Chapter 11
Biorefineries: Focusing on a Closed Cycle Approach with Biogas as the Final Step

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11.1 Introduction

The increasing energy demands as a consequence of fast-growing global population and higher living standards over the last few decades have triggered huge interest in finding new energy resources. Currently, most chemicals, materials, and energy carriers originate from fossil resources (Brar et al. 2016). Concerns over the rising global temperature, the depletion of fossil fuels, and increased environmental pollution, as well as the fluctuations of oil prices have encouraged researchers and energy policy makers to explore practical solutions for generating bioenergy and bioproducts with less environmental impacts (Parajuli et al. 2015). Today, about 80% of the global energy demand is supplied through fossil resources and the global energy demand in 2035 is still projected to rise by 40% with fossil fuels contributing 75% (Parajuli et al. 2015). Therefore, it is anticipated that sooner or later there will be no more fossil fuel to extract in an economical fashion and the world has to adapt to this new paradigm (Sharara et al. 2012).

While it is less complicated to provide future renewable electricity and heat due to the availability of a variety of renewable alternatives (i.e., wind, solar, hydro, biomass, and others), major challenges still exist regarding supplying of biochemicals and biofuels. In this context, biomass has a huge potential to play a pivotal role due to the fact that both biochemicals and biofuels can be extracted from biomass resources. Biorefineries which are analogous to today's petroleum

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refineries are identified as processing facilities capable of using biomass as feedstock to produce fuels, power, and chemicals (Yang and Yu 2013). This chapter aims at introducing the concept of biorefineries, the necessity of moving towards biorefineries, their opportunities and challenges, and potential feedstocks which can be used within the biorefinery concept. Moreover, the benefits of coupling biogas production with biorefineries are discussed and the problems and challenges are evaluated.

11.2 Biorefinery: Definitions and Perspectives

The increased awareness on the need to use biomass resources as well as the growing interest in upgrading more low-quality lignocel-lulosic biomass to valuable products along with the increased attention to the production of starch for energy applications led to the establishment of the term "biorefinery" in the 1990s (Berntsson et al. 2012; Kamm et al. 2006). Among the first definitions presented for the term "biorefinery", the term "Green biorefinery" was presented in 1997 in which biorefinery was referred to as technologies (Soyez et al. 1997). The definition offered was as follows, "Green biorefineries represent complex (to fully integrated) systems of sustainable, environmentally, and resource-friendly technologies for the comprehensive (holistic) material and energetic utilization as well as exploitation of biological raw materials in the form of green and residue biomass from a targeted sustainable regional land utilization" (Soyez et al. 1997).

The US Department of Energy considered biorefineries as an overall concept of a processing plant where a spectrum of valuable products are produced out of biomass feedstocks (Energy 1997). The American National Renewable Energy Laboratory (NREL) referred to biorefinery as a "facility" that integrates biomass conversion processes and equipment with the aim of providing fuels, power, and chemicals from biomass (NREL 2005). In this definition, the biorefineries are regarded as facilities developed to fulfil today's petroleum refineries' functions.

Among the distinctive definitions frequently observed in the literature for the term "biorefinery" (Berntsson et al. 2012; Demirbas and Demirbas 2010; Mansoornejad et al. 2010), the most comprehensive one was offered by the IEA Bioenergy Task 42: "Biorefining is the sustainable processing of biomass into a spectrum of marketable products and energy" (Cherubini 2010; Cherubini et al. 2007). This can be considered as the most exhaustive definition because it simultaneously aggregates the sustainability issues, the types of feedstocks, broad spectrum of obtained products, and economic considerations.

The economic aspects of biorefineries are important because it is often difficult to get positive economy balance, as the production cost of biomass-based fuels is often high. Therefore, integrating biomaterial and biochemical production (i.e., higher-value products) with generation of biofuels (i.e., higher-volume products) can potentially result in increased overall profitability. Although, in petroleum refineries, a wide range of processes can be employed, e.g., fluid catalytic cracking, thermal cracking, hydrocracking, etc., to produce a large number of valuable products out of crude oil, only few petroleum refineries employ all available conversion platforms. Due to the fact that biorefineries are aimed at competing with today's petroleum refineries, it is important to reduce the production costs, and therefore, they should only use the most cost effective conversion technologies to increase the overall profitability.

Biorefineries are imposing significant environmental impacts since they can simultaneously reduce our dependence on fossil resources and alleviate the environmental pollutions caused by the high consumption of fossil-based fuels. Generally speaking, biorefineries can be considered as multiple production of biofuel and biomaterials from various biomass feedstocks with the objectives of decreased non-renewable energy resources utilization, minimized related environmental impacts, and maximized efficient use of biomass. These objectives can be met if the following ecological perspectives are taken into consideration (Cherubini 2010; Gravitis and Suzuki 1999):

- Carbon, water and nitrogen cycles of agricultural and forestry plants.
- Technical and economic evaluations of existing and pilot biorefineries.
- Environmental impact evaluations through the whole life cycle of bio-products.

11.3 Types of Biorefineries and Their Classifications

The first serious attempts made at large-scale utilization of biomass-based resources were made in the 19th and at the beginning of the 20th centuries when the production of bio-based products like pulp, paper, guncotton and viscose silk, soluble cellulose, and furfural was reported (Kamm et al. 2006). The technological and scientific progress achieved during recent decades resulted in a wide range of biomass-based fuel and materials in the context of biorefineries. Due to a variety of distinctive technologies and platforms used in biorefining of biomass feedstocks, along with a broad spectrum of products and different feedstocks employed, several schemes have been proposed in the literature (Chambost and Stuart 2007; Huber 2008; van Ree and Annevelink 2007) to classify biorefineries and to make a systematic arrangement among them (Fig. 11.1).

In one of these systematic arrangements, the biorefineries are classified as generation-I, generation-II, and generation-III on the basis of the technologies employed. "Dry milling ethanol plant", as an example of the first generation, can be mentioned whose outputs are ethanol, feed co-products, and carbon dioxide. The second generation category has strived to overcome the intronsic inflexibility of the first generation using wet milling technology to produce a variety of end products including starch, high-fructose corn syrup, ethanol, corn oil, plus corn gluten feed, and meal. The final product of the generation-II biorefineries depends upon demands, market prices, contract obligations, and management considerations. The first and the second generations typically use grains as feedstock. The third

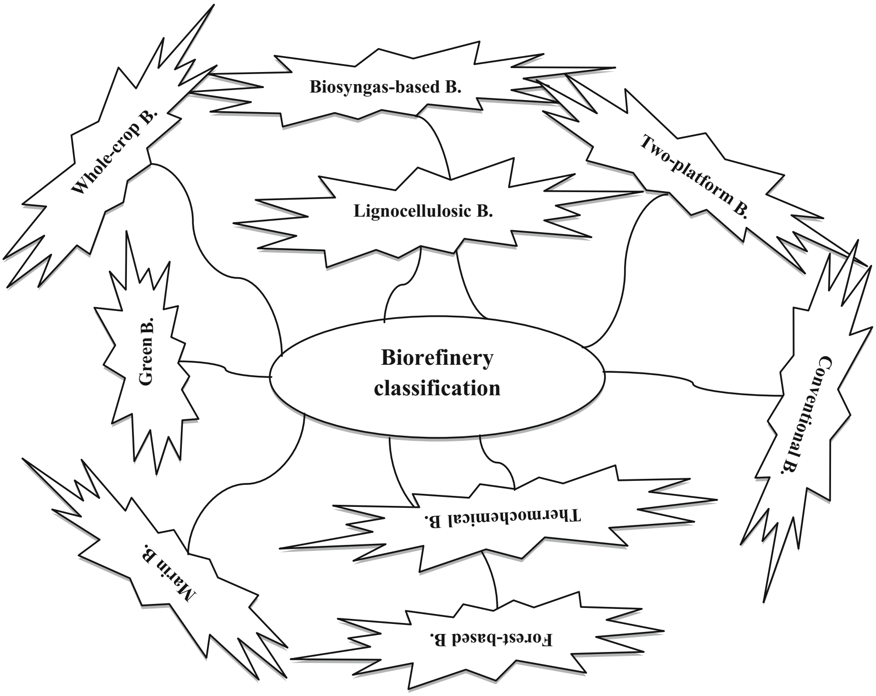

Fig. 11.1 Attempts made to classify biorefineries as observed in the published literature and the different terms introduced

generation biorefineries are the most advanced aimed at using agricultural or forest lignocellulosic biomass to produce multiple product streams, for example ethanol, chemicals, and plastics (Kamm et al. 2006).

However, many more classifications of biorefineries have been defined in the literature, such as the "lignocellulosic feedstock biorefinery", "whole crop biorefinery", "green biorefineries", and "biorefinery two platforms concept" (Kamm and Kamm 2004a, b; Werpy and Petersen 2004). Moreover, Demirbas and Demirbas (2010) added some new terms to this type of classification such as "oilseed biorefinery" and "forest biorefinery". "Lignocellulosic biorefineries" employ nature-dry biomass such as cellulose-containing biomass and wastes (Table 11.1) while in "green biorefineries", nature-wet raw materials including green grass, alfalfa, clover, or immature cereal are utilized.

The green biorefineries include two main pathways following a wet fractionation step. The outputs of these two steps are fiber-rich press cake and nutrient-rich green juice. The former contains cellulose, starch, dyes and pigments, crude drugs, and other chemicals; and can be used to produce biogas or syngas. The nutrient-rich green juice undergoes a fermentation process leading to the production of biogas, amino and organic acids, proteins, enzymes, etc. In the "whole crop biorefinery", the feedstock including wheat, rye, triticale, etc., undergo biorefining process and

Table 11.1 Potential products of a lignocellulosic feedstock biorefinery (adapted from Kamm et al. (2006))

<table>
<tr><th colspan="18">Lignocellulose</th></tr>
<tr><td colspan="7">Cellulose</td><td rowspan="4"></td><td colspan="6">Hemicellulose</td><td rowspan="4"></td><td colspan="3">Lignin</td></tr>
<tr><td colspan="5">Glucose</td><td rowspan="3"></td><td rowspan="3">Cellulose applications</td><td colspan="4">Xylose</td><td rowspan="3"></td><td rowspan="3">Plant gum</td><td rowspan="3">Sulphur-free Solid fuel</td><td rowspan="3">Sub-bituminous coal</td><td rowspan="3">Natural Binder</td></tr>
<tr><td colspan="3">5-Hydroxymethyl furfural</td><td rowspan="2"></td><td rowspan="2">Fermentation products</td><td colspan="3">Furfural</td><td rowspan="2">Xylite</td></tr>
<tr><td>Softener</td><td>Lubricants</td><td>Chemicals and polymers</td><td>Furan resins</td><td>Chemical products</td><td>Nylon</td></tr>
</table>

both seeds and straw is employed to produce a wide range of products. Straw can be treated under a decomposition stage and converted into principle components, i.e., lignin, hemicellulose, and cellulose. Instead of the decomposition process, gasification can be employed to produce syngas. In contrast, seeds can be either used in the grinding phase whose outputs can be binder, adhesive, and cement, or processed in the starch producing step. The extracted starch under chemical or biotechnological conversion as well as extrusion processes can generate valuable final products such as methanol, acetate starch, bioplastic, co- and mix-polymerisate.

"Two platforms concept" consists of the sugar platform and the syngas platform. However, NREL has suggested four different platforms i.e., sugar, thermochemical, biogas carbon-rich chains, and plant products platforms.

The conversion route is another criterion by which the biorefineries can be classified into five groups as follows (Demirbas and Demirbas 2010):

- Biosyngas-based
- Pyrolysis-based
- Hydrothermal-upgrading-based
- Fermentation-based
- Oil-plant-based

Efforts have been made to adapt a systematic approach for biorefinery classification, since the aforementioned classifications are broad, arbitrary and generic, and in some cases, heterogeneous. Moreover, currently used classifications can be combined by linking different technologies. Cherubini et al. (2009) chose five criteria, i.e., platforms, products, feedstocks, and processes to form five groups, each one consisting of some sub-categories (Fig. 11.2). Accordingly, they

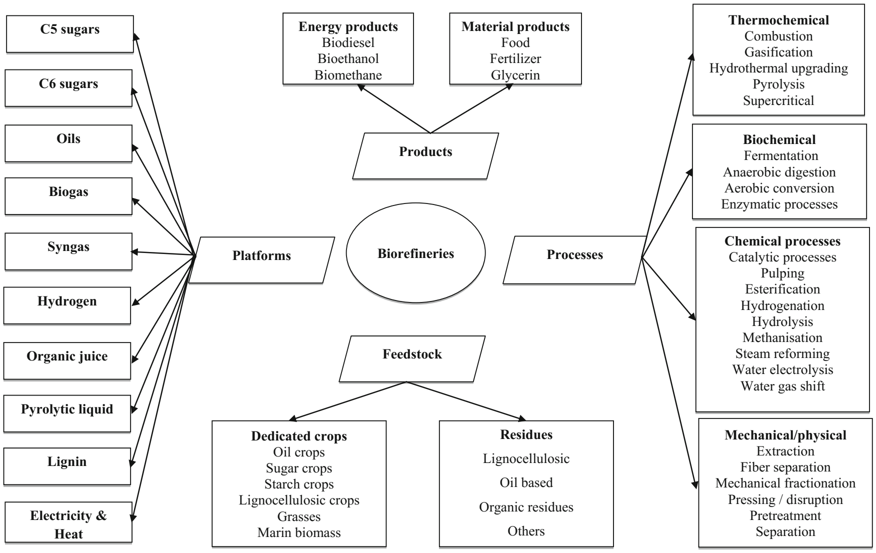

Fig. 11.2 Features and subgroups involved in proposed classification approach based on (Cherubini et al. 2009)

suggested that the biorefineries be classified by listing the main features of the biorefinery system, drawing a scheme of the features identified, and labeling the system by quoting the involved number of platforms, products, feedstocks, along with the processes.

11.4 Barriers and Obstacles to Biorefineries

As discussed earlier, biorefineries are aiming at producing bulk chemicals, biomaterials, and bio-energies from biomass feedstock for overall improving the economy of biomass use. In order to implement a commercial biorefinery, all technical and non-technical barriers should be overcome. Since the products of biorefineries are derived from biomass, the production cost can be mentioned as the most important barriers followed by the transportation cost of biomass-based feedstock. It is worth quoting that, biomass as the feedstock for biorefineries experiences seasonal changes. These seasonal diversities can lead to the need for storage facilities causing storage cost to be added to the total production cost. One important aspect of upscaling biorefineries is the infrastructure required for collection and storage of a large amount of biomass. Such an integrated feedstock supply system need to be constructed at a sustainable fashion and at a reasonable cost (Demirbas and Demirbas 2010). It is worth mentioning that by combining different technologies, based on the pathways shown in Fig. 11.3, for simultaneous

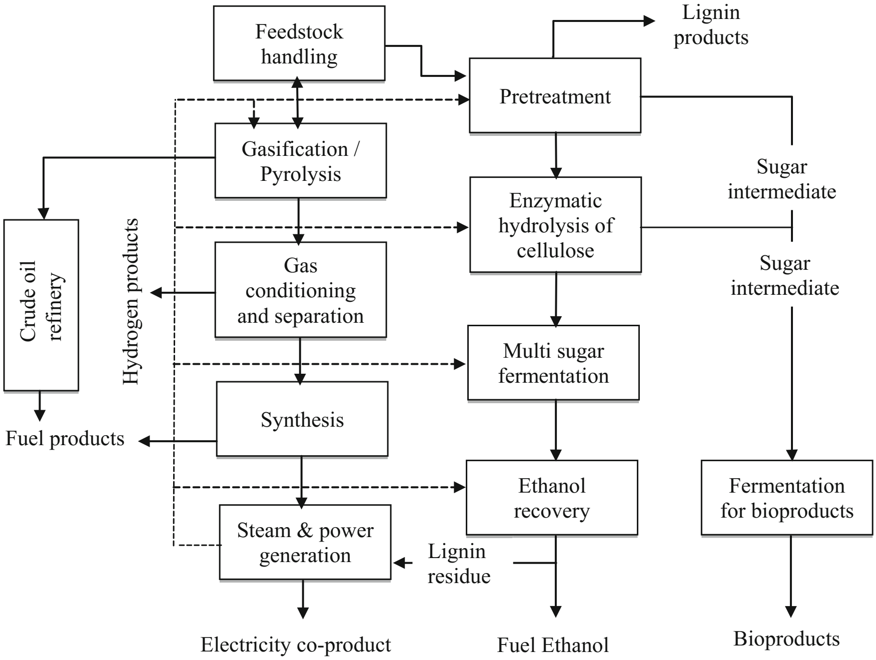

Fig. 11.3 Block diagram of an integrated biorefinery to use different platforms and produce different products (Fernando et al. 2006; Wang et al. 2004)

production of bioenergies and biomaterials, the overall production cost can be reduced and more flexibility in product generation can be offered.

The composition of biomass, undergoing a biorefining process, varies enormously. This can be regarded as a benefit for biorefineries because it enables them to produce a more diverse spectrum of products, even more than those generated by petroleum refineries. However, this compositional variation in biomass feedstock can also result in some disadvantages which need to be overcome. The economic and sustainable processing of raw materials in such a biorefinery requires advanced and sophisticated technologies most of which are still at a pre-commercial stage (Dale and Kim 2006).

Another major non-technical barrier which should be discussed herein is the use of land for production of biorefineries' feedstock. The competition between food production sector *vs.* raw materials supply for biorefineries over land and even other limited resources such as water can be taken into account as a serious limitation towards developing future biorefineries. This point of view has led to a serious discussion in scientific communities. While some believe that use of biomass as a feedstock for biorefineries can create jobs and boost economic growth (Negash and Swinnen 2013), others insist that it might reduce food availability and increase its price, thereby posing a real threat to food security, especially in the developing countries (Janssen and Rutz 2011). On the other hand, both direct and indirect land use change (LUC) effects cannot be ignored when imposing restrictions on the use of land. LUC effects refer to change in soil carbon pools caused by human activities which have huge impacts on the global carbon cycle and can potentially bring about climate change effects. Moreover, the indirect land use change (ILUC) cannot be disregarded in this context because it is responsible for global warming effects. When a piece of land, used for agricultural purposes such as growing food or feed, is now dedicated to biorefinery purposes, another non-cropland—such as grasslands and forests—somewhere else should be devoted to agricultural purposes. This transformation is known as ILUC effects and can neutralize the greenhouse gas savings resulted from replacing fossil-based fuels with the biofuels generated in biorefineries.

Deforestation, defined as "conversion of forest land to non-forest land" (DeFries et al. 2007) has been identified as a serious problem originating from emerging future biorefineries. This is in parallel with LUC effects because deforestation decreases the carbon sequestration. For example, it has been well-documented that the production of soybean-based biodiesel in Brazil and Argentina has contributed to deforestation (Janssen and Rutz 2011). This is due to the fact that the increasing demands for soybean has brought about the conversion of forest land to soybean farms (Nepstad et al. 2006). In spite of these on-going debates and concerns, some reports have shown that simultaneous production of biomass-based products and forest protection are possible depending on policies adopted (Demirbas 2009; Ravindranath et al. 2011).

Generally, it can be concluded that although biorefineries can take advantage of several benefits including energy security, climate change benefits, sustainable management of wastes, coproduction of valuable biochemicals, and rural economic development (Brar et al. 2016), there are still drawbacks and challenges which need to be effectively dealt with. Some of these challenges are summarized in Fig. 11.4.

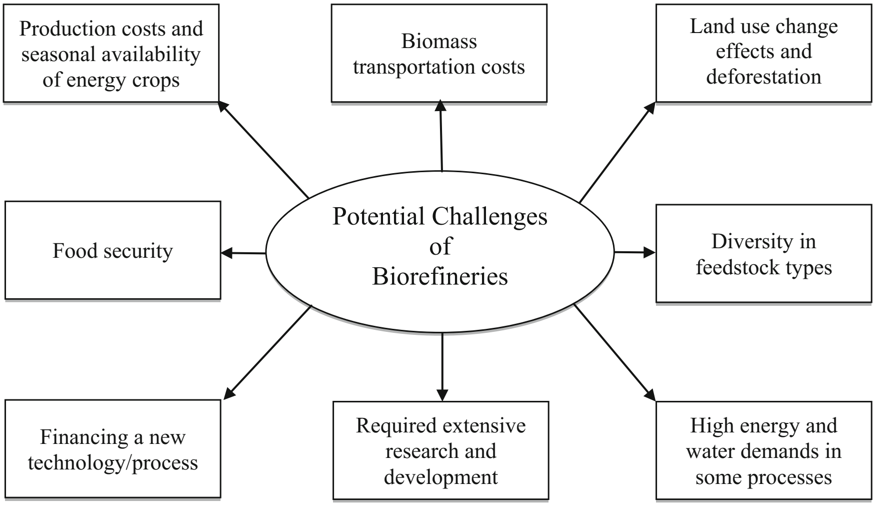

Fig. 11.4 Potential Challenges of the Biorefinery Concept (Brar et al. 2016)

11.5 Feedstock

Petrochemical industry has been playing a pivotal role in the livelihood of mankind by fulfilling needs for energy, material, and chemicals. In order to replace fossil-based refineries by biomass-based refineries, our today's requirements for energy and non-energy products should be completely met by future biorefineries. There is a huge potential to supply both bioenergy and biochemicals from biomass-based feedstock. Taking a look at outputs of today's refineries. i.e., textile goods, housing products, transportation products, etc. reveals that most of the products from the petrochemical industry are derived from 8 to 9 foundation chemicals (Werpy et al. 2004). Accordingly, the US Department of Energy (DOE) endeavored to identify twelve building block chemicals that can be produced from sugars via biological or chemical conversions (Fig. 11.5). Building block chemicals are molecules with multiple functional groups which can be transformed into new families of useful molecules (Werpy et al. 2004). This term is generally used to describe a virtual molecular fragment or a real chemical compound whose molecules possess reactive functional groups (Szmant 1989). They are employed to show how molecules can be assembled in a bottom-up modular order, i.e., nano-particle, metal-organic frameworks, organic molecular constructs, and supra-molecular complexes, ensuring the final compound or a (supra) molecular construct will be generated (Tu and Tirrell 2004). Thirty potential candidates out of 300 initially evaluated were introduced and by an iterative process based on the petrochemical model using building blocks, chemical data, known market data, properties, performance of the potential candidates, and the prior industry

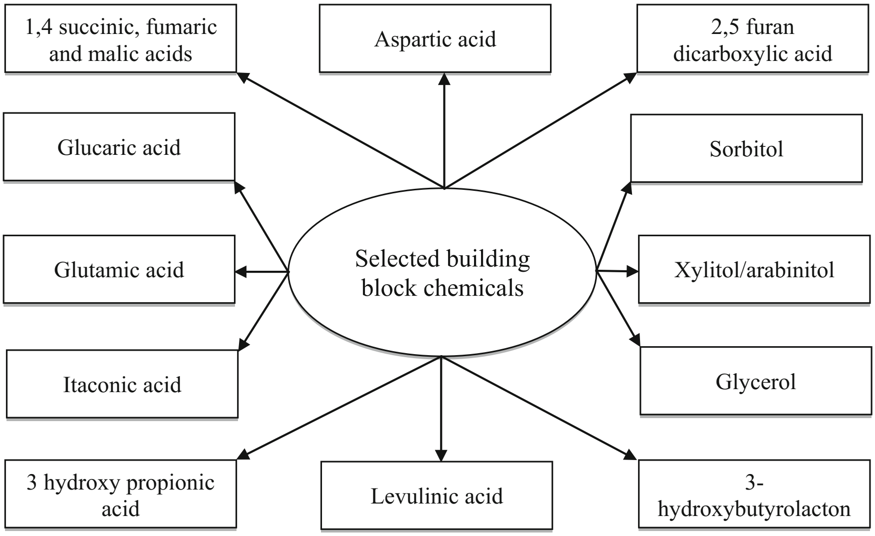

Fig. 11.5 Twelve sugar based building block chemicals (Werpy et al. 2004)

experiences, the top twelve final candidates were chosen. According to the DOE, our requirements for different chemical products can be met by these building block chemicals. Moreover, the final candidates are more appropriate than the other competitors in terms of feedstock costs, estimated processing cost, current market volumes, and prices. These features make the selected building block chemicals capable of competing directly against fossil-based chemicals, as well benefiting from chemical functionality, and improved properties (Werpy et al. 2004). Conversion pathways, derivatives, and potential applications of some most important building block chemicals identified in the literature are tabulated in Table 11.2.

While these building block chemicals can be extracted from various feedstock, attempts have been made to identify easily fermentable substrates to decrease the process costs and increase the total profitability. In parallel with decreasing the process cost, increasing the production level has also been a focus in research. Some researchers have come to the conclusion that productivity and increases in yield can be achieved by using engineered microorganisms, minimizing the production of undesired by-products, and the use of neutralizing agents (Engel et al. 2008; Jiang et al. 2009; Pachapur et al. 2016; Ye et al. 2013). Moreover, improving the product recovery step and increasing product purity can also help to achieve higher product quality and thereby, better prices along with reduction of process costs (Dan et al. 2010; Misra et al. 2011; Pachapur et al. 2016).

As elaborated earlier, there is a huge potential to fulfil our future requirements for chemicals and energy through biorefineries. A great deal of feedstock has been already examined and their advantageous and drawbacks have been discussed. Forest-based feedstock for biorefinery purposes seem to be appropriate feedstock as they cover about 32% of the land area but account for 89.3% of the total standing biomass (Brar et al. 2016). Forest-based biomass is composed of cellulose, hemicellulose, and lignin of which cellulose and hemicellulose can be converted to sucrose, xylose, glucose, galactose, and arabinose. These intermediate products can be converted to a range of platform chemicals through fermentation pathway including propanediol, ethanol, lactic acid, ethylene, succinic acid, glycerol, propane, etc. It is worth mentioning that the commercial production of some of these platform chemicals seems nonviable at the current state (Danner and Braun 1999). For example, 1 ton of fermented hexose (glucose or fructose) using the well-studied organism, *Saccharomyces cerevisiae,* according to the stoichiometric product yield, can result in the production of 511 kg ethanol. While, 8 ton of sugarcane biomass is needed to achieve 1 ton of hexose (Brar et al. 2016).

Animal fat and vegetable oils can also be added to the list of biorefinery feedstock because a number of platform chemicals including glycerol, succinic acid, propionic acid, butanol, and ethanol can be obtained from such feedstock. While animal fat and vegetable oils have long been evaluated for biodiesel production purposes, the use of the resulted by-products i.e., platform chemicals with adhesives, paints, lubricants, food additives, and biopolymers applications, can lead to a biorefinery approach. It is worth quoting that the simultaneous production of biodiesel and platform chemicals from animal fat and vegetable oils should be

Table 11.2 Conversion pathways, derivatives, and potential applications of some most important building block chemicals

Building blocks	Pathways	Derivatives/derivatives family	Potential application of derivatives
Four Carbon 1,4-Diacids[a]	Fermentation Chemical process	THF, BDO, GBL family Pyrrolidinone Family Straight chain polymers Branched polymers	Solvents, fibers such as lycra Green solvents, water soluble polymers (water treatment) Fibers (lycra, others) TBD
2,5-Furan dicarboxylic acid[a]	Enzymatic conversions	Diols and Aminations Levulinic and Succinic Acids Polyethylene terephthalate analogs Furanoic Polyamines	Polyesters and nylons All uses of succinic and levulinic Furanoic polyesters for bottles, containers, films Polyamide market for use in new nylons
3-Hydroxypropionic acid[a]	Fermentation	1, 3 propane diol Acrylate family	Sorona fiber Contact lenses, diapers
Aspartic acid[a]	Chemical process Fermentation Enzymatic conversions	Amine butanediol, amine tetrahydrofuran, amine Aspartic anhydride Polyaspartic	Amino analogs of C4 1,4 dicarboxylic acids
Glucaric acid[a]	Chemical process Catalytic oxidation	Lactones Polyglucaric esters and amides	Solvents Nylons or different properties
Glutamic acid[a]	Chemical process Fermentation	Diols (1,5-propanediol) Diacids (1,5-propanediacid) Aminodiol (5-amino, 1-butanol)	Monomers for polyesters and polyamides
Itaconic acid[a]	Chemical process Fermentation Aerobic fungal fermentation	Methyl butanediol, butyrolactone, tetrahydrofuran family Pyrrolidinones Polyitaconic	May confer new useful properties for the BDO, GBL, and THF family of polymers New polymer opportunity
Levulinic acid[a]	Chemical process	Methyl tetrahydrofuran γ- butyrolactone Acetyl acrylates Acetic-acrylic succinic acids Diphenolic acid	Fuel oxygenates, solvents Copolymerization with other monomers for property enhancement Replacement for bisphenol A used in polycarbonate synthesis

(continued)

Table 11.2 (continued)

Building blocks	Pathways	Derivatives/derivatives family	Potential application of derivatives
3-Hydroxybutyrolactone[a]	Chemical process	Furans. Analogs of pyrrolidones Amino analogs to tetrahydrofuran	Solvents Amino analogs to lycra fibers
Glycerol[a]	Chemical process Enzymatic conversions	PLA Analogs Glyceric Acid Propylene glycol 1,3-propanediol Branched polyesters and polyols	PLA with better polymeric properties Polyester fibers with new properties Antifreeze, humectant, etc. Sorona fiber Unsaturated Polyurethane Resins for use in insulation
Sorbitol[a]	Chemical process	Isosorbide, anhydrosugars Propylene glycol, lactic acid Branched polysaccharides	PET Antifreeze, PLA Water soluble polymers
Xylitol/arabinitol[a]	Chemical process Fermentation Enzymatic transformation	Xylaric and Xylonic acids Arabonic acid and Arabinoic acid Xylaric and Xylonic acids Arabonic acid and Arabinoic acid	Antifreeze Unsaturated polyester resins New polymer opportunities
Butanol[b]	Fermentation	2-Methyl-2-butanol, 2-butanol	As alternative fuel
Butyric acid[c]	Fermentation	R)-3-(Boc-amino)-4-(4-bromophenyl)butyric acid	Cosmetics Pharmaceuticals, As a “natural preservative” in the food industry
Lactic acid[d]	Fermentation	Lactate ester Polylactic acid (PLA) Acrylic acid 1,2-Propanediol Pyruvic acid	Hygroscopic and emulsifying properties, solvents Biodegradable plastic Acrylate polymers, biochemical intermediate Commodity chemical

[a] Werpy et al. (2004) [b] Cooksley et al. (2012) [c] Zhang et al. (2009) [d] Gao et al. (2012)

carefully suggested due to the fact that biotechnological progress has led to the direct production of these platform chemicals with decreased investment costs and increased total yield.

Microalgae are also considered as another potential feedstock for future biorefineries. From one hand, a vast number of researchers have shown that microalgae species have technical potential to produce lipid or carbohydrate biofuel precursors taking into account greenhouse gas and land use sustainability metrics, rapid biomass production rates, and high solar conversion efficiencies (Lardon et al. 2009; Melis 2009; Reijnders 2008; Stephenson et al. 2010). On the other hand, the economic analysis of algal biofuel production has proven that there is still a long way before achieving economic algal biofuel production, capable of competing with petroleum-based fuels (Brar et al. 2016; Sheehan et al. 1998; Williams and Laurens 2010). Nevertheless, the biorefinery approach has been suggested as a practical solution to achieve commercially relevant rates of return because it can result in simultaneous production of algal biofuels and value-added products. Pigments, vitamins, phytosterols, polysaccharides, organic acids, lipids, and miscellaneous algal compounds are high-value platform chemical which can be extracted from algae.

Chlorophylls, carotenoids, and phycobiliproteins are among the large number of pigments which can be extracted from algae. They are also rich in vitamin. It has been well-documented that different combinations and concentrations of vitamin B12 (cobalamin), vitamin B1 (thiamine), and vitamin B7 (biotin) can be found in algae (Brar et al. 2016; Croft et al. 2006; Provasoli and Carlucci, 1974). Moreover, there are several metabolic pathways in distinctive algae species resulting in synthesizing other vitamins, including vitamins A, C, and E (Hirschberg 1999). Phytosterols known as steroid alcohols are valuable platform chemicals owing to their medical applications, i.e., potential for lowering total and LDL cholesterol. They are also employed as therapeutic agents to treat hypercholesterolemia (Francavilla et al. 2010; Ostlund et al. 2003; St-Onge et al. 2003). Polysaccharides have been reported as a possible platform for the production of biofuels while they also have high values in the marketplace in terms of their applications in the food industry (Brar et al. 2016; Wargacki et al. 2012). Production of succinic and malic acids, two organic acids listed among the top 15 building block chemicals, from algae is anticipated to increase progressively in the near future in response to an additional market size of 25×10^6 ton per year for succinic acid-derived polymers (Bozell and Petersen 2010). Algal lipids have high values in the marketplace and they can be employed for biofuel production, nutritional supplements, and pharmaceutical applications. Microalgae are capable of bio-synthesizing lipids by diverting their central metabolic pathways when they are under certain stress conditions (Brar et al. 2016).

The utilization of agro-industrial waste for energy and biochemical production has gained lots of interests and the conducted studies have shown a great potential to revolutionize the chemical industry (Chandra et al. 2012; Octave and Thomas 2009). Agro-industrial wastes are important feedstock within the biorefinery concept since they are produced in huge amounts and a wide spectrum of valuable platform chemicals can be produced from them. The use of waste as biorefinery feedstock can decrease the total production cost and increase the total profitability. However, the challenges, i.e., non-uniformity, social perspectives, technology issues, collection, storage, and segregation, regarding the use of agro-industrial waste in biorefineries cannot be ignored. Currently a considerable deal of efforts has been concentrated on the production of bioethanol, as well as cogeneration of biofuels and adsorbents.

11.6 Biogas Production and Biorefinery Approach

Energy recovery and more specifically biogas production under anaerobic conditions plays a key role in developing future biorefineries because they contribute to a more sustainable performance of the whole system under consideration. Energy recovery in the form of biogas is a way to close the cycle and use the residual organic matters which have not been recovered. Anaerobic digestion (AD) is a versatile process, by which different types of organic matters are converted into biogas. On the contrary, many other bioconversion processes have a much narrower substrate preference, leaving unutilized a large portion of the organic matters. Therefore, biogas can be seen not only as an effluent purification process, but also energy producing path. Most of the biorefinery concepts have AD as a part of the proposed processes. In better words, integrating AD into some current technologies has been proposed as a practical solution which can simultaneously increase the total profitability and overcome some challenges involved. For example, biogas production from pre-hydrolysate under a biorefinery approach has been proposed to maximize the profitability resulted from the conversion of available sugars in woods (Safari et al. 2017). Softwood pine for example, due to its lignocellulosic structure, requires a pretreatment step prior to enzymatic or biological conversion. After completion of the pretreatment, the solid fraction is filtrated from the pre-hydrolysate, i.e., the liquid fraction, and undergoes enzymatic hydrolysis for ethanol fermentation (FazeliNejad et al. 2016; Khoshnevisan et al. 2016; Shafiei et al. 2015). To make this process economically viable, separate hydrolysis and co-fermentation (SHCF) or simultaneous saccharification and co-fermentation (SSCF) have long been used to convert pre-hydrolysate to ethanol (Dien et al. 2003; McMillan et al. 1999). The proposed methods bring about some new challenges including low ethanol yield, differences in the optimal fermentation conditions of the involved strains, etc. Accordingly, the integration of ethanol and biogas production from softwood has been evaluated and reported as a practical solution to overcome the aforementioned problems (Safari et al. 2017).

On the other hand, the economic profitability when using biomass in a biorefinery approach can be improved compared with using it for biogas production alone. As an example, Santamaría-Fernández et al. (2017) reported that the combination of protein refining and biogas production could be more economically favorable compared with sole biogas production from green biomass crops.

It should be noted that biogas production has been introduced as an economic solution for many industries because it can easily contribute to decreasing the costs associated with energy consumption and wastewater treatment (McKendry 2002; Schmidt et al. 2013; Wilkie et al. 2000). Nevertheless, recent studies have argued that the most interesting and impactful contribution of biogas solutions are their potential for product valorization and material upcycling (Batista et al. 2017; Begum et al. 2016; Hagman et al. 2017).

11.6.1 Microalgal as Biogas Feedstock

Microalgal feedstock has been widely considered for biofuel and biochemical production, there are several challenges to overcome though. The high accumulation of lipids in microalgae makes them attractive feedstock for biodiesel production. Moreover, different kinds of metabolites including pigments, fatty acids, proteins, and nutritional supplements for human consumption can be obtained from microalgae (Ramos-Suárez et al. 2014; Spolaore et al. 2006). Coupling of AD to the extraction of such metabolites from microalgae has also been examined as a potential way to improve the economics of the process. It has been shown that metabolites extraction could function as a pretreatment method for increasing the biodegradability of microalgal cells (González-Fernández et al. 2011; Mussgnug et al. 2010). Moreover, it can simultaneously decrease the C/N ratio and thereby, alleviate potential inhibition of methanogenesis due to increased ammonia levels (Zhong et al. 2012). The biogas potential from microalgae has been reported in several publications pioneering by Golueke and Oswald (1959). Table 11.3 tabulates a summary of biogas potential from different microalgae species.

Several challenges have been discussed by researchers as major factors affecting biogas production from microalgae including high capital cost, low algae productivity, slow conversion rate, and high sensitivity of AD process (Roy and Das 2015). Low concentration of biomass has been identified as one of the limiting factors because solid biomass content of most uncontrolled outdoor microalgae cultures is less than 1 g L^{-1} (Golueke and Oswald 1959; Stephens et al. 2010). Concentrating and dewatering of microalgae cultures have been suggested as practical solutions to the aforementioned problem, they are expensive and time-consuming procedures though (Harun et al. 2010; Pragya et al. 2013; Stephens et al. 2013; Ward et al. 2014). Integrating AD process into microalgae production can potentially offset the energy requirements with respect to the resultant methane production (Sialve et al. 2009).

The rigid cell wall structure is another problematic issue because it hinders accessibility of the AD microorganisms to the algal biomass. The increased process cost makes pretreatment methods as inappropriate approach to break down the rigid cell wall structure. Ramos-Suárez et al. (2014) integrated AD with amino acid extraction and reported improved economics of the process. Another dilemma in AD of microalgae is ammonia inhibition. The significant protein and lipid

Table 11.3 Methane biogas production through anaerobic digestion of different species of microalgae biomass

Microalgae species	C/N ratio	Methane yield	Loading rate
Tetraselmis	N/A	252 L kg^{-1} VS	5400 mg VS^{-1} L^{-1}
Scenedesmus	7.3	291.5-409.3 L kg^{-1} VS	3.85 g VS^{-1} L^{-1}
Chlorella vulgaris	N/A	403 L kg^{-1} VS	2 g VS^{-1} L^{-1}
Microspora	N/A	413 L kg^{-1} VS$_{algae}$	N/A
Chlamydomonas	N/A	310 L kg^{-1} VS$_{algae}$	N/A
Acutodesmus	N/A	223 L kg^{-1} VS$_{algae}$	N/A
Nannochloropsis oculata	N/A	204 L kg^{-1} VS	N/A
Lake Chaohu natural population consortium	N/A	295 L kg^{-1} VS	N/A
Nannochloropsis salina (lipid extracted biomass)	4.4	130 L kg^{-1} VS	2000 mg VS^{-1} L^{-1}
Arthrospira maxima	4.3–5.33	173 L kg^{-1} VS	500 mg TS^{-1} L^{-1}
Phaeodactylum tricornutum	N/A	350 L kg^{-1} COD	1.3 ± 0.4–5.8 ± 0.9
Scenedesmus obliquus	N/A	240 L kg^{-1} VS	2000 mg VS^{-1} L^{-1}
Scenedesmus sp.	N/A	170 L kg^{-1} COD	1000 mg COD^{-1} L^{-1}
Scenedesmus sp. (single stage)	N/A	290 L kg^{-1} VS	18,000 mg VS^{-1} L^{-1}
Scenedesmus sp. (two stage)	N/A	354 L kg^{-1} VS	18,000 mg VS^{-1} L^{-1}
Scenedesmus obliquus	N/A	287 L kg^{-1} VS	2000 mg TS^{-1} L^{-1}
Microcystis sp.	N/A	0.070–0.153 L	1500–6000 mg VS^{-1}
Nanochloropsis oculata	N/A	390 L kg^{-1} VS	N/A

concentrations of microalgae lead to the formation of ammonia when these compounds are broken down during the hydrolysis stage. The extraction of protein and lipid for further use in biochemical industries, or lipid extraction for biofuel production purposes can decrease the possibility of ammonia inhibition in the subsequent AD process (Spolaore et al. 2006). Protein and lipid extraction followed by AD can also help to achieve increased C/N ratios when considering microalgae for biogas production. Last but not least among the challenges discussed herein is the high nutrient requirement of microalgae for their mass production (Collet et al. 2011). This requirement, particularly for nitrogen and phosphorous, has been met by employing huge amounts of chemical fertilizers causing a serious competition with the agricultural sector (Fenton 2012; Stephenson et al. 2010; Ward et al. 2014).

11.6.2 Lignocellulosic Biomass for Biogas Production

Lignocellulosic biomass also holds a huge potential for being used as feedstock for biogas production due to their abundance, availability, and their high carbohydrate content. Although lignocellulosic materials generally cover two groups of feedstock, i.e., energy crops and lignocellulosic residues, this section only deals with the second generation biomass, i.e., wastes and agricultural residues such as straw and woody biomass. As presented in Table 11.4, energy crops also have a significant potential for biogas production but due to their competition with conventional crops production over water resources and land use, their application as feedstock for AD will not be discussed herein.

Lignocellulosic materials can be divided into four different groups, i.e., agricultural residues (straw), fruit and vegetable waste, woody residues, and paper waste. Although being appropriate for AD, the major disadvantage of lignocellulosic residuals is their high amount of lignin content, which can be regarded as a serious obstacle for AD process. In general, those lignocellulosic residues, containing a higher amount of volatile solids and a lower amount of refractory volatile solids, are more preferable for AD process (Monnet 2003).

Table 11.4 Methane yield of various energy crops (Deublein and Steinhauser 2011; Kabir et al. 2015)

Crop	Methane yield
Maize (whole crop)	205–405 (m^3 CH_4 kg^{-1} VS)
Potatoes	276–400 (m^3 CH_4 kg^{-1} VS)
Wheat (grain)	384–426 (m^3 CH_4 kg^{-1} VS)
Oats (grain)	283–492 (m^3 CH_4 kg^{-1} VS)
Triticale	337–555 (m^3 CH_4 kg^{-1} VS)
Sorghum	295–372 (m^3 CH_4 kg^{-1} VS)
Barley	353–658 (m^3 CH_4 kg^{-1} VS)
Red clover	300–350 (m^3 CH_4 kg^{-1} VS)
Alfalfa	340–500 (m^3 CH_4 kg^{-1} VS)
Sunflower	154–400 (m^3 CH_4 kg^{-1} VS)
Oilseed rape	240–340 (m^3 CH_4 kg^{-1} VS)
Peas	390 (m^3 CH_4 kg^{-1} VS)
Ryegrass	390–410 (m^3 CH_4 kg^{-1} VS)
Fodder beet	420–500 (m^3 CH_4 kg^{-1} VS)
Nettle	120–420 (m^3 CH_4 kg^{-1} VS)
Hemp	355–409 (m^3 CH_4 kg^{-1} VS)
Grass ensilage	0.6–0.7 (m^3 CH_4 kg^{-1} DM)
Leaves of sugar beet	0.4–0.8 (m^3 CH_4 kg^{-1} DM)
Sugar beet	0.4–1.0 (m^3 CH_4 kg^{-1} DM)
Clover	0.6–0.8 (m^3 CH_4 kg^{-1} DM)
Diverse kinds of cereals	0.4–0.9 (m^3 CH_4 kg^{-1} DM)
Barley ensilage	0.75–0.99 (m^3 CH_4 kg^{-1} DM)
Rye ensilage	0.57–0.79 (m^3 CH_4 kg^{-1} DM)

11.6.3 Wood Residues

It has been well established that biogas production from woody residues is not economically feasible due to factors affecting the efficiency of the AD process including low moisture content, high lignin content, cellulose crystallinity, and degree of association between lignin and carbohydrates (Kabir et al. 2015). Recent research studies have shown that coupling biomaterial with biomethane production form woody residues would result in better economic and environmental benefits (Khoshnevisan et al. 2016; Safari et al. 2017; Shafiei et al. 2011). Biogas production from woody residues necessitates a pretreatment step. A large number of pretreatment steps such as alkaline pretreatment, N-methylmorpholine-N-oxide, untreated, steam explosion, and fungal treatment have been identified and evaluated. Based on the substrate employed and the pretreatment method conducted, different methane production rates have been reported (Mirahmadi et al. 2010; Take et al. 2006; Teghammar et al. 2010).

11.6.4 Agricultural Residues

Agricultural residues are among lignocellulosic materials with significant potential for biogas and biomaterial production. The straw-based lignocellulosic residues of agricultural origin can undergo AD and produce huge amounts of biogas. As elaborated earlier, gas production rates reported in the literature varies depending on the kinds of cereals used in AD system. The main obstacle using straw-based lignocellulosic residues for biogas production is the pretreatment step (Rahimi et al. 2018; Khoshnevisan et al. 2017). However, extracting building block chemicals from straw-based lignocellulosic materials can compensate for the pretreatment step. Although a large number of studies have been conducted to evaluate different pretreatment methods, it is difficult to conclude which pretreatment method works best and produces the highest level of gas. This is due to the fact that most studies failed to address economic and environmental perspectives. Table 11.5 tabulates methane potential of various kinds of straw under different pretreatment methods.

11.6.5 Paper Wastes

Paper waste, a lignocellulosic material, has also been a focus for AD. Biological methane potential of paper waste hugely depends on the type of the paper, i.e., pulp and paper sludge, paper tube residues, etc. Moreover, the pretreatment method applied and the inoculum used could influence the specific methane yield. It has been well-established that the specific methane yield of untreated paper ranges between 100 and 200 L kg^{-1} VS (Wellinger et al. 2013). Pretreatment can significantly improve AD of paper waste leading to higher specific methane

Table 11.5 Methane potential of different kinds of straw (Odhner et al. 2012; Wellinger et al. 2013)

Type of straw	Pretreatment	Digestion type	AD temperature (°C)	Organic loading	Specific methane yield	AD time
Wheat	Untreated	Mesophilic			189 L kg^{-1} VS	
	Milled	Mesophilic	37.5	SI^1 ratio 1:3	275 L kg^{-1} VS	
	Steam explosion	Mesophilic	37.5	SI^1 ratio 1:3	331 L kg^{-1} VS	
	Physical pretreatment 30 × 50 mm	Mesophilic	37	89 g VS + 2 L water + 2 L slurry	162 L kg^{-1} VS	60
	Physical pretreatment 0.088 mm	Mesophilic	37	89 g VS + 2 L water + 2 L slurry	249 L kg^{-1} VS	60
Rice	Untreated	Mesophilic	35	400 ml swage + 1 g straw	54 L kg^{-1} straw	30
	Untreated	Psychrophilic	22	12.6 g VS L^{-1}	240 L kg^{-1} VS	120
	Untreated	Thermophilic	55	40 ml Inoc. + 0.2 substrate	30 NL kg^{-1} VS	45
	Untreated	Mesophilic	35	50 g solid L^{-1}	190 L kg^{-1} VS	24
	Acetic + propionic acids (1:1); solid acid ratio (1:20)	Mesophilic	35	400 ml swage + 1 g straw	213.5 L kg^{-1} straw	30
	Phosphate supplementation 155 mg-P L^{-1}	Psychrophilic	22	12.6 g VS L^{-1}	250 L kg^{-1} VS	120
	Grounded 25 mm	Mesophilic	35	50 g solid L^{-1}	200 L kg^{-1} VS	24
	Grounded 25 mm 110 °C + NH_3 20 mg g^{-1}	Mesophilic	35	50 g solid L^{-1}	245 L kg^{-1} VS	24
	NMMO	Thermophilic	55	40 ml Inoc. + 0.2 substrate	212 NL kg^{-1} VS	45
	Physical pretreatment 30 × 50 mm	Mesophilic	37	79.4 g VS + 2 L water + 2 L slurry	241 L kg^{-1} VS	60
	Physical pretreatment 0.088 mm	Mesophilic	37	79.4 g VS + 2 L water + 2 L slurry	365 L kg^{-1} VS	60

(continued)

Table 11.5 (continued)

Type of straw	Pretreatment	Digestion type	AD temperature (°C)	Organic loading	Specific methane yield	AD time
Corn	Untreated	Mesophilic	35	40.25 g VS L^{-1}	153.7 L kg^{-1} VS	30
	NaOH 8% Wt	Mesophilic	35	40.25 g VS L^{-1}	472 L kg^{-1} VS	30
	Ammonia 5% Wt	Mesophilic	35	40.25 g VS L^{-1}	243.5 L kg^{-1} VS	30
	Urea 4% Wt	Mesophilic	35	40.25 g VS L^{-1}	178 L kg^{-1} VS	30
	Pleurotus florida	Mesophilic	35	40.25 g VS L^{-1}	380 L kg^{-1} VS	30
	Pleurotus florida 300 g ground straw +225 g water 121 °C for 2 h	Mesophilic	35	40.25 g VS L^{-1}	404.8 L kg^{-1} VS	30

[a] Substrate Inoculum dry matter ratio

production. The untreated pulp and paper sludge under mesophilic condition reportedly produced 190 L CH_4 kg^{-1} VS, while in contrast, a pretreatment with 0.6% NaOH at 37 °C water bath for 6 h increased the specific methane production by 68.5% (Lin et al. 2009). Simultaneous pretreatment with steam explosion and sodium hydroxide has shown better results than sole sodium hydroxide when treating paper tube residues under thermophilic conditions. The specific methane yield resulted from pretreatment of paper tube residues with steam explosion and 2% NaOH at 220 °C was estimate at 403 L kg^{-1} VS. Adding 2% H_2O_2 to the mentioned pretreatment method increased the specific methane yield by 22%. Untreated paper tube residues and the one treated with 2% NaOH at 190 °C produced 222 and 269 L CH_4 kg^{-1} VS, respectively (Teghammar et al. 2010).

11.6.6 Industrial Waste

The high potential of industrial waste for biogas production cannot be ignored. Biofuel plants and biorefineries are among the distinctive industries where very large amounts of organic by-products are accumulated. These organic by-products are appropriate feedstock for the AD process. For example, the silage fractions remain after bio-ethanol production in grain-processing bio-ethanol plants can undergo the AD process (Cassidy et al. 2008; Drosg et al. 2008; Rosentrater et al. 2006). Moreover, it has been well established that, cane juice silage is anaerobically degradable, and so, it is a suitable substrate for AD (Cail and Barford 1985; Callander and Barford 1983; Russo et al. 1985). In biodiesel plants, the glycerol and the wastewaters generated along with the oil extraction residual cake can also undergo the AD process (Wellinger et al. 2013). Nevertheless, the limitations regarding AD of industrial organic wastes should be neglected. More specifically, these feedstock can potentially contain a huge amount of undesirable compounds such as biological, physical or even chemical pollutants. Physical impurities, pathogens, heavy metals and/or persistent organic compounds found in industrial organic wastes can neutralize the environmental benefits of AD and pose health risks to humans and animals. This problem is more critical when the produced digestate is used as fertilizer (Wellinger et al. 2013).

11.7 Summary and Concluding Remarks

Providing energy and materials through biorefineries has attracted an increasing deal of interest and this popularity is mainly attributed to the positive sustainability impacts of biorefineries. In better words, biorefineries are meant to treat biomass feedstock and deliver a spectrum of products with positive effects while displacing their fossil-fuel originated counterparts. This approach makes biorefineries capable of competing with today's petroleum refineries. While the development of biorefineries for supplying bioenergy and biomaterials for coming decades seems promising and the current examples of biorefineries can be found all around the world, there is still a long way to go before biorefineries can be considered as comprehensive alternative to petroleum refineries.

To satisfy the future demands for bioenergy and biochemical, a substantial amount of biomass from agriculture, forestry, and waste need to be dedicated to biorefineries. From the sustainability point of views, the allocation of the available biomass resources to different types of biorefineries should be judiciously managed. Otherwise, it can possess negative ecological impacts, socio-economic consequences, and other environmental burdens. Although a wide range of biomass feedstock can undergo biorefining process, the selection of feedstock, processing pathways and final products should be done wisely by following a systematic approach. For instance, if the biorefineries are meant to supply future block building chemicals, the top twelve final candidates already identified through an iterative process based on the petrochemical model using building blocks, chemical data, known market data, properties, performance of the potential candidates, and the prior industry experiences, should be considered.

Multi-criteria assessment can also be employed to determine the overall sustainability of biorefineries due to the fact that it can simultaneously combine the physical, ecological, environmental, and socio-economic considerations. For instance, when facing a dilemma between two alternatives, e.g., lignocellulosic versus macroalgae biorefineries for producing specific types of biomaterials and bioenergies, the question to be answered would be which feedstock could better satisfy mass and energy balance, economic balance, employment opportunities, environmental issues, and technical possibilities. The economic aspects of biorefineries are also important because it is often difficult to get positive economy balance, as the production cost of biomass-based fuels is often high. The competition between food production sector versus raw materials supply for biorefineries over land and even other limited resources such as water must also be taken into account as a serious limitation in developing future biorefineries. Direct and indirect LUC effects should also incorporated into any final decisions.

Finally, the review of already published studies well shows that the integration of AD units with various biorefinery platforms or even currently-existing biofuel plants holds a huge potential to produce a positive economic, as well as energy and mass balance, with lower environmental intensity.

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