPA (Italy), under construction, where the complex is expected to employ directly 680 people with a total investment of 500 million Euro. A 1-platform (bio-oil) biorefinery for the production of chemicals (bio-lubricants), bio-polymers, bio-fillers from oil-seed (http://www.matrica.it/);
- Dupont (Nevada, Iowa) and POET-DSM (Emmetsburg, Iowa) in USA; Iogen Corporation in Canada; GranBio (Alagoas) and Raízen/Iogen (Piracicaba) in Brazil, are giving the first steps as major players to commercialize cellulosic ethanol. (IEA Bioenergy Task 42 report, 2014).

1.2.2 Marine Biorefineries

As the name indicates, this biorefinery is based on marine biomass such as aquatic plants, macroalgae (e.g., seaweed) and microalgae. This type of biomass has some advantages, such as no competition for arable land, high areal productivities, and production of a wide range of biobased products and energy, however the cultivation and processing are still at its beginning.

Microalgae biofuels are also likely to have a much lower impact on the environment and on the world's food supply than conventional biofuel-producing crops. When compared with plants biofuel properties, microalgae biomass has a high caloric value, low viscosity, and low density. These characteristics make the microalgae more suitable for biofuels production than lignocellulosic materials, as well as their inherently high lipid content, semi-steady-state production, and suitability to grow in a variety of climates (Gouveia 2011). The main advantages of microalgae are: a high photon conversion efficiency and growth at high rates; a high CO_2 sequestration capacity; they utilize nitrogen and phosphorous from a variety of wastewater sources (e.g., concentrated animal feed operations and industrial and municipal wastewaters) providing the additional benefit of wastewater bioremediation; they do not compete with food production since they use marginal areas which are unsuitable for agricultural purposes (e.g., desert and seashore lands); production is not seasonal; cultures can be induced to produce a high concentration of oil, starch and biomass; they can be cultured without the use of fertilizers and pesticides, resulting in less waste and pollution; and they produce value-added products or coproducts (e.g., proteins, polysaccharides, pigments, biopolymers, animal feed, fertilizers…) (Campbell et al. 2011; Gouveia 2011).

The characteristics of microalgae described above make this biomass a great potential to use in biorefineries (Fig. 1.4). However, the industrial viability of microalgae-based biofuels depends upon the economical aspects which are fundamental to the process. Furthermore, whatever advances might arise in terms of technological innovations, the market will not exhibit an enthusiasm for funding capital-intensive energy projects unless the risk–return ratio is acceptable (Ferreira et al. 2013a; Singh and Gu 2010). Consequently, the technologies concerning this type of biomass are still in development, and must be further investigated to make microalgae-based products, energy, and environmentally relevant.

The marine biorefineries are not already developed, however there are a few examples of this type of biorefineries at pilot plant or demonstration stage:

- AlgaePARC (The Netherlands) Pilot Plant, a multi-platform biorefinery for the production of proteins, lipids, carbohydrates, and pigments from microalgae (http://www.algaeparc.com/project/2/algaeparc-biorefinery);
- Ecoduna Algae Biorefinery (Austria) Demonstration Plant, a 3-platform biorefinery producing biofuels, electricity and heat, omega-3/6 fatty acids and fertilizer from microalgae (http://www.ecoduna.com/);
- Solvent Rescue Ltd (previously Solray Energy Ltd) (New zealand), Pilot plant for supercritical water processing of algae to bio-crude oil. Development work on woody feedstocks (http://www.solventrescue.co.nz/);
- Aquafarming (Maris, Leuven, FeyeCon) Demonstration Plant (http://www.maris-projects.nl/) (IEA Bioenergy Task 42 report 2014).

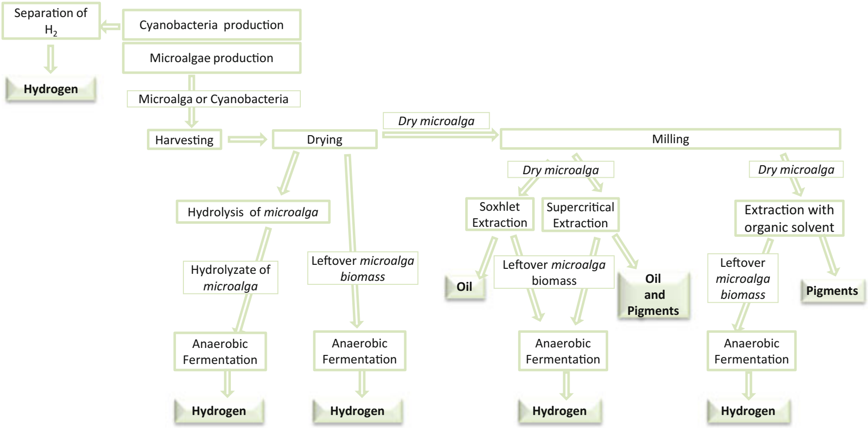

Fig. 1.4 Example of the marine biorefinery. Based on Ferreira et al. (2012, 2013a, b), Pacheco et al. 2015)

1.3 Biomass Conversion Processes

Nowadays, the biobased products have a great importance for several industries; however there are still several technical, strategic, and commercial challenges that need to be overcome before any large-scale commercialization of the industry can succeed. Then, the development and application of the best possible technologies for all processes (e.g. chemical conversion, gasification, fermentation), and also for pretreatment and storage, should be concerned for any projected biorefinery (Löffler et al. 2010).

Processes like combustion, gasification and pyrolysis and biological conversion to sugar and volatile fatty acids could be considered in order to take into account the variability in the biomass chemical compositionchemical composition (moisture, content and quality of both inorganic and hemicellulose fractions), as well as the need to provide a wide selection of energy carriers, end products and secondary raw materials for the fulfillment of the market needs. Thermochemical conversion of biomass in practical systems results from a strong interaction between chemicals and physical processes at the levels of both the single particle and the reaction environment. Feedstock restrictions for thermochemical conversion mostly pertain to particle size, moisture, and ash content (Küçük and Demirbaş 1997; Strezov and Evans 2014).

In terms of conversion processes biorefineries could be divided in two distinct pathways, as can be seen in Fig. 1.5: biochemical conversion and thermochemical conversion.

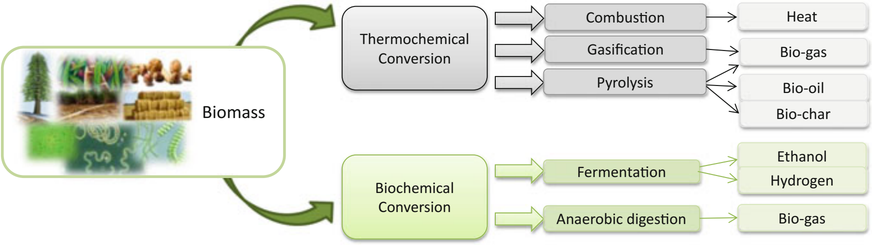

Fig. 1.5 Biochemical and thermochemical pathways for converting biomass to biobased products (e.g. of the main products of each process)

1.3.1 Thermochemical Conversion

Thermochemical conversion is characterized by higher temperatures and faster conversion rates. The three main pathways are: combustion (complete oxidation), gasification (partial oxidation), and pyrolysis (thermal degradation without oxygen). Other example of thermochemical conversion is the Fischer–Tropsch synthesis and liquefaction.

Thermochemical conversion involves controlled heating or oxidation of biomass synthetic gas as an intermediate product, which can be upgraded to valuable products (Demirbas 2004; Tanger et al. 2013).

Thermochemical-based refinery processes are generally consisting of the following interconnected unit operations: pretreatment (i.e., drying, size reduction), feeding, conversion, product clean up and conditioning, and product end use. Thermochemical conversion technologies convert biomass and its residues to fuels, chemicals, and power. The products by thermochemical conversion of biomass and their relative amounts depend on process conditions such as temperature, pressure, feed rate, time of heating, particle size of biomass, and any quenching processes that are applied. The thermochemical conversion is represented in Fig. 1.6.

Combustion of biomass is the thermochemical conversion technique most studied and established for generating heat and power. Combustion processes are responsible for over 97% of the world's bio-energy production (Demirbas, 2004). Combustion is an exothermic reaction between oxygen and the hydrocarbon in

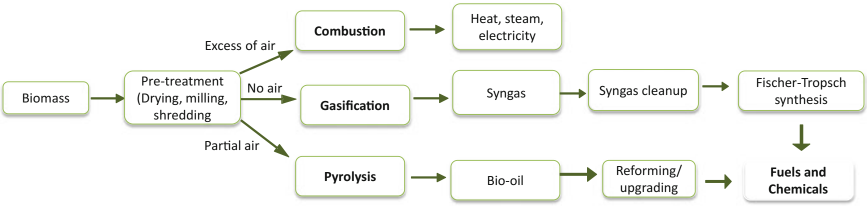

Fig. 1.6 The overall scheme of the thermochemical conversion process

biomass. (Liñán and Williams 1993). Here, the biomass is converted to H_2O and CO_2, where the main direct source of H_2O is drying of biomass and main indirect source of H_2O is oxidation of volatiles. Heat and electricity are two principal forms of energy derived from biomass (Basu 2013). However, the detailed chemical kinetics of the reactions that take place during biomass combustion are complex. Unfortunately, this technique is still associated with high emissions of particulate matter (PM), from which PMs smaller than 1 μm are regarded as a major indicator for the health relevance of ambient air pollution (Fernandes and Costa 2012). The imperfect combustion results in the release of intermediates including environmental air pollutants such as volatile organic compounds (VOC), large oxygenated organic carbon species, CH_4, CO, and PM. Additionally, fuel impurities, such as sulfur and nitrogen, are associated with emission of SO_X and NO_X. (Tanger et al. 2013).

Considering the high level of maturity of combustion technology, technology developments will only produce incremental improvements. Furthermore, combustion produces heat which is not an easy energy carrier to store. If heat is the desired energy carrier, the efficiency of conversion can be quite high, but storage is difficult. If electricity is produced, the efficiency of the process is relatively low, and it can only be stored in batteries, which is not a fully mature technology.

Combustion is widely utilized and commercially available for small-, medium- and large-scale applications. Large-scale co-firing of bio-oil has been carried out, for example, at EnSyn, but few other cases of application exist.

Gasification involves a chemical reaction in an oxygen-deficient environment. Gasification is the exothermic partial oxidation of biomass, with about one-third of the oxygen necessary for complete combustion, produces a mixture of CO_2 and hydrogen, known as syngas. The gas can be cleaned and used directly as a stationary biofuel or can be a chemical feedstock through biological fermentation or catalytic upgradingcatalytic upgrading via the Fischer–Tropsch process for the production of fuels or chemicals (alcohols, organic acids, ammonia, methanol and so on) (Cherubini, 2010; Tanger et al. 2013). The gasification process is faced with some challenges such as the development and commercialization of biomass gasification due to “tars” formation (Milne and Evans 1998). Tars and other contaminants formed during gasification must be removed prior to fuel synthesis; these are both a fouling challenge and a potential source of persistent environmental pollutants (Basu 2013; Foust et al. 2009).

Gasification of biomass has had little commercial impact owing to the competition from other conversion techniques. There has, however, been renewed interest in this process, yet economically viable examples are rare (Bridgwater 1995).

Pyrolysis is a process of heating biomass in the absence of oxygen at a relatively low temperature. Pyrolysis is a promising bioconversion technique for energy recovery, waste management, and converting biomass into useful energy products that has attracted considerable attention during the past decades due to its bioenergy production capability (Liew et al. 2014). Within a pyrolysis process, the raw material is converted into different reactive intermediate products: solid (bio-char), liquid bio-oils (heavy molecular weight compounds that condense when cooled down), and gaseous products (low molecular weight gases) (Fernández et al. 2011). Both gas and pyrolysis oil can be used as fuels that are cleaner and more efficient than the solid biomass, but can also be chemically converted to other valuable fuels and chemicals. Depending on the pyrolysis temperature, the char fraction contains inorganic materials to varying degrees, any unconverted organic solid and carbonaceous residuescarbonaceous residue produced from thermal decomposition of the organic components. Bio-char offers numerous benefits when applied to soils and it potentially delivers a net reduction of atmospheric carbon dioxide, achieved across the combined cultivation and processing regime overall as a function of time. The oil fraction is a complex mixture of organic chemicals (Silva et al. 2016) The pyrolysis method has been used for commercial production of a wide range of fuels, solvents, chemicals, and other products from biomass feedstock. Conventional pyrolysis consists of the slow, irreversible, thermal decomposition of the organic components in biomass. Slow pyrolysis has traditionally been used for the production of char. Short residence time pyrolysis (fast, flash, rapid) of biomass at moderate temperatures has generally been used to obtain high yield of liquid products (Yaman 2004). This technology is not already maturating but in contrast with combustion technology the resulted biofuels can be stored if fuel quality and storage conditions are appropriate.

The use of pyrolysis and the properties of the bio-oil produced are still in development, but it is thought that it can reduce the costs of gasification compared with feeding solid biomass directly into the gasifier (Bridgwater 1995).

A thermo-catalytic conversion can also be considered, including liquefaction and Fischer–Tropsch synthesis. The liquefaction process occurs in the presence of a catalyst and at a still lower temperature. In this process the biomass is converted into liquid. Liquefaction of solid biomass into liquid fuel can be done through pyrolysis, gasification as well as through hydrothermal process. In this case, when there is contact of the biomass with water at elevated temperatures (300–350 °C) with high pressures (12–20 MPa) for a period of time, the biomass is converted into oil (Basu 2013).

The Fischer–Tropsch synthesis is a process used to convert syngas obtained by gasification into liquid transport fuels. This process is widely recognized, but there is a possibility of catalyst shortages in large-scale productions if catalyst regeneration is not improved. This technology is commonly found in the commercial generation of electricity and synthetic fuels from conventional fossil fuels (The Royal Society 2008).

1.3.2 Biochemical Conversion

In biochemical conversion, biomass molecules are broken down into smaller molecules by bacteria or enzymes. In biochemical conversion technology, these biocatalysts, in addition to heat and other chemicals, convert the carbohydrates of the biomass (hemicellulose and cellulose) into sugar. These sugars are intermediate products that can be fermented or chemically catalyzed, using biocatalysts, into a range of advanced biofuels and value-added chemicals such as ethanol and other fuels, chemicals, heat, and/or electricity.

Unlike thermochemical conversion processes, biochemical processes occur at lower temperatures and have lower reaction rates. The biochemical process consists of the following crucial steps: feedstock supply, pretreatment, hydrolysis, biological conversion, and product recovery. The most common biological conversions are fermentation and anaerobic digestion, however it can be considered the enzymatic conversion. The overall scheme of the biochemical conversion process is shown in Fig. 1.7.

Fermentation uses microorganisms or/and enzymes to convert fermentable substrate into recoverable products (alcohols or organic acids). With this process ethanol (the most required fermentation product), butanol, hydrogen, methanol, butyrate acid, and acetate acid can be produced. The fermentation of lignocellulose into cellulosic ethanol has been substantially developed in the past few decades. Lignocellulosic ethanol plants as a whole are at the large demonstration stage, with the Beta Renewables plant becoming operational in 2013, and several others under construction. Enzymatic hydrolysis is being used in these demonstration scale plants. There are around 6–7 small-scale demonstration plants currently operational in Europe with capacities of 1–6 million liters per year (ML/year) and 2–3 pilot plants, Beta Renewables, SEKAB, Clariant, and Inbicon (Bacovsky 2014). The US has a similar number of demonstration plants of the same scale, but at a more advanced stage of development, with four plants under construction, Abengoa, Bluefire, Beta Renewables, Zeachem, Fiberight, Poet-DSM, Mascoma, and Dupont (Council 2013; DOE 2014; Sheridan 2013). In Brazil, one of the key actors is GranBio which plans to bring a 90 ML/year plant into operation in 2014 based on Beta Renewables technology (Bacovsky 2014).

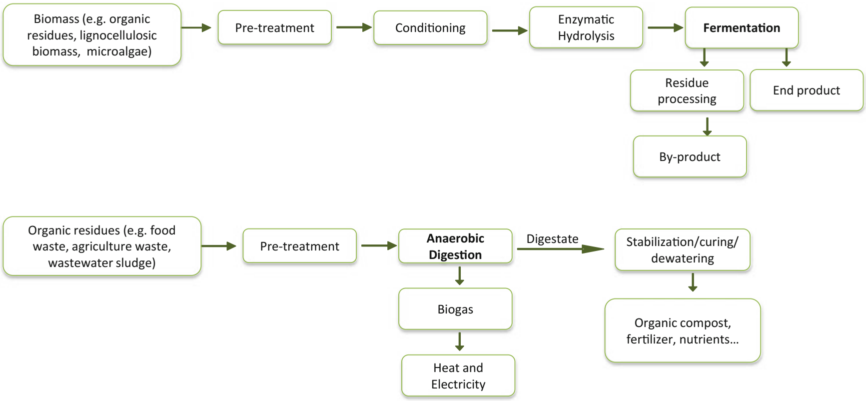

Fig. 1.7 The overall scheme of the biochemical conversion process (fermentation and anaerobic digestion processes)

Fermentation of C5 and C6 sugars to butanol is commercial using the Acetone–Butanol–Ethanol (ABE) process, although the process yields are typically found to be uneconomic for fuel production. Other fermentation pathways for producing only butanol are at the demonstration stage. Most developers are currently focusing on demonstrating butanol production based on sugar and starch feedstocks, with an aim to move to lignocellulosic feedstocks in the longer term, using technologies developed and demonstrated for lignocellulosic ethanol. For example, Gevo have licensed organisms from Cargill that would allow them to use lignocellulosic feedstocks (Alpena Biorefinery 2013; European Biofuels Technology Platform 2013).

Anaerobic digest occurs in controlled reactors or digesters and uses bacterial breakdown of biodegradable organic material. This process occurs in the absence of oxygen over a temperature range from about 30 to 65 °C. The main product of this process is biogas (methane and carbon dioxide and solid residue), which can be upgraded up to 97% methane content and can be used to replace natural gas (Cherubini 2010). An anaerobic digestion for the production of biogas is a well-established commercial technology. Small-scale biogas digesters have been used throughout many developing countries, most notably China and India, but also Nepal, South Korea, Brazil, and Thailand. However, this technology has some limitations in terms of conversion efficiency and productivity of lignocellulose (Consortium 2014).

1.3.3 Advanced Biorefinery

The integrated thermo-biorefinery or advanced biorefinery is considered a biorefinery of the future. The concept of advanced biorefineries is similar to a conventional biorefinery, however, in this case multiple feedstocks, products, and platforms are considered (Fig. 1.8). This type of biorefinery integrates all technologies mentioned in previous subsections.

In advanced biorefinery, different biomass feedstocks and innovative technologies are used. In this case, significant investments in development and new ways to reduce costs and achieve competitiveness with fossil fuels fossil fuelsare essential (Office 2013). An integrated biorefinery produces various products, which include electricity produced from thermochemical and bioproducts from the combination of sugar and other existing conversion technology platforms.

The example of an advanced biorefinery is Abengoa in USA (Office 2013). The current challenges and opportunities in the world and the pilot/demonstration plants will be mentioned with more detail in Chap. 7.

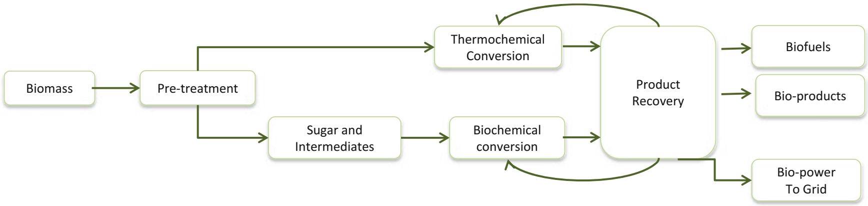

Fig. 1.8 Scheme of advanced biorefinery. Adapted from Office (2013)

1.4 Economic and Sustainability Analyses

Evaluating the economic and sustainability of the biorefinery is extremely important to understand the energy, environmental burdens, and costs of any production/ conversion system giving insight into its sustainability (DG Tren—European Commission 2008).

Each process involved in the biorefinery has a relevant impact on the sustainability of biobased products. In any biorefinery, the recycling of energy/heat should be improved with influence on the energy consumption and emissions of the whole processes and respective products. The efficiency of the conversion processes on the biorefinery is essential to make it more sustainable and consequently more economic. Moreover, the use of coproducts and residues as added value products, or as potential fuels to be sold or to produce electricity and heat onsite, and the reutilization of residual heat, are topics that potentiates the increase of the system efficiency and economical gain. To make a biorefinery sustainable and efficient, a significant investment in terms of special technologies for biobased product production and in infrastructures and supply security is needed. Therefore, it is of extreme importance to minimize the costs and the cost of end products (Löffler et al. 2010). And this may be achieved with the proper coproduct allocation and valorization.

The optimization of biorefineries is becoming increasingly significant (Peters et al. 2015). It will allow the identification of bottlenecks and improvement of pathways in the biorefinery processes, improving the biomass conversion yield, carbon footprint, water footprint, fossil energy addiction, and net economic value (NEV). The selection of the most suitable processes, production pathways, and energy and material fluxes are some of the desired results of optimization methods applied to the refinery system. The selection of the most valuable or sustainable pathways within a biorefinery system is a challenge when optimizing biorefinery systems, namely because different products have different value, requirements, demands, and yield efficiency (Fig. 1.9). If in some cases the correct allocation is key, in other cases there may not be an optimal pathway allocation—flexibility depending on the fluctuating demand and value market may be one of the solutions.

The energy and emissions balance of an engineered process is crucial to verify if the processes and technologies used on biorefinery are environmentally friendly and

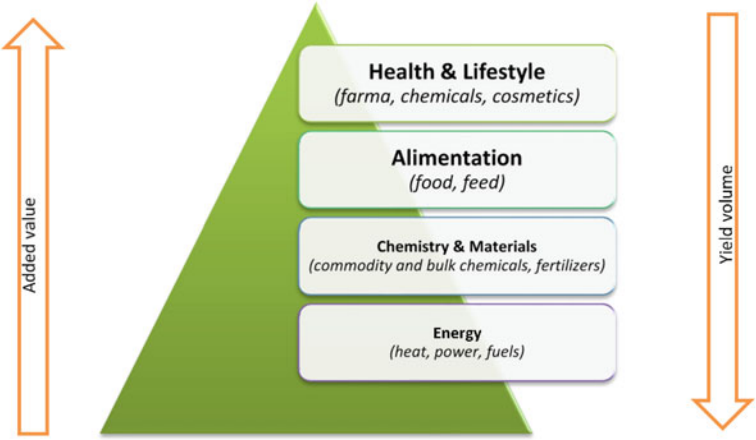

Fig. 1.9 Value pyramid of biomass use in a biorefinery concept. Adapted from Ree and Zeeland (2014)

sufficiently efficient, and identify the bottlenecks aiming to apply further improvements on the energy and CO_2 emission chain. As part of a sustainability assessment, the economic, energetic, and environmental impacts depend on these global process balances. The environmental carbon footprint based on life cycle methodology has shown to be an important tool and it is frequently used in studies of this research area (Pacheco et al. 2015).

The life cycle assessment methodology (LCA) analyzes a product during its lifetime from its production, to its utilization, and end of life, including its recycling process. It is an important methodology to estimate the energy balance and environmental impact of a system. This methodology is defined by the ISO 14040 principles (14040:2006, Life Cycle Assessment: Principles and Framework and 14044:2006, Life Cycle Assessment: Requirements and Guidelines).

In this methodology, each step of the processes should be considered, such as biomass feedstock (e.g., culture, harvesting, drying), conversion process (e.g., pyrolysis, fermentation) and use of the product.

Figure 1.10 exemplifies a biorefinery system with several life cycle steps, from its primary feedstock extraction to the final product achievement and coproducts or residues post-processing.

Several items should be addressed when dealing with bioenergy systems to ensure its sustainability, such as direct and indirect land use change, water footprint, and energy demand. The most adequate indicators and methodology to carry the social and environmental life cycle assessments should be selected according to their representativeness with a geographical and time approach. This will allow getting valid results to check land use changes and social impacts. All these indicators allow to determine the actual sustainability of the systems. Checking different

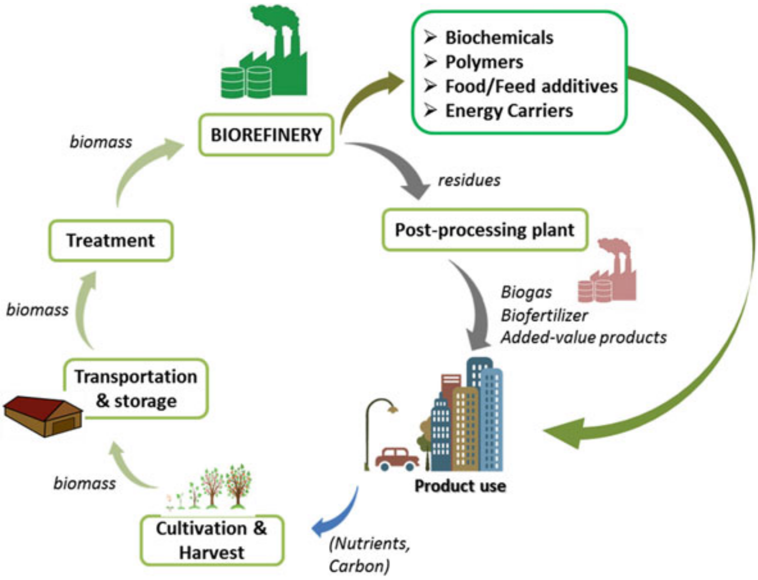

Fig. 1.10 Example of a biorefinery system and its integration within the life cycle of the input and output products. Adapted from https://www.chalmers.se/en/departments/bio/research/industrial-biotechnology/Biorefineries/Pages/default.aspx

biorefinery schemes will allow proposing a common methodology to be used for the assessments of each facilities and plants.

When it comes to life cycle, it is fundamental to refer the associated uncertainty. There can be two types of parameter uncertainty: measurement uncertainty, which is related to imperfections, assumptions or the inability to take an exact measurement when the actual inventory is being developed, and uncertainty related to the data quality of the inventories used. Identifications of sources of uncertainties in biorefinery assessment will therefore consist of a literature survey to determine the uncertainties existing in life cycle assessment of biorefinery, e.g., plantation of biomass and land use control (LUC) considerations, life of the plantation, different methods for harvesting, different processes of transformation and energy requirements, different allocation methods, and different end products. Definition of uncertainty in market demand will cause different biorefinery end product quantities needs as referred previously. A flexible biorefinery should respond to this market stimulation.

In the cost analysis, the economic viability and evaluation of the costs of each process can assess its economic feasibility. These types of analyses can be useful in determining which emerging technologies have the highest potential for success and to minimize the costs involved in whole processes. The socioeconomic factor should cover the impact created due to the biorefinery at a local and national level, associated job creations, land valorization, region incentives, associated secondary companies, and services contracted; and should also account with the capital investment, insurances, maintenance and relative services, human resources, energetic, and material requirements during the biorefineries lifetime, toward a viable or competitive leveled cost of the output.

In resume, in order to develop a sustainable biorefinery, the economic, environmental, and social impacts should be considered and analyzed.

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