

Chapter 2

Perspective of Biofuels from Wastes

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Abstract In the world today, with an everyday increase in global population, transitioning the society to a more sustainable atmosphere would be the only solution for guaranteeing a long-lasting life in this planet. Despite the fact that the earth is armed with various natural resources, it should be accepted that they would not last forever. By converting useless wastes and residues to a new source for supplying energy rather than wasting the existed energy for their disposal, not only the concerns for the depletion of fossil fuels would be reduced but also the environment dares to breathe. Concerning this issue, the present chapter has tried to depict a clearer perspective for waste-based biofuels which are known as second-generation ones. The discussed products in this chapter are biodiesel, bioethanol, biobutanol, biogas, and biohydrogen. The focus is mostly on new researches which have introduced new waste as feedstock and their usage feasibility, though production processes and challenges ahead are included as well.

2.1 Introduction

Today, the population growth and the need for energy together with the fossil fuel depletion and environmental pollutions have urged countries to seek for more newer and cleaner sources of energy (Balat and Balat 2009). Around 60 % of world's oil consumption and one-fifth of global CO₂ emissions are related to transportation sector (Kirtay 2011). Hence, replacing fossil fuels by renewable

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energy sources, specifically in developing countries where the rate of energy consumption is faster than industrial ones, is a must (Balat and Balat 2009).

In 2012, the global petroleum consumption was estimated as 89 million barrels per day from which about a half was used for gasoline production. At this rate of consumption, the oil resources are predicted to run out within the next 50 years (Arifin et al. 2014). Furthermore, fossil fuel usage can cause environmental problems such as air pollution, greenhouse gas emissions, and global warming, consequently, which makes the society worried. Thus, many countries are trying to find renewable resources as alternatives which are capable of balancing the GHG emissions. Biofuels seem a key solution for the present challenge since it is produced from renewable resources and have a great influence on GHG mitigation as 23 % of CO₂ emissions are related to transportation sector (Fiorese et al. 2013). Biofuels can be categorized into three main groups, first-, second-, and third-generation biofuels which can be obtained from food, non-food feedstocks, and microalgae, respectively. The biomass potential for supplying energy has been estimated as 10²⁰ J/year of which 40 % is being utilized nowadays (Ragauskas et al. 2006).

First-generation biofuels, the most common type, are mainly produced from agricultural crops such as corn, sugarcane, sugar beet, wheat, rapeseed, soybean oil, sunflower, and palm oil, having a good access to a highly mature technology in converting crops to biofuels. In Europe, it was first emerged as a result of agricultural stagnation in 1990–1994, encouraged farmers to grow crops for non-food purposes, thanks to tax exemptions supported by governments. In the Netherlands for instance, two public transport companies invested on bioethanol and biodiesel production for bus consumptions. In 1995, environmental issues and biomass energy gained an importance leading to the investments of two boating companies on biodiesel followed by the 10-year tax exemptions' demand for the Nedalco with the aim of producing 30 L bioethanol from agriculture crops. In 1998, Kyoto treaty was signed, and the climate issues became more and more important. On the one hand, different investigations revealed that it is worthy to develop the projects in which CO₂ emissions are reduced up to more than 80 %. On the other hand, as a result of the growing world population, by 2050, the agriculture will need to provide food for 9 billion people, an enormous challenge from an agronomic perspective (Jeihanipour 2011). The consideration of using crops for food or for biofuel may be referred to as the “food versus energy” conflict (Suurs and Hekkert 2009). Furthermore, recent studies disclosed that an increase in the production of biofuels from food resources might cause a substantial “carbon debt,” since the reduction of GHG emission by replacing fossil fuels is less than the CO₂ released from direct or indirect changes in land use (Williams et al. 2009). Therefore, decision makers are trying to devise more research on second- and third-generation biofuels (advanced biofuels) which can be obtained from non-food crops, wastes, and algae. Unlike the former one and without considering dedicated crops, these new feedstocks do not require extra land and water, as they are mainly consisted of residues of agriculture (straw, stover, husks and cobs, marcs and lees, bagasse, empty fruit bunches, and nutshells) and forestry (treetops, branches, stumps, leaves,

sawdust, cutter shaving, scrap wood, and wood pulp). Even the aquaculture fishery (algae, fish scales, viscera, and scrap) residues, sewage sludge, and industrial and municipal wastes are classified in this category. Furthermore, it is believed that GHG emissions caused by second-generation biofuels are much lesser than the former ones. As an example, in comparison with fossil fuels, the cellulosic ethanol can reduce CO₂ emission up to 75 %, whereas the sugarcane/cassava-based ethanol decreases it by 60 %. Similarly, thermochemical-based biodiesel obtained from wastes can reduce carbon release by 90 % compared to the 75 % reduction offered by usual biodiesel (Patumsawad 2011). However, the conversion processes of such biomass are much more complicated and costlier in comparison to first-generation ones (Fiorese et al. 2013). As a matter of fact, the worldwide production of advanced biofuels is less than 1 billion gallon per year at present (Yue et al. 2013).

There are two major methods of bio/thermopath for converting biomass to second-generation biofuels (Fig. 2.1). In thermopath, the biomass gets heated, and depending on the temperature range, finally three different products are obtained. Torrefaction (250–350 °C/anaerobic), pyrolysis (550–750 °C/anaerobic), and gasification (750–1,200 °C/limited oxygen) are different processes, applied in this path leading to the production of solid (biochar), liquid (bio-oil), and gaseous (syngas)

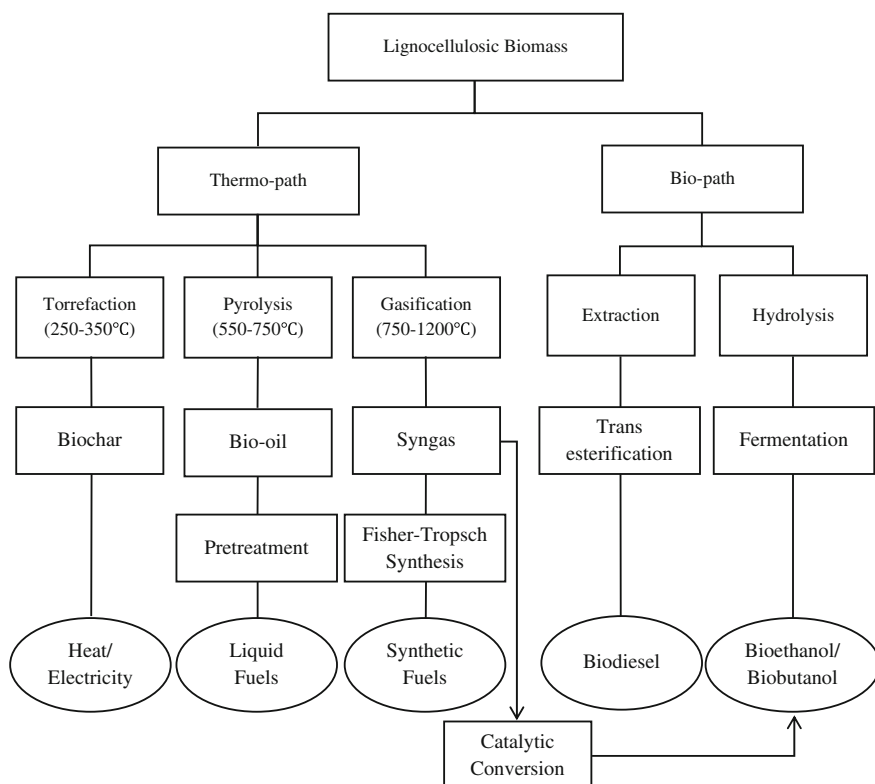


Fig. 2.1 Conversion processes of second-generation biofuels

products. However, within syngas production, a few amounts of biochar and bio-oil are formed as well. Furthermore, thermal processes are exothermic; thus, they can supply their own energy requirement for such high temperatures. Moreover, bio-oil and syngas are more appropriate to be used as a fuel than biochar since they have fluid's characteristics; however, they need some pretreatments before being able to be used in vehicles. In all thermopath processes, the price of biomass is a key factor. Therefore, when agricultural residues or municipal wastes are used instead of dedicated crops, the process would become more cost-effective (Lee and Lavoie 2013). In contrast, biopaths entirely lead to the formation of liquid and gaseous biofuels through fermentation and anaerobic digestion processes.

It is predicted that lignocellulose-based biomass can produce ethanol up to 442 billion L/year, though there is still no large-scale plant for this purpose (Festel et al. 2014). These biomasses are usually comprised of cellulose (crystalline polymers made of glucose), hemicellulose (amorphous polymers of several pentoses and hexoses), and lignin (a complex and large polyaromatic compound). With the aid of pretreatments such as steam explosion and ammonia treatment, hemicelluloses and lignin can be separated from the cellulose and further enzymatic or acidic hydrolysis would lead to glucose separation as well (Taherzadeh and Karimi 2008). Different types and details of leading pretreatment processes are presented in Chap. 3. The glucose is then converted to ethanol via fermentation, and finally, ethanol is separated by distillation. Lignin has the potential to be used as a solid fuel or an H₂ source in biorefineries. However, its aromatic monomer consisted of valuable chemical compounds that can be separated for plastic or adhesive production industries. This issue would open a new market for second-generation bioplastics and bioadhesive manufacturing based on biomass (Lee and Lavoie 2013).

From another aspect, second-generation biofuels will not only overcome the first-generation problems but also could moderate the waste management hardships (Zah 2010). In 2012, the global urban population was estimated as 3 billion, which is predicted to increase to 4.3 billion by 2025. The municipal solid waste production rate of this population was 1.3 billion ton/year, which is estimated to increase to 2.2 billion ton/year by 2025 (Hoorweg and Bhada-Tata 2012). According to Kelessidis and Stasinakis (2012) the annual production of sewage sludge in EU-12 in 2005 was estimated as 1.1 million ton dry solid which is predicted to exceed 13 million ton dry solid by 2020. Currently, the most commonplace methods for disposing solid wastes in many countries are incineration and landfilling which are faced with barriers such as air pollution, ash disposal, land availability, and financial issues. However, by separating the organic fractions of the municipal solid wastes or using other sources of wastes, e.g., agriculture, forestry, and sewage sludge, these barriers would be eliminated, and in addition, it would be considered as a new source for energy and value-added products.

The aim of this chapter is to introduce the biofuels having the potential of being produced from different types of wastes as well as discussing the available processes and probable challenges ahead.

2.2 Which Waste? Which Biofuels?

Wastes, residues, and co-products are new and widely available alternatives for biofuel production, while municipal solid wastes, used cooking oil, industrial wastes, and sewage sludge are examples of wastes that can be used for second-generation biofuel production. These new sources can be used for the production of biofuels such as biodiesel, bioethanol, biobutanol, biogas, biohydrogen, and a number of biochemicals such as citric acid, xanthan, lactic acid, and acetic acid. Here is a brief introduction to some of the important ones.

2.2.1 Wastes to Biodiesel

Biodiesel, shortly introduced in Chap. 1, is a renewable alternative for the fossil fuel diesel having the potential to reduce the emission of toxic gases such as carbon monoxide (Mandolesi de Araújo et al. 2013). It can be obtained via transesterification of oils in which glycerides are converted into esters resulting in viscosity drop, better combustion, and less emission in engines (Canakci 2007). The main challenges of biodiesel production are the high cost of vegetable oils constituting 70 % of the total costs (Haas and Foglia 2005). In August 2012, the price of soybean oil, palm oil, and canola oil, which are the main sources of biodiesel in the present market, was US\$ 1,230/ton, 931/ton, and 1,180/ton, respectively. Based on the price of canola oil, each ton of oil is capable of producing 1,000–1,200 L biodiesel with the market price of US\$ 0.85/L; nevertheless, the methanol price should also be considered (US\$ 0.35/L) since about 125–150 L of methanol is required per ton of oil (Lee and Lavoie 2013). Therefore, it is essential to find cheaper oil sources to make the biodiesel production more profitable. These oils can be supplied from different wastes and residues, e.g., used cooking oil, oils and fats extracted from animal tallow, sewage sludge, crude or waste fish oil, fish canning industry, leather, winery and agro-industrial wastes, restaurant waste lipids, olive pomace oil, sorghum bagasse, and meat industry residues, directly or indirectly. Indirect use of wastes for biodiesel production is referred to those in which the oleaginous microorganisms are cultivated on municipal, industrial, or agricultural wastes to store lipids. Then, the lipids can be extracted and applied for biodiesel production as well.

There are usually three main steps for biodiesel production from waste oils including pretreatment, transesterification, and separation processes. However, depending on the type of waste, lipid extraction should be considered as well. About 13 % of Brazil annual biodiesel requirements can be supplied from used cooking oil. This type of oil usually needs some pretreatments to reduce the viscosity and the content of water and free fatty acids (FFAs) which can influence transesterification process negatively (Mandolesi de Araújo et al. 2013). Even by carrying out a pretreatment on used oil, it is still more economical and can reduce the direct production costs up to 45 % in comparison with pure oils (Zhang et al. 2003). In fish canning

and processing industry, there is also a possibility of biodiesel production from oily fishes such as codfish, salmon, mackerel, and tuna. The annual production rate for fish oil is about 150 ton of which more than 50 ton would be disposed as sewage (Costa et al. 2013). In 2005, the estimated world fish production was 142 Mt which increased to 144 Mt in 2008. About 25 % of this amount can be considered as a waste, and its oil content has the potential of biodiesel production (Yahyaee et al. 2013). Waste chicken fat has also been used as a feedstock for biodiesel production. In 2006, 10.5 million chickens were produced in China from which 115,500 ton fat was recoverable. However, it should meet the pretreatment requirements as well (Shi et al. 2013). Chakraborty and Sahu (2014) used waste goat tallow as an oil supplement for biodiesel production using a novel method for transesterification. Using infrared radiation method, they could not only enhance the product yield due to an increase in heat and mass transfer but also reduced the reaction time significantly which is considered as a challenging task if the catalytic methods are used. Furthermore, in different countries, some industries are more developed, of which the residual and wastes can be utilized for biodiesel production. For instance, in countries where the leather industry is developed, there is a possibility to use fleshing oil wastes as a raw material for biodiesel production (Alptekin et al. 2012). Spain, France, and Italy are large producers of wine, and the oils exist in grape wastes can be converted to biodiesel. The global estimation of annual grape's production in 2005 was 67 million ton of which more than 20 % is regarded as waste. By extracting the oil that exists in waste grape's seed (10–20 %), biodiesel production would be feasible. However, it should be pretreated as most of the wastes (Fernández et al. 2010). Besides, in Mediterranean countries, such as Greece where the annual production of olive pomace oil is about 40,000 ton, there is a possibility to convert this oil to biodiesel after performing a pretreatment on it (Che et al. 2012). Meat industry has also been evaluated for biodiesel production. Since 49 % of cattle, 44 % of pig, and 37 % of fowl weight are not consumable by human, the yellow fat obtained from these sorts of wastes, estimated as 1.38 kt/year, would lead to a biodiesel yield of 95 %. This means that it is possible to produce 1.3 kt/year biodiesel from such fats, providing 51.2 GJ/year energy. It is estimated that the obtained biodiesel blending with fossil fuel diesel (2 % biodiesel and 98 % fossil fuel diesel) would cover 25 % of the fuel consumption of the passenger vehicles and trucks registered in 2007 in Baja California, Mexico (Toscano et al. 2011). Besides, some of the industrial and agro-industrial wastes and residuals have the potential to be used as a carbon source or an organic supplement for oleaginous microorganisms which are capable of lipid production. It is estimated that for producing 10,000 ton microbial oil from glucose, the unitary cost is about US\$ 3.4/kg. Crude glycerol is a by-product of biodiesel production and is used in producing alcoholic beverages as well as saponification of oils and fats. However, it is contaminated to chemical catalysts and cannot be used in pharmaceutical, toothpastes, or cosmetic purposes since the purification costs are significantly high and the process is considered as energy-consuming one. Therefore, it is more economical to use it as a carbon source for lipid production. Lignocellulose materials obtained from agriculture residues are expected to be consumed as carbon supplement by lipid-producing microorganisms after pretreatment and conversion to

simple sugars as well. However, the strains resistance to inhibitors, formed after pretreatments, should be considered (Leiva-Candia et al. 2014).

Apart from all waste types, municipal and industrial wastewater sludge has also the potential to be used for biodiesel production. In 2010, each gallon of biodiesel produced from primary and secondary sludge was estimated to cost 3.11 and 3.23 US\$, respectively (Siddiquee and Rohani 2011). Lipids present in sewage sludge contain triglycerides, diglycerides, monoglycerides, phospholipids, and FFAs which are usually absorbed directly to sludge or are consisted of microorganism's cell membranes made of phospholipids (Kargbo 2010). These lipids can be extracted from sludge through boiling solvent, supercritical CO₂, and solo or a mixture of solvent extraction methods. However, lipid extraction from raw sludge is not economically feasible since it needs a large amount of organic solvent and bulky tanks equipped with mixers and heating systems. Since the dewatered sludge is very sticky and can hinder the extraction process, dry sludge has been widely used for lipid extraction (Siddiquee and Rohani 2011). It has been reported that all types of sludge, i.e., primary, secondary, blended, and digested sludge, are capable of being used as a biodiesel production source; however, primary sludge has shown the maximum biodiesel yield (Olkiewicz et al. 2012). By integrating lipid extraction and transesterification process in half of the US wastewater treatment plants, 0.5 % of its annual petroleum diesel would be supplied (about 1.8 billion gallon). Besides extracting lipids from sewage sludge, there is the possibility of microalgae cultivation in wastewater treatment plants to store the lipid and produce biodiesel after the harvesting and lipid extraction step. Microalgae, like other types of microorganisms, are phototrophic or heterotrophic and can supply their energy and carbon requirements from sunlight and CO₂ or by metabolizing organic carbons, respectively. Since they can grow fast and yield high amounts of lipid at controlled conditions, they can be used in large-scale biodiesel production processes. However, the energy balance and greenhouse gas emissions (GHG) would seem rather challenging. The cultivation can be performed on industrial wastewaters, e.g., starch industry wastewater. In producing biodiesel using starch industry and cellulose industry wastewater, by applying heterotrophic microalgae, the energy gain is 27.2 and 11.8 GJ for production of 1 ton biodiesel, respectively (Zhang et al. 2013).

Pretreatment is the first step in biodiesel production from waste oils in order to remove the impurities and solid particles or decrease the water content and acidity value (Costa et al. 2013; Mandolesi de Araújo et al. 2013). The required pretreatments in most cases are filtration and heating; however, pretreatments such as steam injection, neutralization, vacuum evaporation, and vacuum filtration have been applied as well (Kulkarni and Dalai 2006).

In the second step, transesterification reaction should be performed in which glycerides are converted into esters in the presence of a catalyst and an alcohol. However, in this step, using non-catalytic conversion techniques are also possible. In fact, each mole of lipid reacts with 3 mol alcohol and produces 3 mol alkyl esters (biodiesel) and 1 mol glycerol (Zhang et al. 2013).

Methanol is the most common type of alcohol used for performing the esterification reaction, as it is the least expensive industrial alcohol. In comparison with ethanol, it has a lower price, higher reactivity, simpler recoverability, preventing soap property, and azeotrope formation tendency (Siddiquee and Rohani 2011). Catalysts can deprotonate the alcohol in order to make it more nucleophile while reacting with lipid (Kargbo 2010). They are categorized as alkaline, acidic, and enzymatic types. Alkaline catalysis is the most common catalysts which is fast (less than 1 h) but extremely sensitive to the presence of water and FFAs. Water can change the saponification process of ester into alkaline conditions, and FFAs may react with the catalyst leading to the formation of water and soap or emulsions that influence the removal of biodiesel negatively (Mandolesi de Araújo et al. 2013; Canakci 2007). To overcome this problem, acidic esterification and heating can be applied on waste oils prior to transesterification process. El-Mashad et al. (2008) used H_2SO_4 1 wt% to reduce the acidity of the salmon oil to the standard range of alkaline catalysts (the maximum concentration of 2 mg KOH g^{-1}) followed by heating at $52 \text{ }^\circ\text{C}$ for 1 h within stirring condition of 600 rpm. The molar ratio used for methanol:oil was selected as 6:1. Alptekin et al. (2012) used animal fat obtained from leather industry fleshing wastes for biodiesel production and achieved ester yield of 92.6 % using KOH 1 wt% and a methanol molar ratio of 7.5:1 at optimum conditions. However, they had to pretreat the oil by heating it up to $110 \text{ }^\circ\text{C}$ to remove the water followed by a filtration to remove the suspended solids. NaOH has also been used for production of biodiesel from used coconut oil as an alkaline catalyst, leading to the transesterification performance of 94.5 % at the optimum catalyst concentration of 0.08 % and heating temperature of $60 \text{ }^\circ\text{C}$ for 20 min (Chhetri et al. 2008). Costa et al. (2013) produced biodiesel using the oil extracted from Portuguese fish canning industry. In order to dehydrate and esterify the oil, they heated the oil up to $100 \text{ }^\circ\text{C}$ and added it into a round-bottomed vessel and immersed it in a temperature-adjustable water bath equipped with a water-cooled condenser ($4 \text{ }^\circ\text{C}$) and was mixed at 900 rpm. Then, the catalyst (1, 2, and 3 wt% H_2SO_4) and methanol (with molar ratio of 6:1) were added to the oil. The reaction temperature kept constant at $65 \text{ }^\circ\text{C}$ for 1 h. The maximum and minimum transesterification yield was obtained as 73.9 and 66.4 wt% with methanolic solution of 60 and 90 vol.% and catalyst concentration of 1 and 3 wt%, respectively. The results showed that catalyst concentration can negatively influence the biodiesel yield as a result of purification of lipid phase during the washing process leading to emulsion formation and loss of the product. Yahyae et al. (2013) produced 0.91 L biodiesel out of 1 L oil extracted from fish processing waste using 1 wt% KOH and a methanol:oil ratio of 1:4 at $60 \text{ }^\circ\text{C}$ and 300 rpm for 2 h. Shi et al. (2013) used the integrated catalytic composite membrane (CCMs) process and sodium methoxide as a novel approach to produce biodiesel from waste chicken fat. Heterogeneous solid catalysts, i.e., sodium methoxide, SrO, MgO, and CaO, have been used for transesterification of animal oils since they are recyclable and more efficient in the presence of FFAs and water. They esterified the oil with CCM and methanol first, to reduce the acidity value of chicken fat, and the initial value was 39.52 KOH/g fat. However, the more CCM layers resulted in more reduction in acidity of esterified

product since more active sites were involved during the reaction between methanol and chicken oil. The membrane porosity and the methanol:oil ratio used were 68 % and 3:1, respectively, with a reaction temperature of 338 K. Sodium methoxide was used as the alkaline catalyst at 1 wt%, and the transesterification yield of 98.1 % was achieved (Shi et al. 2013). The biodiesel produced from waste winery grape's seed had a yield of 97.8 wt% after pretreating the extracted oil through acid conditioning and deacidification. The first step was performed by heating the oil at 60 °C and adding phosphoric acid and water with molar ratio of 0.05 and 1:6, respectively, mixing for 30 min. This was done in order to convert non-hydrated phospholipids to the hydrated form since H_3PO_4 is able to break down the metal/phospholipid complexes. Then, after separating the phases with centrifugation at 6,000 rpm and 20 °C for 20 min, the oil was mixed with NaOH and water (molar ratio of 0.2 and 6, respectively), and the temperature was held at 60 °C for 15 min until the formation of emulsion. Then, the formed soap and residual water were separated by centrifugation and vacuum evaporation. The maximum oil extraction yield from grape's seed (17.5 %) was achieved via soxhelt extraction and hexane:acetone ratio of 1:1 as the extracting solvents at 60 °C with the oxidation stability of 16.3 h (Fernández et al. 2010).

Che et al. (2012) could reduce the acid content of olive pomace oil to 1.38 % from the initial value of 22.11 % by acid esterification for 60 min, choosing catalyst:oil and methanol:oil ratios of 1 % and 0.45 v/v, respectively. However, the acidity obtained after pretreatment was still out of the standard range (1 %). They concluded that the most feasible and economical way to reduce the acidity would be achieved after using extra amount of alkaline catalyst during the esterification; however, an increase in methanol:oil ratio or reaction time and temperature, even performing an additional pretreatment step, can improve the acid value reduction up to some extent.

Cheirsilp and Louhasakul (2013) studied the cultivation possibility of four types of *Yarrowia lipolytica* on four different industrial wastes such as palm oil mill, serum latex obtained from rubber latex industry, crude glycerol of biodiesel-producing plant, and molasses that comes from sugarcane processes. They concluded that the first two wastes can be used as a cultivation media and the two others are more feasible as an additional carbon source for lipid production. In fact, in 4 % concentration of glycerol added to palm oil, the maximum lipid was produced. They also found out that direct transesterification of wet microbial cells is the most economical and easiest way to achieve biodiesel with a yield of 72 % in 1 h and methanol to oil ratio of 209:1 in comparison with direct transesterification of dried cells or transesterification of extracted lipids from dried cells, since the latter are more expensive and energy consuming.

Sorghum bagasse hydrolysates have been utilized for producing microbial lipids by Liang et al. (2012). They could achieve the lipid yield of 8.74 g per 100 g bagasse after pretreating with lime and enzyme. The lime pretreatment step was suitable for removing the lignin and hemicellulose, whereas the enzymatic procedure could degrade xylane and glucan.

Olkiewicz et al. (2012) evaluated different sludge types (primary, secondary, blended, and digested) for biodiesel production and obtained the highest yield (13.9 %) from primary sludge based on dry weight, since it mainly consisted of floated grease, while secondary sludge is composed of microbial cells obtained during biological treatment of wastewater (Kargbo 2010). In addition, digested sludge produced in an anaerobic digester showed the least biodiesel yield as a result of organic matter mineralization during the anaerobic digestion process. Furthermore, Angerbauer et al. (2008) could successfully store lipid by *Lipomyces starkei* up to 0.4 and 1.2 g/L on raw and ultrasonicated sludge. However, they did not report any biodiesel production yield in their study. In order to extract lipid from sludge, Boocock et al. (1993) used soxhlet and boiling solvent extraction method (chloroform and toluene) and extracted 12 and 17–18 % lipid from 50 to 100 g dry sludge, respectively. They concluded that both solvents are efficient, but toluene is more environmental compatible and economical. Dufreche et al. (2007) also reported a lipid yield of 27.0, 3.5, and 13.7 % for extraction methods of solo or three-solvent mixture (60 % hexane, 20 % methanol, and 20 % acetone), supercritical CO₂, and the combination of methanol and supercritical CO₂, respectively. Li et al. (2011) investigated nutrient removal and biodiesel production from microalgae *Chlorella* sp. cultivated on highly concentrated municipal wastewater and obtained the removal efficiency of 93.9, 89.1, 80.9, and 90.8 % for ammonia, total nitrogen, total phosphorous, and COD, respectively, as well as biodiesel yield of 11.04 % of dry biomass.

Unlike the alkaline catalysts, acidic ones are not sensitive to the presence of water nor FFAs but can esterify them about 4,000 times slower and require higher oil:alcohol ratio (Canakci 2007; Siddiquee and Rohani 2011). Thus, they can be used for the oils with acidity more than 1 % (Freedman et al. 1984).

Enzymatic catalysts in which lipase is the most common type are recovered easily, and unlike the former ones, they do not lead to the by-product formation and are not sensitive to water and FFA content as well (Mandolesi de Araújo et al. 2013). However, low reaction rate, high price, and product contamination by enzymatic activity make its usage challenging (Siddiquee and Rohani 2011). Recently, the application of lipase to catalyze palm oil sludge is investigated as a green technology for biodiesel production. By using enzymes, not only the need for multistep catalyst's removing processes would be eliminated but also a wider range of lipids such as FFAs, monoacylglycerides, diacylglycerides, and triacylglycerides are converted to biodiesel. However, the selection of proper solvent is of crucial importance since polar solvents like methanol can reduce the enzyme activity by removing the water molecule from the surface of enzymes. Thus, ethanol that does not have such effect and has the potential for being produced from other wastes can be used instead. The FFA conversion and biodiesel yield obtained in optimal condition in this method are 21.7 and 54.4 % w/w, respectively (Nasaruddin et al. 2014).

In non-catalytic approaches, it is possible to use a solvent which is miscible in both methanol and oil instead of using the catalyst. The reaction occurs fast without any catalytic residue remaining, or by applying the BIOX, a patented production process, FFAs and triglycerides are converted into esters through a two-step process

in less than 90 min, resulting in more than 90 % conversion in a case that the feedstock contains more than 10 % acidity (Mandolesi de Araújo et al. 2013). So far, microwave radiation, static mixers, microchannel, cavitation method, and infrared radiation have been investigated as well. For instance, Chakraborty and Sahu (2014) using an infrared radiation assisted reactor, obtained 96.7 wt% FFA conversion and 98.5 wt% biodiesel yield from waste goat tallow in 2.5 h, at optimal conditions.

As the third and last step, the produced biodiesel should be separated and purified which can be regarded hard if the feedstock is supplied from wastes. In this case, the alcohol (methanol) would be separated via distillation and the catalyst and the glycerol are aimed to be washed away by hot water (50 °C). After washing the mixture by hot water, two phases form. The biodiesel form the top phase, with a water content of 1 g per liter of biodiesel, which will be separated by distillation later on. The bottom phase would be glycerol, catalyst, and water. The catalyst would be separated in a neutralizing reactor, and the glycerol then would be dried via distillation (El-Mashad et al. 2008; Lin and Li 2009; Fan et al. 2010; Zhang et al. 2013).

2.2.2 Wastes to Bioethanol

Bioethanol is currently the most common biofuel in terms of produced volume which is industrially produced mainly from corn and sugarcane. For decades, it was used as a source of energy in a lamp oil, for cooking, or known as spirit oil before being applied in an internal motor combustion by Samuel Morey early in the nineteenth century. Later on, it was introduced to the automobile market and in agricultural machines. However, emergence of oil and its derivatives in twentieth century drove it aside until the Arab oil embargo of 1970s (Lee and Lavoie 2013). Today, the depletion of fossil fuels and its environmental drawbacks have enforced the policy makers to focus on renewable sources of energy. Hence, many countries enacted several directions for enhancing the share of biofuels in their energy basket (Zah 2010).

The annual production of ethanol increased to more than 85.6 billion liter in 2010 worldwide (Carriquiry et al. 2011) since it has some advantages over other fuel additives. Its high octane number and flexibility in blending with petrol have made it a well-suited additive in automobile's engines without almost any modification requirement. By blending ethanol with petrol, not only the emissions of GHGs, unburned hydrocarbons, and carcinogens would be reduced but also the sulfur oxides which are the main cause of acid rains will be decreased significantly (Nigam and Singh 2011). These features can make the ethanol as the best environmental-friendly candidate in transportation sector. There are three main sources of biomass that can be used as a feedstock for bioethanol production: sucrose-based sources (sugarcane, sugar beet, and sweet sorghum), starchy biomass (wheat, corn, and barley), and lignocellulose materials (wood, straw, and grass) (Soccol et al. 2010). Although the first two (first generations) benefit a highly simple and mature

technology in converting the sugars to ethanol, they suffer the controversy of food versus energy as well. For instance, the price of raw sugar in August 2012 was US\$ 0.2/pound, while the ethanol price was US\$ 0.68/L. This meant that production of 1 L ethanol from raw sugar would account for US\$ 0.3–0.35 and it is more beneficial for market to produce sugar rather than ethanol. The story goes the same for the corn and other food-based ethanol sources (Lee and Lavoie 2013). Thus, lignocellulose-based material can be a better replacement for them. However, more complex processes are required to convert them to ethanol.

In most countries, there is a good potential for bioethanol production from various wastes and residues including forestry and agricultural residues (forest woody feedstocks, corn stovers, cornstalks, rapeseed residue, sugarcane bagasse, citrus peels, empty bunches of fruits, straws, etc.), water hyacinth and seaweeds as well as industrial or municipal solid wastes (waste papers, newspapers, money bills, household food and kitchen wastes, coffee residue, waste textiles, etc.). In Iran for instance, the bioenergy potential from agricultural, animal, and municipal wastes has been estimated as 8.78×10^6 , 7.7×10^6 , and 3×10^6 t, respectively, while a potential of annual ethanol production of 4.91 GL from agricultural residues was reported before (Avami 2013). About 600–900 million ton rice straw is produced annually in the world of which 205 billion liter ethanol might be possible to be produced (Sarkar et al. 2012). This means that most of the Asian countries can benefit this sort of biomass. Around 20 % of sweet potato grown worldwide remains as waste on fields. It is stated that sweet potato can yield higher concentration of ethanol, nearly 114 %, than corn (Dewan et al. 2013). In India, growing bamboos is well established, and annually, 32 million ton of this herb is cultivated. Since bamboo contains a very small amount of lignin and a large share of cellulose, its residues, which are estimated as 5.4 million ton, can be utilized for bioethanol production. It has been reported that the surplus amount of bamboo residues, i.e., 3.3 million ton, have the potential to produce 473 million liter ethanol (Kuttiraja et al. 2013). An herbal plant, called *Coleus forskohlii Briq*, is cultivated for its root in large scale in India due to its medical advantages. In 2011, 100 tons of this herb was produced in an area as wide as 100 ha. The remained biomass after the extraction of *forskolin* still consisted of 90 % carbohydrate and can be used for ethanol production (Harde et al. 2014). In the USA, each year 10 million dollars is spent on disposal of apple pomace. However, it is more economical to reutilize it as a feedstock for ethanol production. In fact, most of the food wastes have the same potential to be utilized in ethanol industry rather than being composted or consumed for animal feed in which the market does not seem interested (Van Dyk et al. 2013). Similarly, in Mediterranean countries, olive cake, usually called olive mill solid waste (OMSW), formed after oil extraction can be applied as a promising source of ethanol production. The global production of this waste is reported as 4×10^8 kg dry weight. Besides, it can yield 3 g ethanol/100 g dry OMSW (Abu Tayeh et al. 2014). Gaining a giant industry in instant noodle production, Korea produced more than 2,106 ton instant noodle residue in 2011. By treating this residue through boiling, washing by hexane and then filtration, a solid and a liquid phase was produced which can be used for ethanol and biodiesel production, respectively

(Yang et al. 2014). In addition to this, Korea has the potential to profit a 40,000 ton log waste remained after being used for mushroom cultivation annually (Kim et al. 2010). Palm oil provides a wide industry in different continents such as Asia, Africa, and Latin America. The empty fruit bunches left after oil extraction are capable of being used for ethanol production (Chiesa and Gnansounou 2014).

The main steps of producing bioethanol from lignocelluloses include pretreatment, saccharification or enzymatic hydrolysis, fermentation, and distillation. However, for developing these steps, it is of crucial importance to learn about the nature and structure of the feedstocks first (Taherzadeh and Jeihanipour 2012). Lignocellulosic biomass consisted of three main components including cellulose (30–50 %), hemicellulose (15–35 %), and lignin (10–30 %). Cellulose is a crystalline polymer, made of long-chained glucose units that should be broken down to its monomers to become consumable by microorganisms for ethanol production. In contrast, hemicellulose is comprised of five-carbon sugars. Despite the fact that hemicelluloses can easily be degraded to their building blocks, i.e., xylose and pentose, their fermentation is complicated since most strains are naturally able to ferment only six-carbon sugars to ethanol. The lignin part of lignocellulosic biomass is made of non-fermentable phenolic compounds which can be recovered and applied as a solid fuel for electricity and heat supplement in ethanol or butanol production plants (Nigam and Singh 2011). Therefore, in order to convert lignocelluloses to fuel ethanol more efficiently, applying an effective pretreatment is in priority since it can break the recalcitrant structure of lignocellulose (Limayem and Ricke 2012). However, it should be noticed that while the pretreatments enhance the efficiency of enzymatic hydrolysis and enable the better digestion of released sugars by increasing the biomass surface area or changing its chemical structure to a more accessible material, it would affect the economical feasibility of a process as well. In fact, it is stated that pretreatment step constitutes 20 % of the overall process operational costs. Thus, finding a proper pretreatment can significantly economize the lignocellulosic ethanol production which is still in pilot scale and needs further investigation to become economically commercial, the same as first-generation bioethanol (Paulová et al. 2014).

Physical, solvent fractionation, chemical, and biological pretreatments are different options that can be applied to lignocelluloses. However, thermochemical conversion processes are also available to convert them to other fuels as well (Taherzadeh and Karimi 2008). Figure 2.2 shows a schematic diagram of various pretreatments that deal with lignocellulosic material leading to ethanol production.

Through physical pretreatments, i.e., ball milling, grinding, chipping, and freezing, the biomass size is reduced by mechanical stress, making it more susceptible for further enzymatic hydrolysis by improving the surface area to the volume ratio. In fact, this type of treatment prepares the biomass for better digestion, though it is not able to hydrolyze recalcitrant structure solely (da Costa Sousa et al. 2009). Solvent fractionations act as a hydrogen-binding disrupter to solubilize the components. Organosolv process, phosphoric acid fractionation, and ionic liquids (ILs) are some of the examples (da Costa Sousa et al. 2009). For instance, organosolv method is usually applied to high lignin biomass providing the opportunity of removing the

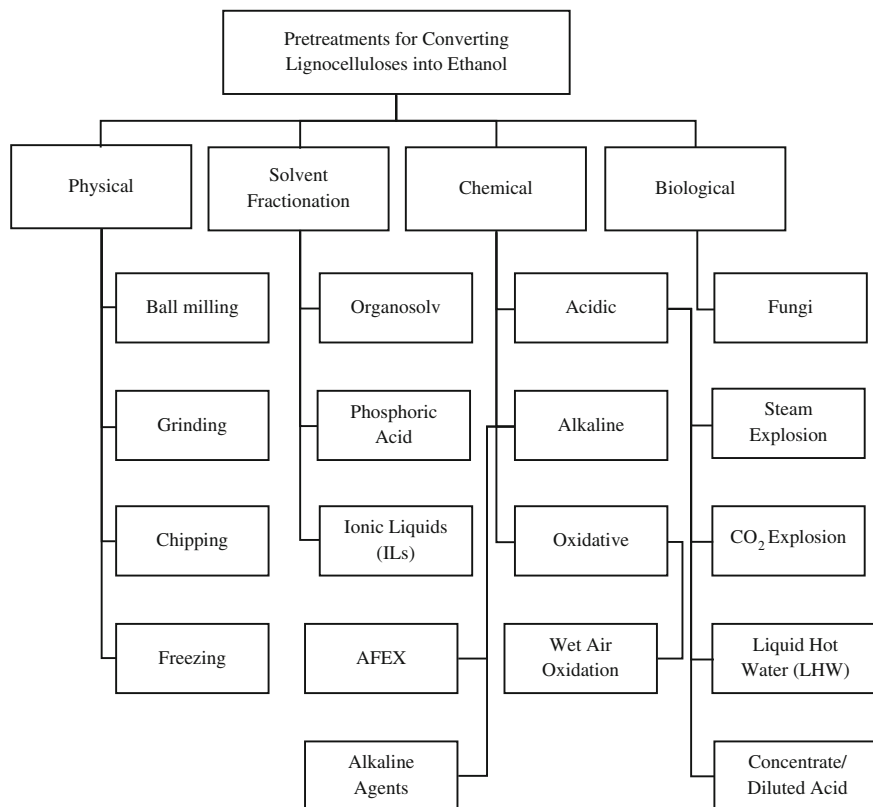


Fig. 2.2 Various pretreatment methodologies for lignocellulosic materials

pure lignin as a by-product. This happens by aiding an organic solvent, usually alcohols, in the presence or absence of a catalyst. Catalyst concentration, temperature, and time range are selected depending on the structure of lignocellulose, and the percentage of lignin and hemicellulose exist in that (da Costa Sousa et al. 2009; Haghighi Mood et al. 2013). This type of pretreatment is capable of producing considerable amount of inhibitors, furfural and hydroxymethylfurfural (HMF), and is less efficient in hydrolyzing hemicellulose sugars (Limayem and Ricke 2012). In phosphoric acid fractionation, different components of lignocellulosic biomass dissolve in various solvents (phosphoric acid, acetone, and water) at 50 °C resulting in its fractionation into amorphous cellulose, hemicellulose, lignin, and acetic acid. ILs are organic salts consisted of cations and anions. The anions present in ILs are capable of forming hydrogen bond with the hydroxyl protons of the sugars present in lignocellulosic biomass. Thus, the linkages between cellulose, hemicellulose, and lignin degrade, and the antisolvents would recover ILs via flash distillation (da Costa Sousa et al. 2009; Haghighi Mood et al. 2013). Chemical pretreatments are more common than the former and can be categorized into three main methods, i.e., acidic,

alkaline, and oxidative. Acidic methodologies are carried out based on applying concentrated or dilute acid, steam or CO₂ explosion, and liquid hot water (LHW) through which mostly lignin and hemicellulose get involved in a chemical hydrolysis process. However, during the pretreatment, some inhibitor compounds such as furfural, 5-hydroxymethylfurfural (5-HMF), phenolic acids, aldehydes, levulinic acid, and aliphatic acid form which limit the enzymatic hydrolysis (da Costa Sousa et al. 2009). Despite the fact that concentrated acids result in less toxic and inhibitor compounds with the sugar yield of 90 %, they are mainly corrosive, toxic, and hazardous, requiring corrosion-resistant reactors as well as acid recovery considerations which increase the operational costs. Thus, it is more preferable to use dilute acids; however, they are more likely to form toxic compounds and phenolic substances which are problematic to saccharification (Limayem and Ricke 2012). Steam explosion is the most common pretreatment for plant biomass since less dangerous chemicals are used and it has the ability to improve enzymatic hydrolysis, reduce the inhibitor formation, and remove hemicelluloses completely (Nigam and Singh 2011). Through this method, the grounded biomass is being heated by a high pressure steam for a few minutes, and in a sudden process, the pressure will get back to the atmospheric condition via an adiabatic expansion, leading to the hydrolysis of hemicelluloses and partly depolymerization of cellulose and lignin as well (Soccol et al. 2010; Kahr et al. 2013).

Among all explosion methods available as pretreatment, CO₂ explosion has gained more popularity since it needs a lower operational temperature and costs less. It is categorized in acidic pretreatments as a consequence of its ability to form carbonic acid (behaving like an acid-catalyzed process) while dissolving in water (Nigam and Singh 2011; Haghghi Mood et al. 2013). The same feature is accessible by using LHW. In fact, water exhibits acidic characteristics at high temperatures, solubilizing most of the hemicellulose and improving the digestibility of cellulose. Moreover, during LHW treatment, inhibitor formation and sugar degradation would be avoided if the pH is controlled at 4–7 (Roy et al. 2012a; da Costa Sousa et al. 2009). By applying alkaline approaches, intermolecular ester bonds cross-linking xylane hemicellulose and other components would go through a saponification process (Nigam and Singh 2011). This pretreatment can mostly expose cellulose and hemicellulose to enzymatic hydrolysis and extract the lignin existed in agricultural residues or herbaceous crops (Roy et al. 2012a; Soccol et al. 2010). Alkaline catalysts, i.e., sodium hydroxide, potassium hydroxide, calcium oxide (lime), and ammonia, are usually applied as well as ammonia fiber explosion (AFEX) as an alkaline methodology. The AFEX is an alkaline process at high pressure (1.72–2.06 MPa) and moderate temperature (60–120) acting like other explosion methods (Haghghi Mood et al. 2013). However, the ammonia supplement and recovery's cost, its handling, and high energy requirement during re-compression are of major drawbacks (Roy et al. 2012b). Oxidizing agents such as air/oxygen or hydrogen peroxide as an oxidant can remove hemicellulose and lignin as well as solubilizing the cellulose at temperatures higher than 120 °C and pressure range of 0.5–2 MPa which are considered as wet oxidation methods. The presence of alkaline during this process increases the yield of monosaccharide sugars and

decreases the formation of inhibitor compounds (da Costa Sousa et al. 2009; Haghighi Mood et al. 2013). Biological methods are also available to deal with the recalcitrant structure of lignocellulosic materials without requiring much energy. During this pretreatment, fungi (usually white rot) are used to secrete the extracellular enzymes such as lignin peroxidase or laccase to remove lignin (da Costa Sousa et al. 2009).

Pretreated lignocelluloses have to be hydrolyzed with enzymes, so that its sugars get saccharified, being available as monosaccharides such as glucose or xylose depending on the structure of the feedstock. Enzymatic hydrolysis usually occurs by using cellulase, endo/exoglucanase, β -glucosidase, and xylanase (Kahr et al. 2013). If the pretreatments are not done well and the amount of lignin is still high, the accessibility of cellulase to cellulose would be reduced and more enzymes will be required since lignin has a non-productive adsorption effect on the enzyme. Moreover, phenolic groups formed after degradation of lignin make cellulase enzymes inactive (Limayem and Ricke 2012). Thus, usually surfactants are added to avoid the side effect of lignin on enzymes (López-Linares et al. 2014). However, high amount of glucose and cellobiose can cause inhibition to endo/exoglucanase and β -glucosidase (Limayem and Ricke 2012). In order to overcome this drawback, the fermentation step can be combined with the enzymatic hydrolysis.

Separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), and consolidated bioprocessing are the main fermentation processing procedures for bioethanol production. However, some modifications such as the combination of SHF and vacuum evaporation (SHEF) (Choi et al. 2013), delayed SSF (dSSF) (Paulová et al. 2014) and prehydrolysis and simultaneous saccharification and fermentation (PSSF) (López-Linares et al. 2014) have also been applied to improve saccharification. In SHF, the hydrolysis and fermentation take place at separate vessels leading to product inhibition of enzymes (cellulase) as a result of glucose accumulation. However, since it is done at 50 °C in which the cellulase has higher activity, hydrolysis rate would increase and microbial contamination decreases. Moreover, it is more likely to remove lignin from the sugars as a solid fuel in SHF (Soccol et al. 2010). In comparison with SHF, SSF is more rapid and economical since the saccharified glucose is fermented into ethanol in the same tank simultaneously. Additionally, the rapid consumption of glucose prevents its accumulation and consequently enzyme inhibition. In fact, during SSF, more cellulose would be hydrolyzed to its building block sugars. Anaerobic condition, the presence of ethanol, and continuous process of glucose formation and consumption lessen the contamination risks as well. However, the optimum temperature for the enzymes (45–50 °C) and fermenting microorganisms (28–35 °C) is different, and also limitation in accessibility of carbon source for microorganisms might happen at the beginning of the process (Paulová et al. 2014). There are two options for overcoming the mismatch temperature problem in SSF by using PSSF or dSSF. Through PSSF, presaccharification is carried out at enzymes' optimum temperature (usually 50 °C) for 24 h followed by SSF at a lower temperature (40 °C) to facilitate the fermentation and decrease the viscosity of solid–liquid mixture before the addition of microorganisms (López-Linares et al. 2014).

The dSSF or delayed SSF is designed not only to eliminate the mismatch temperature limitations but also to omit the low glucose availability in the early stages of SSF and improve the ethanol productivity as well. Paulová et al. (2014) found out that by delaying the inoculation for 12 h, the cellulose and ethanol concentration can increase to 33.3 and 9.2 g/L at 32 h of fermentation, respectively, and shortening the process length up to 60 %. However, the final ethanol concentration is not as high as being distilled economically, since for an economic distillation, the ethanol concentration should exceed 4 % w/v. Thus, fed-batch dSSF with gradual feeding of prehydrolyzed medium was performed to enhance the final ethanol concentration and reduce the rate of inhibitor's accumulation and media's viscosity as well. In addition to the above-mentioned fermentation techniques, CBP is available in which the enzyme (cellulase) is produced with the aid of a fermentative/cellulolytic strain in an aerobic condition. After switching the condition of the vessel to the anaerobic mode, the strain is able to hydrolyze and ferment the saccharified sugars to ethanol. Despite the fact that a wide range of eukaryotes and prokaryotes have shown the ethanol production capability, most of them face with the limitations such as deficiency of sugars co-fermentation, low ethanol yield, low tolerance to chemical inhibitors (aerobic formed metabolites), intolerance to high temperatures, and low ethanol concentration (Limayem and Ricke 2012; Zerva et al. 2014). However, for instance, *Paecilomyces variotii* could successfully co-ferment the agro-industrial wastes (wheat bran, corn cob, and brewers' spent grain) to ethanol yield of 80 % of theoretical value by hydrolyzing glucose and xylose through xylanase, β -xylosidase, endoglucanase, and β -glucosidase which were produced in an aerobic mode by the strain (Zerva et al. 2014).

The most common method to separate the produced ethanol is distillation; however, membranes have been used as well in case that the final ethanol concentration is not high enough to be distilled. Fractional distillation can separate water and ethanol based on volatility. In this process, the mixture boils, and since the boiling point of ethanol is lower than water, it changes into steam sooner and is recaptured with a concentration of 95 %. Then, the water will be condensed and removed. Continuous distillation column is usually used in large industries and biorefineries in which liquid mixture is heated and flow continually. At the top and bottom of the column, volatiles and residues are separated, respectively (Limayem and Ricke 2012). Recently, Trinh et al. (2013) used pervaporative separation of bioethanol produced from the fermentation of waste newspapers. In this method, one of the components with higher affinity and diffusivity to the membrane can preferably be separated. When using membranes, its performance should be considered as well which is mostly dependent to the ethanol concentration, operational temperature, and fouling. The performance of membranes is affected by microbial cells, inorganic salts, sugars, and chemical inhibitors that exist in fermentation broth. The results showed that by using newspaper wastes, it is possible to produce 4.1 % ethanol in 48 h and separate it successfully through a hydrophobic polymeric polydimethylsiloxane (PDMS) membrane without any considerable reduction in performance (Trinh et al. 2013).

So far, some researchers have focused on finding new feedstock for bioethanol production including agricultural residues and municipal or industrial wastes, while others have tried to optimize the process conditions including pretreatment, hydrolysis, microorganisms, fermentation, and distillation. Although it is not possible to investigate all these studies in details, a short introduction of new findings is presented in the following.

Different countries can invest on production of second-generation ethanol depending on the type of wastes they have challenges with the most. For instance, the annual production of cotton is about 23 million ton. The cotton-based waste textiles are consisted of cellulose that can be separated and used for bioethanol production. Jeihanipour and Taherzadeh (2009) investigated the possibility of complete conversion of waste cotton-based textiles to ethanol. Although cotton does not contain lignin or hemicellulose, the crystallinity of its cellulose is high. Therefore, pretreatments should be performed before enzymatic hydrolysis to break down the hydrogen bonds between glucan chains of the crystalline cellulose and obtain the amorphous cellulose instead. Alkaline pretreatment of cotton linter (12 % NaOH) at 0 °C led to 86 % of ethanol theoretical yield after 4 days. In another study (Jeihanipour et al. 2010b), they studied the effect of *N*-methyl-morpholine-*N*-oxide (NMO or NMMO) on the enhancement of ethanol and biogas production from waste textiles since this pretreatment can be applied in industry. The results revealed that by using 85 % NMO (dissolution mode) at 120 °C for 2.5 h, the enzymatic hydrolysis would be increased to 100 % and ethanol amount of 460 g per each kg of cellulose.

Coffee residue wastes (CRW) contain 37–42 % fermentable sugars and is produced during the production of instant coffee. If these wastes dispose to the environment, they can cause problems since they contain toxic compounds. The annual production of coffee in 2010–2011 was estimated as 8.2 million ton. Thus, a large quantity of CRW are produced annually that can be converted to ethanol after a proper pretreatment. Choi et al. (2012) applied popping pretreatment to reduce the lignin and hemicellulose content of CRW as well as improving the degradation of its cellulose as a novel pretreatment. The popping equipment operated at optimum temperature and pressure of 150 °C and 1.47 MPa for 10 min, and then, the pressure reduced to the atmospheric condition again. By conducting the SSF after 96 h, 45.9 g ethanol obtained from 300 g CRW. They also used the same pretreatment procedure for producing ethanol from Mandarin peel (MP), Citrus unshiu, and decreased the amount of *D*-limonene, an inhibitor substance that exists in citrus peel. The SEM images showed that popping pretreatment can efficiently reduce the size of MPs and enhance the substrate surface area. It has also led to the hydrolysis of more xylose and glucose as well as the reduction of *D*-limonene to below 0.01 wt%. Further bioprocessing of hydrolyzed sugars by SHEF, the combination of SHF and vacuum evaporation, yielded 46.2 g/L ethanol in 12 h (Choi et al. 2013).

Waste money bills are used by Sheikh et al. (2013) as a new cellulosic material for bioethanol production. In Korea, 2,357 ton waste money bills are incinerated annually which have been duplicated recently. In USA, 500 million dollars has been allocated to manage waste money bills. Thus, its cellulose content can be

saccharified and fermented to ethanol. Waste money bills pulverized after soaking in 1.2 % NaClO for 5 min, sterilizing with 70 % ethanol, and drying at 105 °C. As a pretreatment, 0.5 % H₂SO₄ was used at 121 °C for 30 min. Enzymatic hydrolysis was done at 50 °C for 72 h, and fermentation was conducted at three different conditions, i.e., anaerobic, anoxic, and anoxic with benzoic acid (0.4 mM). Each led to ethanol concentration of 1.00, 17.22, and 22.01 mg/ml, respectively. The *Saccharomyces cerevisiae* cells in acidic conditions are very permeable to weak acids while being impermeable to anions; thus, they can exhibit an adaptive tolerance in acidic conditions. This leads to accumulation of preservative anions and transient reduction in the pH level that can improve the ethanol yield. Dubey et al. (2012) also produced ethanol from waste papers through dilute acid (0.5 N H₂SO₄) treatment at 120 °C for 2 h and obtained 3.73 g/L ethanol. Their novelty took the possibility of xylose fermentation as well as glucose with the aid of *Pichia stipitis* into account. Economic feasibility and sensitivity analysis of ethanol production from various waste papers (newspaper, office paper, cardboard, and magazines) were investigated by Wang et al. (2013a) with the aid of *Zymomonas mobilis*. They suggested that separation of papers from other municipal wastes and recycling it into new papers is nearly harder than converting its cellulose to ethanol. They concluded that except magazines that contain impurities, other types of waste papers can economically be used for ethanol production if the office papers and newspapers receive only dilute acid and oxidative lime pretreatment, respectively. The maximum glucose and xylose yield was related to office papers, whereas the minimum quantity was obtained from magazines.

The possibility of ethanol production from kitchen wastes (restaurants, cafeterias, dining halls, household kitchens, and a food processing plant) was studied by Cekmecelioglu and Uncu (2013). Glass, metals, and plastics were first separated, and the rest was grounded into a composite. The waste consisted of fruit's peel, vegetables, bakery's wastes, coffee residues, beans, and cereal foods. Dilute acid and hot water used as pretreatments. However, the results revealed that none of them were as efficient as untreated wastes. When no pretreatment was done, ethanol concentration was 23.3 g/L, whereas it was obtained as 17.2 g/L under hot water treatment, which was a bit higher than the one treated with dilute acid. In another study, Matsakas et al. (2014) utilized household food wastes (HFW) for production of ethanol at high dry material (DM) content. They just performed enzymatic hydrolysis (8 h) on the HFW with the DM of 45 and 35 % which yielded ethanol concentration of 42.78 and 34.85 g/L, respectively, after 15 h of fermentation. They suggested that the solid waste, remained after fermentation, still contains cellulose that can be fermented as well if its recalcitrance being removed by hydrothermal pretreatments (microwave at 200 °C for 10 min) in the presence of acetic acid as a catalyst. This new waste led to ethanol concentration of 15.92 and 11.44 g/L at DM of 45 and 35 %, respectively.

In Mediterranean countries, there is a possibility of ethanol production from different seaweeds, duckweeds, and water hyacinth which are regarded as residues and contain considerable amounts of cellulose. Pilavtepe et al. (2012) used *Zostera marina* residues, considered as an environmental problem in Mediterranean beaches because of its bad smell, to produce ethanol. The plant was first extracted by

supercritical CO₂ ($P = 250$ bar, $T = 80$ °C) and ethanol (20 %) and then pretreated at different acid (H₂SO₄) concentrations and reaction times at 120 °C followed by an enzymatic hydrolysis. The SSF yield was obtained as 8.72 % after 24 h. In another study (Pilavtepe et al. 2013), they transformed *Posidonia oceanica* residues to bioethanol at the same conditions as their previous study. The ethanol yield in a 2-L fermenter attained as 62.3 %. Duckweeds and water hyacinth are sea plants capable of growing rapidly in wastewater to clean it and then being used as bioethanol feedstock. Physical and chemical pretreatments such as drying, boiling, steaming, sonication, dilute acid and alkaline are required to process sea plants into bioethanol (Bayrakci and Koçar 2014).

A wide range of agricultural residues have been used for ethanol production. The global production of cellulose, hemicellulose, and lignin from agricultural residues including wheat, barley, corn, rice, soybean, and sugarcane accounts for 3.7 Pg/year (Bentsen et al. 2014). In 2004, it was estimated that the potential bioethanol production from crop residue can reduce 29 % of the gasoline consumption (Kahr et al. 2013).

López-Linares et al. (2014) used rapeseed straw for bioethanol production through different bioprocesses, i.e., SHF, SSF, and PSSF. They concluded that high solid rates at SSF and PSSF caused an inhibition to microorganism, while at SHF, the theoretical yield was improved. De Bari et al. (2014) tried to convert the produced glucose and xylose to ethanol after steam explosion and acidic pretreatment of corn stover. Xylose isomerase is able to convert xylose to ketose (xylulose) which is consumable by *S. cerevisiae* through pentose phosphate pathway (PPP). However, the optimum pH and temperature for yeast and xylose isomerase are different. Thus, sequential addition of enzymes and microorganisms should be applied in order to make the conversion simultaneously possible. At first, the pH and temperature were adjusted at suitable range for cellulose hydrolysis (pH = 4.8, $T = 50$ °C). After 24 h, they changed the pH to 6.5 and temperature to 60 °C followed by a pH adjustment at 7 after passing another 24 h and holding it on for 7 h more. Finally, the pH and temperature were adjusted to 6.5 and 35 °C, respectively, to be proper for the addition of yeast. The maximum xylose conversion in the best case led to the most ethanol production, 70 % on the basis of glucose, xylose, and galactose.

The ethanol produced from various lignocellulosic materials needs to be evaluated to be used as a fuel in engines. The standard limitations in different countries may vary depending on the environmental issues and industrial development. However, there are some general impurities (acetaldehyde, acetone, ethyl acetate, methanol, iso/n-propyl alcohol, and isobutyl/amyl alcohol) within the lignocellulosic-based ethanol that should be reduced or omitted due to their negative effect. Styarini et al. (2013) detected some of these impurities through gas chromatography and suggested that the maximum and minimum amounts were related to isobutyl and isopropyl alcohol according to their own standard protocol.

More details about bioethanol production are presented in Chap. 5.

2.2.3 Wastes to Biobutanol

Biobutanol was first produced via microbial fermentation by *Pasteur* in 1861 and later in 1914 was industrialized when *Weizmann* discovered *Clostridium acetobutylicum*, the strain that can ferment sugars to biobutanol through a process known as acetone–butanol–ethanol (ABE) fermentation (Stoeberl et al. 2011; Kumar and Gayen 2011). However, butanol as a solvent could not compete with the petrochemical-based type due to the high costs of raw material, product inhibition, and low ABE yield, about 0.28–0.33 g/g (Kumar et al. 2012; van der Merwe et al. 2013). Recently, the production of biobutanol as a biofuel has gained more attention since the conversion of lignocellulosic wastes as a non-food cheap raw material is available. However, commercial production of butanol is still not feasible if the yield is lower than 25 % (Kumar and Gayen 2011).

Furthermore, the fuel characteristics of butanol are more interesting than the ethanol. Unlike the ethanol, butanol can blend with petrol in different ratios to be used in car engines and it has higher calorific value and hydrophobicity as well as lower freezing point and heat vaporization (Kumar et al. 2012). It is also not corrosive and has more similar features to petrol (Han et al. 2013).

Similar to ethanol, various pretreatments and enzymatic hydrolysis should be applied on lignocellulosic materials to break down the recalcitrant structure of cellulose, hemicellulose, and lignin. The fermentation processes, i.e., SHF, SSF, or other modifications, are also done the same as for ethanol (Kumar et al. 2012). However, in ABE fermentation, there are two different metabolic pathways leading to butanol production. In the first step which is known as acid genesis, acetate, butyrate, hydrogen, and CO₂ are produced when the microorganism is in its exponential growth phase which then would be converted to acetone, butanol, and ethanol in a process named as solvent-producing step (Stoeberl et al. 2011). Like ethanol fermentation when using SSF, lack of sugar at the beginning of the process may lead to lower productivity for butanol production. Cheng et al. (2012) used a novel method, sequential SHF-SSF, to overcome the problem of lack of sugar at the beginning of fermentation. They used sugarcane bagasse and rice straw as a feedstock pretreated by 2 g/L H₂O₂ and 15 g/L NaOH at 120 °C for 20 min followed by an enzymatic hydrolysis for 2 days. Then, more pretreated feedstock within mixed bacterial culture was added to the media. The enzymatic hydrolysis and fermentation continued for the next 3 days. In fact, at the second day, the system was changed into the SSF process from the SHF one. This sequential technique led to butanol production of 1.95 and 2.93 g/L for bagasse and rice straw, respectively. However, these amounts were obtained as 2.29 and 2.92 g/L when the experiment is conducted by the SHF alone.

The major problems associated with butanol production include sustainable biomass selection, low productivity, butanol inhibition, and high recovery costs (Srirangan et al. 2012; Xue et al. 2013). Lignocellulosic wastes have balanced the obstacle of biomass supply to some extent. Nevertheless, it has added a new expense by necessitating the pretreatment step. There are some new articles trying to focus on

producing butanol from different new wastes with no requirement to pretreatments. Virunanon et al. (2013) used the starchy wastewater of Tapioca factories. Raw materials included cassava pulp (CP) and cassava starch wastewater (CWW) which were hydrolyzed by enzymes for 2 h in order to be used as a carbon source for both butanol and ethanol production. When the CP was used alone, the produced butanol was extremely low (0.03 g/L) and the acetone was undetectable, whereas the obtained ethanol was as high as 8.98 g/L. However, using the CWW alone resulted in ethanol, butanol, and acetone concentration of 1.76, 0.85, and 0.25 g/L. In contrast, the combination of CP and CWW yielded more butanol, i.e., 2.51 g/L, in comparison with ethanol, i.e., 1.76 g/L, and acetone, i.e., 0.6 g/L. This increase might be related to the presence of a substance in CWW that leads the metabolic pathway to more butanol production or the fact that the more starch has released more reducing and fermentable sugars. Felled oil palm trunk was also used as a new feedstock in two different ways, sap and trunk fiber, with the aid of various types of *clostridia* strains by Komonkiat and Cheirsilp (2013). The first one could be used directly; however, the latter needed pretreatment. The mixture of sap (30 g/L sugar) and yeast extract (1 g/L) after 144 h of fermentation resulted in butanol, ethanol, and acetone production of 7.3, 1.5, and 2.1 g/L, respectively, while a potential of mixture of pretreated oil palm trunk and the nitrogen source led to butanol, ethanol, and acetone concentration of 10.0, 0.19, and 3.88 g/L after 144 h of fermentation. Chen et al. (2013) suggested that non-pretreated rice straw can be used under the non-sterile condition as well as the sterile mode if the inoculation is added at a high concentration. By using non-sterile conditions, the cost of process can significantly be reduced. The concentration of butanol was obtained as 6.6 and 6.3 g/L under non-sterile and sterile conditions within the cell concentration of 2,331 mg/L.

Apart from this, in most cases, the lignocelluloses should be pretreated to enhance the productivity. Ranjan et al. (2013) investigated the possibility of butanol production from rice straw under diluted acid (1 % w/v H_2SO_4) and agitation (200 rpm) at 120 °C and 150 psi for 15 min. The agitation caused the rapid release of sugars, and the concentration of butanol, ethanol, and acetone was obtained as 13.50, 0.82, and 6.24 g/L, respectively. Decanter cake waste, the effluent of palm oil mill, was used as a substrate for butanol production after being pretreated by 1 % HNO_3 and a 15-min agitation at 150 rpm and 121 °C for 20 min as well. Cheap nitrogen source (whey protein or ammonium sulfate) was added to it which yielded 3.42 g/L of butanol (Loyarkat et al. 2013). The improvement of ABE process was investigated by Moradi et al. (2013) through an alkaline (12 % w/v) and H_3PO_4 (85 %) treatment of rice straw which led to butanol production of 2 and 1.4 g/L, respectively. When no pretreatment was done, the butanol concentration was 0.16 g/L. Both pretreatments not only enhanced the glucan content but also reduced the xylane and lignin. Furthermore, 2-year-old willow biomass was studied for ethanol production by Han et al. (2013). Acid hydrolysis was performed by 24 N H_2SO_4 at 30 °C for 1 h, then it was diluted with boiling water and hydrolyzed for an extra hour at 105 °C. By fermenting the stem and bark of the willow biomass, butanol concentration of 4.5 and 4.3 g/L was obtained. However, during acid hydrolysis, inhibitor compounds such as acetic and formic acids and furfural

formed. Some researchers tried to find a solution for decreasing the amount of inhibitor compounds by applying membrane-based technologies. For instance, Cai et al. (2013) separated furfural through a pervaporation process. After acid hydrolysis with 0.2 % w/v acetic acid at 170 °C for 30 min, the hydrolysate was detoxified by pervaporation. The maximum efficiency of furfural separation was achieved as 94.5 %. Then, the fermentation was conducted, and the butanol was separated by the PDMS membrane as well. The concentration of produced butanol, ethanol, and acetone was 12.3, 2.5, and 6.1 g/L, respectively. Since effluent of biohydrogen-producing bioreactor contains significant amount of butyrate, Chen and Jian (2013) used it for butanol production. However, mixed culture exists in the effluent may cause inhibition for ABE production which can be separated by membranes. The butyrate was not sufficient enough as a carbon source for the fermentation; thus, saccharose was added as well. Finally, the saccharose and butyrate concentration of 25 and 3.5 g/L, respectively, resulted in butanol formation of 0.47 mol/mol. A new pretreatment procedure by electrolyzed water was performed on distiller's dried grains with solubles (DDGS) to produce butanol (Wang et al. 2013b). The DDGS is a major co-product in ethanol fermentation of corn. Electrolyzed water was combined with acidic (1 % H₂SO₄) and alkaline agents, and the results were compared to solo alkaline (2.5 % NaOH) and hot water (140 °C for 20 min) pretreatments. The maximum butanol concentration obtained via hot water and acid-electrolyzed water were, respectively, 3.64 and 3.62 g/L, whereas the solo alkaline could only lead to butanol formation of 2.09 g/L after 96 h of fermentation.

Batch, fed-batch, and continuous process are some options for the fermentation step. The first two require a long time for sterilization of bioreactor and reinoculation with a low productivity and high solvent inhibition, whereas the latter is more economical and can overcome most of these hurdles; however, its contamination risk and capital cost are high. Different techniques are available in a continuous process such as free/immobilized cell. In free cell method, due to the mechanical agitation or air-lifting capability, the cells are free to move in the fermentation broth, which improves the mass transfer as well, whereas the cells are longer alive during solvent-producing step in the immobilized cell technique, since the mechanical agitation does not exist anymore. In order to improve the free cell fermentation process, cell recycling and bleeding or continuous flash fermentation is designed. Through cell recycling, the cells would be recycled to the bioreactor via a membrane which enhances the cell concentration and productivity of butanol by helping the fermentation broth to be kept at optimum state. This method can increase the butanol productivity up to sixfold. Flash fermentation, in contrast, consisted of three interconnected units, i.e., vacuum flash vessel, cell retention system, and fermenter. It can reduce the distillation cost and is more compatible with environment (Kumar and Gayen 2011).

Another option for enhancing the productivity of butanol and reducing the solvent production or increasing the tolerance of microorganism to butanol is obtained by applying modified microorganisms through mutagenesis and evolutionary and metabolic engineering. *S. cerevisiae* and *Escherichia coli* for instance can be used instead of *Clostridia* for butanol production without solvent formation (Xue et al. 2013).

However, there are some *Clostridia* strains that can produce butanol without producing acetone. Gottumukkala et al. (2013) used *Clostridium sporogenes* BE01 to produce butanol from dilute acid-treated rice straw (4 % H₂SO₄ at 121 °C for 60 min) enriched with calcium carbonate (buffering agent) and yeast extract (nitrogen source) without acetone formation. When the hydrolysate was detoxified by anion resins and enriched with mentioned additives, butanol was produced as high as 5.52 g/L, while it was obtained as 3.43 g/L when no calcium carbonate was added to control the pH and enhance the tolerance of strain to butanol.

Butanol inhibition may occur in both steps of ABE process. During the acid production, the *Clostridia* strains suffer the acidification of cytoplasm or accumulation of anions leading to its growth reduction and butanol inhibition. In addition to this, butanol is toxic for *Clostridia* as a result of its lipophilic feature. In fact, butanol can cause physiological dysfunction on the cell membrane by disrupting the phospholipid contents and altering some physicochemical properties such as preferential transport of solute, permeability of the membrane, and the amount of glucose uptake (Xue et al. 2013; Kumar and Gayen 2011).

In order to separate butanol from other solvents and water, four distillation towers are required. Since the boiling point of acetone (56.53 °C) and ethanol (78.4 °C) is lower than others, they get distilled in the first tower followed by removing water and butanol as residue. While the second tower is designed to separate the acetone and ethanol, two series of towers and a decanter are targeted to break the azeotrope point of butanol and water (Kumar et al. 2012). Separating butanol with four distillation towers is not only energy consuming but also very expensive. Therefore, it is of interest to find new economical techniques for butanol separation. Adsorption, gas stripping, liquid–liquid extraction (LLE), perstraction, pervaporation, and reverse osmosis (R.O.) are of the examples. Abdehagh et al. (2014) reviewed various separation techniques for butanol. Through an adsorption, butanol is first adsorbed on an adsorbent surface, i.e., activated carbon, resins, and zeolites, following by desorption as a result of temperature increase until a concentrated butanol solution is obtained. This method is considered as one of the energy-efficient separation processes.

Gas stripping is a simple method through which the stripper gas, nitrogen, or fermentation gases such as CO₂ or H₂ flow into the fermentation broth and carry the acetone, ethanol, butanol, and water with them at their equilibrium partial pressure. The stripping gas can further be condensed and returned to the fermenter. In spite of high gas flow rate, although the cells are not damaged, foaming might happen. Due to the simplicity of the process (not requiring complex chemicals or facilities), providing a low concentrated butanol condition to prevent the inhibition and high productivity of butanol and sugar-consuming rate, the selectivity is low and the heater and condenser need high amounts of energy. In contrast, LLE is a high selective technique in which an organic water-insoluble extractant is mixed with fermentation broth to remove butanol. However, the extractant with high distribution coefficient is usually toxic for the microorganism. Thus, the extraction may occur in an external column to avoid the low mass transfer to the extractant, emulsion formation, and cell growth inhibition.

Perstraction, pervaporation, and R.O. are the examples of membrane-based methods. The latter can improve the distillation process by dewatering the fermentation broth via a semi-permeate membrane at high pressures and achieving a high concentrated final product. In addition to enhance the dewatering, the membrane would not be affected by fouling if the fermentation broth goes through an ultrafiltration first. However, the ultrafiltration membrane should be replaced regularly due to the fouling. Perstraction can overcome some of the problems associated with LLE since it uses a membrane which is in contact with both extractant and broth on each of its sides. The most important point in this method is choosing a high selective membrane to butanol and an extractant with a high distribution coefficient. However, the fouling and expensive price of the membranes can reduce its popularity. A binary or multicomponent liquid mixture is likely to be separated via pervaporation. By using this method, the components would get separated after a partial vaporization based on their diffusivity and adsorption to the membrane rather than the volatility. In fact, permeate adsorbed to the membrane firstly and diffuse through it. Finally, it would desorbed and evaporate under low pressures (Niemistö et al. 2013). Of advantages of pervaporation are high selectivity, no influence on microorganism, prevention of substrate or nutrient loss, suitable for azeotropic mixtures, and requiring low operation temperatures and energy. However, it is faced with some limitations such as low permeation flux, membrane swelling, and concentration polarization.

Despite the fact that second-generation biobutanol production is still in its infancy, the effort for its development is still in progress. As an example, Nilsson et al. (2014) have recently introduced a novel method for butanol production. Through this technique, succinic acid (SA) obtained after fermenting the CO₂ by *E. coli* would be converted to butanol by being hydrogenated via catalysis. The SA is an intermediate product in the citric acid cycle which can be produced under the anaerobic fermentation as well. By integrating the processes in which SA is produced with a catalysis process, the possibility of butanol production might be feasible.

Chapter 8 of this book has a more specific view on biobutanol production.

2.2.4 Wastes to Biogas

Anaerobic digestion (AD) consisted of four series of bioreactions (hydrolysis, acidogenesis, acetogenesis, and methanogenesis) by consortium of microorganisms through which organic materials are converted into a mixture of CH₄ and CO₂ and a trace amount of water vapor, H₂S, and NH₃, which is known as biogas. Depending on the feedstock used and the operational conditions of the digesters, the biogas content varies. However, its major component is methane. Via the first step, referred as hydrolysis or liquefaction, hydrolytic or fermentative bacteria, which are capable of extracellular enzyme secretion, hydrolyze complex organic materials such as lipids, proteins, and polysaccharides to soluble monomers or oligomers such as

amino acids, long-chained fatty acids, sugars, and glycerol. In the second stage, acidogenic bacteria convert simple and soluble compounds obtained in the previous step to CO_2 , H_2 , alcohol, and low molecular weight volatile fatty acids (VFAs), e.g., propionic or butyric acid. Through the third step known as acetogenesis, hydrogen-generating bacteria metabolize the alcohols and VFAs anaerobically to form acetate, H_2 , and CO_2 . However, hydrogen-oxidizing bacteria or homoacetogens can produce acetate from the CO_2 and H_2 . Finally, two groups of methanogens produce methane. Whereas acetotrophic methanogens utilize acetate as a substrate for methane production, the hydrogenotrophic methanogens reduce CO_2 by using H_2 as an electron donor and generate methane. In fact, 70 % of methane is attained through decarboxylation of acetate, while the rest is achieved by reducing the CO_2 . However, a few amounts of methane are probable to be produced from other organic substrates such as formic, propionic, and butyric acids (Surendra et al. 2014).

The produced methane is targeted to be upgraded and used as a fuel in transportation or simply burned for domestic heating and cooking. It is of interest to notice that it has the potential for supplying the heat and electricity of a plant as well as a local area. It is estimated that 1 m^3 biogas which is comprised of 60 % methane equals to the heating value of 21.5 MJ (Surendra et al. 2014). Whereas in India, 1,281 MW electricity is produced annually from the agro-waste-based biogas. In 2007, Sweden supplied 11 % for its domestic fuel need (about 38 PJ) from anaerobic digestion of organic wastes (Sarkar et al. 2012). Furthermore, the digestate remains after the process is applied as a fertilizer for agricultural purposes (Ariunbaatar et al. 2014).

The LCA studies have proved that biogas production from energy/dedicated crops is in direct competition with food on agricultural land and water requirement (Graebig et al. 2010). It is worthwhile to remind that due to the increase in population and the huge rate of waste generation in recent decades, municipalities are involved in great trouble for waste management. Currently, incineration and landfilling are of the major disposal methods for most of the wastes which not only are threatening for the environment, causing soil and water contaminations or GHG emissions, but also are not cost-effective (Zhang et al. 2014; Kothari et al. 2010). Hence, a wide range of organic wastes are introduced to be digested in an anaerobic digester as the feedstock, including sewage sludge, agricultural residues, the organic fractions of municipal solid wastes (OFMSW), animal manure, and fruit and vegetable wastes.

According to the statistics, the annual production of MSW is reported more than 2.5 billion ton/year which can yield up to 50–70 % methane. Whereas the incineration or landfilling of MSW causes the loss of fertile lands, health problem, and GHG emissions, its AD would result in heat and electricity supplementation as well as producing a transportation fuel. However, there are some uncertainties over techno-economic potentials of biogas production from MSW in an industrial scale. In conjunction with this concept, Rajendran et al. (2014) studied six different scenarios by using Aspen Plus[®] based on the industrial data. They suggested that the main uncertainties over the techno-economic feasibility of biogas from MSW are due to the transportation and collection of wastes and reduced operations of the

plant. Furthermore, it was concluded that not only the biogas production from MSW as fuel is a positive investment, but also the integration of produced biogas with the one from WWTPs along with its upgrading through water-scrubbing process is the most economical and profitable venture. In addition, Hung and Solli (2012) compared four scenarios for managing the organic waste with incineration and biogas production to obtain either heat and electricity or a fuel for buses in Trondheim city. They claimed that in spite of negligible climate benefit of biogas production from MSW in Trondheim, the elimination of diesel fuels from the bus's engines and its consequent influences on less photochemical oxidant production and particulate matter formation have significant benefits. Their studied scenarios showed that construction of a new biogas plant in Trondheim is the most environmental-friendly one. Recently, Afazeli et al. (2014) investigated the potential of biogas production from livestock and slaughterhouse wastes in Iran, suggesting the possible annual production of 8,600 million m^3 biogas from livestock excreta. However, this sort of waste is still not efficiently used in developing countries like Iran. By taking into account some of the advantages of digesting livestock and slaughterhouse wastes, i.e., development in industry and job creation, cutting down the zoonotic disease transmission and medical expenses as well as odor controlling and managing the hazards associated with slaughterhouses and animal husbandries, it would be more rational to bring these wastes into consideration for a more sustainable and healthier society.

In the USA, the annual production of brown grease, consisted of trapped, sewage, and black grease collected from either the restaurants or food processing industries, is estimated as 1.84 million ton whose landfilling accounted for US\$110 per metric ton in 2002. Besides the high disposal costs related to landfills, soil and water contaminations should be considered as well. Hence, this sort of waste was utilized in a high rate pilot-scale anaerobic digester for biogas production by Zhang et al. (2014). In order to reduce the water consumption during the digestion, pulp and paper liquid wastewater was also added. The methane yield was obtained as $0.4\text{--}0.77 \text{ m}^3 \text{ CH}_4/\text{kg VS}_{\text{removed}}$, indicating the successful possibility of reutilizing it in digesters rather than landfilling.

Alkanok et al. (2014) estimated the food waste generation by supermarkets in Turkey between 5 and 45 tons/month or 1–10 tons/week. They utilized fruit, vegetables, meat, sugar, dairy products, and flower wastes at 10 % TS, under mesophilic conditions in a batch digester to produce biogas with the highest methane yield of $0.44 \text{ L CH}_4/\text{g VS}_{\text{added}}$. They suggested that if the wastes are separated at source and collected in a centralized biogas plant, being supplemented by trace elements and VFAs, ammonia, pH, and C/N ratio being monitored well, the process would be more efficient and stable.

Scano et al. (2014) evaluated a full-scale power plant for biogas production from fruit and vegetable wastes (FVWs). The estimated power output for the daily produced methane ($290 \text{ Nm}^3/\text{day}$) based on 9 ton waste/day was calculated as 42 kW within annual electrical production of 300 MWh/year. In summary, they suggested a successful and economical AD power plant from FVWs.

Liu et al. (2012) focused on biogas production and its GHG emission reduction by co-digestion of food (FW)/fruit and vegetable wastes (FVWs) mixed with dewatered sewage sludge (DSS). They considered three scenarios in a pilot-scale continuous CSTR at mesophilic temperatures (35 °C) and obtained the maximum biogas yield of 0.72 m³/kg VS_{added}. It is believed that the main source of GHG emissions in China is related to landfill disposal of MSW, since 79 % of it was landfilled in 2009. Hence, the GHG emissions produced after biogas production from MSW with the possibility of power or bionatural gas (BNG) generation were compared with its landfill disposal. Both scenarios associated with biogas production showed a significant reduction in GHG emissions compared to landfills. It was estimated that an AD plant with a capacity of 500 ton/day can reduce the GHG emissions for power generation and BNG up to 20,800 and 95,400 ton CO₂, respectively.

Around 40 % of fibers used in waste textiles are comprised of cellulose, mainly cotton or viscose. In Sweden, 53,000 ton cellulose is wasted annually which can be used for more than 20 Nm³ methane generation as well as 4 TWh power per year by considering a methane yield of 415 ml (at STP) per g of cellulose. Jeihanipour et al. (2013) used waste textiles in a two-stage process for a high rate biogas production. However, they have already introduced a novel process for biogas production from cellulose in blended-fibers waste textiles (Jeihanipour et al. 2010a) and enhanced its production from high-crystalline cellulose by different modes of NMO pretreatment (Jeihanipour et al. 2010b). In their recent study, they used viscose and cotton fibers blended with polyesters (unseparated cellulose fibers) in both batch one-stage (SBR) and two-stage (SBR connected to a CSTR in series) processes. In addition, either the pretreated textiles with NMMO or untreated ones were digested in a semi-continuous two-stage reactor with different organic loads. The maximum biogas yield for viscose and cotton fibers was obtained, respectively, as 55 and 31 ml/g VS/day in a batch single stage. Whereas the two-stage process did not improve the biogas yield for viscose fibers, it enhanced the methane yield up to 80 % for cotton fibers. Besides, the results of a semi-continuous reactor showed that pretreatments can increase the yield by 100 %.

In Portugal, between 70,000 and 80,000 ton/year sardines are captured of which the half is processed in canning industry. The co-digestion of waste oils obtained from sardine canning industry with pig manure at ratio of 5:95 yielded 26 m³ CH₄/m³ feedstock. Since the sardine oil does not contain sufficient nutrients and its alkalinity is low, pig slurry was added to supply the nutrients as well as maintaining the buffering capacity (Ferreira et al. 2012). However, Eiroa et al. (2012) evaluated biomethane production potential of solid fish wastes. The maximum methane yield was almost the same for all types of fish, 0.47 g COD-CH₄/g COD_{added}; however, it was a bit higher for mackerel (0.59 g COD-CH₄/g COD_{added}) due to its more oil content.

Of factors influencing the AD process are pH, alkalinity, temperature, and retention time. Different microorganisms existing in the digester have a distinguished optimum pH and temperature. For instance, methanogenetic bacteria usually tend to work under neutral pH, while the fermentative ones are still active at

wider ranges (4–8). During acidogenesis, the formation of VFAs would result in a sharp pH dropping (Appels et al. 2008). At low pH, glycolytic enzymes, which are sensitive to acids, lose their function and high-level dissociated acids penetrate the cell membranes of methanogens and disrupt the macromolecules. In fact, high amount of VFAs can lead to inhibition of methanogens. In order to reduce the inhibitory effect of VFAs, different strategies such as adjustment of C/N by co-digestion or other options, addition of trace elements to accelerate the growth, and separating methanogenesis and acidogenesis step through using two-stage digesters have been introduced (Xu et al. 2014).

Kafle and Kim (2013) co-digested apple wastes (AW) and swine manure (SM) in a batch, either at mesophilic (36.5 °C) or at thermophilic (55 °C) conditions, as well as a continuous process at 36–38 °C to overcome methanogen's inhibition caused by both VFA formation and high ammonia content of swine manure. Although the biogas yield obtained at thermophilic conditions was higher than the mesophilic one, the methane percentage did not differ. Besides, the mixture of AW and SM could enhance the biogas yield up to 16–48 % more than the solo SM. The continuous digestion of the mixture yielded more biogas by increasing AW addition.

Different types of digesters are designed to improve the operation conditions. Standard rate (cold) digesters are the simplest one with long digestion periods (30–60 days) which are used in small scales. Feedstock is usually neither heated nor mixed in this type. In contrast, at high rate digesters, the feedstock is either heated or mixed to establish a uniform media for microorganism leading to more stability and efficiency of the digester (Appels et al. 2008). These types of bioreactors, usually known as upflow anaerobic sludge bed (UASB), are commonly used at industrial plants. Since the biological reactions take place at the bottom of the reactor, a denser sludge bed would guarantee the success of UASBs. Besides, the application of microbial consortia granules stimulates the interspecies electron transfer and high rate methane production (Sabra et al. 2010).

Anaerobic digestion may occur via batch or continuous process in a one- or a two-stage digester. In the batch mode, the wastes are entered to the reactor and the process step by step. One-stage digesters are used in large scales, and all the reactions take place at once in the same vessel. In contrast, two different reactors are used for acidogenesis and methanogenesis steps in a two-stage digester. This helps to avoid the inhibition caused by VFAs; however, the one-stage digester is easier to design and needs lower investments (Sitorus et al. 2013).

Digesters can operate at different temperature conditions, called as mesophilic (30–38 °C) or thermophilic (50–57 °C). At high-temperature conditions, the bioreactions occur faster as well as more pathogen destruction; however, the energy requirement and odor potential are higher, and finally, poorer stability is attained (Appels et al. 2008).

Depending on the TS of feedstock, the AD is performed as liquid (L-AD) or solid-state AD (SS-AD) process. The operational TS range for L-AD is between 0.5 and 15 %, while the SS-AD is more than 15 %. Although the reaction rate is higher and retention time is shorter in L-AD, it is faced with hurdles such as floating and stratification of fibrous substances. In contrast, SS-AD is more economical due

to its lower reactor volume, energy input, and almost zero mixing energy requirement (Liew et al. 2012).

The type of biomass used in a digester plays a key role in the final yield and the selection of operational criteria. It is believed that hydrolysis step is the most rate-limiting one. However, methanogens can be rate-limiting as well if the organic materials degrade easily. In order to overcome these problems and improve the yield of biogas as well as taking economical aspects into account, pretreatments are of interest (Ariunbaatar et al. 2014). However, co-digestion of different feedstocks would help as well. Various pretreatments such as physical or mechanical, chemical, biological, and their combination have been widely used for different feedstocks. Physical or mechanical pretreatments not only disintegrate cell membranes, but also improve the contact between bacteria and feedstock by increasing the surface area, resulting in better digestion consequently (Carrère et al. 2010). Sonolysis was used as a mechanical pretreatment on sewage sludge followed by a co-digestion with kitchen wastes by Cesaro et al. (2012) to enhance the biogas yield. After running the AD process for 45 days, the biogas increased up to 24 % within the sonolized sludge in comparison with untreated sample. As a matter of fact, ultrasonication can enhance the biodegradability of sludge through both physical and chemical reactions by cavitation phenomena and free radical formation. However, the co-digestion process was also beneficial. The pretreatment was performed at 20 kHz and 750 W with a probe diameter of 13 mm for 60 min.

Thermal pretreatments in contrast disrupt the cells by providing a pressure gradient on the cell surface which leads to the release of cell components followed by series of physical and chemical reactions between them (Bougrier et al. 2006). Solid slaughterhouse wastes rendering products (SSHWRP) were sterilized at 115–145 °C to disrupt its lipid cell's membrane by Pitk et al. (2012). The methane yield was obtained in the range of 390–978 m³ CH₄/kg VS after this dry rendering method for different waste products, revealing that the melt waste yielded the most. They concluded that dry rendering methodology could recover 4.6 times more primary energy than unsterilized SSHWRP.

In chemical methods, agents such as acids, alkaline, and oxidants are applied to treat the biomass. Although this method has been frequently used, it should be avoided for high carbohydrate content substrates due to its fast disruption effects and the subsequent accumulation of VFAs which would result in methanogen inhibition. Biological pretreatments are usually carried out on lignocellulosic biomass or sewage sludge (Ariunbaatar et al. 2014). Fungal and bacterial consortium and enzymatic techniques are of examples of biological pretreatments. While fungi strains are mostly able to degrade lignin and hemicellulose, microbial consortium is more capable of attacking cellulose and hemicellulose. Moreover, despite the fact that enzymes are almost expensive and have a minimal influence on biogas yield, there are not usually applied in full scales. Liew et al. (2012) utilized four lignocellulosic wastes (corn stover, wheat straw, yard wastes, and leaves) with TS of 22 % to produce methane under an enzymatic hydrolysis by cellulase for 72 h at 50 °C and 150 rpm in a 30-day SS-AD process. Whereas corn stover resulted in maximum methane production of 81.2 L/kg VS, wheat straw, leaves, and yard

wastes led to methane yield of 66.9, 55.4, and 40.8 L/kg VS, respectively. However, Ye et al. (2013) suggested that it is more economical to co-digest agricultural residues rather than pretreating them before the AD process. By co-digesting rice straw, kitchen wastes, and pig manure with a ratio of 1:0.4:1.6, the methane yield was 383.9 L CH₄/kg VS. Since kitchen wastes are easily degradable substrates with high moisture, carbohydrate, and lipid and protein content, its solo digestion could lead to VFA formation and pH drop causing the methanogen inhibition. Thus, the addition of pig manure that is rich in organic substances and is able to balance the C/N ratio was done to increase the methane yield.

Some researchers reported ensilaging as an effective method in comparison with enzymatic pretreatments (Zheng et al. 2014). For instance, Kafle et al. (2013) reported that by ensilaging the fish industry waste (FW) with bread wastes (BW) at 25 °C for 22 days, the methane yield would increase to 441 ml CH₄/g VS from the initial value of 306 ml CH₄/g VS. Since the FW contains a large amount of protein, its ensilaging alone would lead to butyrate formation as a result of *Clostridia* strain's dominant role in fermentation. Thus, by adding BW that mainly consisted of carbohydrates, sufficient energy for growth of lactic acid bacteria (LAB) will be provided and the fermentation would drive under the LAB influence.

More detail about biogas production is presented in Chap. 6 of this book.

2.2.5 Wastes to Biohydrogen

Hydrogen is the cleanest fuel that can be used in transportation sector since its only by-product when it is either used in fuel cells for electricity generation or heat engines as a fuel is water, which is not only a pollutant but also a favorable product (Show et al. 2011; Chong et al. 2009). Hydrogen is a colorless non-toxic gas without any odor or taste (Chong et al. 2009), which in comparison with other fuels generates more energy, about 122 kJ/g (Sekoai and Gueguim Kana 2013), having the calorific value of 143 GJ/ton (Show et al. 2011). Even though the current hydrogen application is limited to ammonia manufacture (49 %), petroleum refining (37 %), methanol production (8 %), and miscellaneous uses (6 %), it is believed that it can be a strategic bridge to the future of world's energy (Kırtay 2011). At present, there are various technologies available for hydrogen production such as chemical (steam reformation or coal gasification), electrochemical (water electrolysis), and thermochemical (biomass gasification or pyrolysis) methods (Azbar and Levin 2012; Das et al. 2014). Whereas the first two methodologies are extremely dependent on fossil fuels, turning them into energy-intensive approaches with a great potential of GHG emissions, the latter is carbon neutral since the generated CO₂ is fixed through photosynthesis by the new biomass. However, tar and char are the most undesirable by-products after thermochemical techniques (Kırtay 2011; Bartels et al. 2010). Therefore, biological methods are gaining more attention in recent decades as a new approach which has changed it into biohydrogen production. Albeit, the economic aspects of biohydrogen production are still under

question and further researches and modifications should be carried out to make it commercially established (Show et al. 2011).

Biological methodologies of biohydrogen production are categorized into four groups including direct/indirect water photolysis by cyanobacteria/green or blue algae, photofermentation of organic compounds by photosynthetic bacteria, dark fermentation of organic compounds by anaerobic bacteria, and hybrid reactors or microbial electrolysis cell (MEC), which is the integration of dark and photofermentation (Ren et al. 2009; Kırtay 2011; Hay et al. 2013).

Regardless of the higher yield provided by photolysis or photofermentation, the commercial light supplementation in photobioreactors is not economic enough to develop it into an industrial scale. Within dark fermentation, there are main challenges as well, such as low yield and hydrogen inhibition due to the accumulation of end products (propionate, lactic acid, and ethanol) (De Gioannis et al. 2013). However, it is more suitable to mature dark fermentation or hybrid systems in which organic wastes and residues even lignocellulosic materials are used as the merely source of electron and energy for hydrogen formation. Of other advantages of dark fermentation are process simplicity, less energy requirement, and more cost-effective production through reutilizing wastes and residues (Sydney et al. 2014). However, there are some key factors that should be considered for enhancing the biohydrogen production via dark fermentation, e.g., microorganism, pH, temperature, organic load, inoculum pretreatments, HRT, substrate, and trace elements.

During anaerobic fermentation, two groups of bacteria are active. While some of the bacteria can convert acetic acids to methane, others would utilize H_2 and CO_2 . Therefore, the second pathway should be eliminated if the H_2 is preferable (Liu et al. 2013). As a matter of fact, the H_2 production would be enhanced if the metabolic pathway switches to more acid formation or the domination of acidogenesis step (Mohan et al. 2012). This would be obtained through inoculum pretreatment such as heat-shock or physical and chemical methods resulting in methanogen's activity reduction (Chinellato et al. 2013). However, it is not appropriate in full scales (Pan et al. 2008). Faloye et al. (2014) optimized the inoculum by using two pretreatment conditions, i.e., heat shock (pH = 8.36, $T = 89\text{ }^\circ\text{C}$, $t = 68\text{ min}$) and autoclave (pH = 8.93, $T = 121\text{ }^\circ\text{C}$, $t = 15\text{ min}$), which resulted in maximum hydrogen production of 0.78 mol H_2 /mol glucose and 1.35 mol H_2 /mol glucose, respectively. They, also conveyed a microwave pretreatment at pH 11 for 2 min on the inoculum and obtained 1.92 mol H_2 /mol glucose, increased the H_2 production by 32.41 %. In addition to this, the scale-up optimization in a batch semi-pilot reactor with and without pH control resulted in 2.07 and 1.78 mol H_2 /mol glucose, respectively (Faloye et al. 2014).

Depending on the consortia of bacteria, acetate or butyrate paths would be dominant in H_2 production in which 4 and 2 mol H_2 would be formed per mol of glucose, respectively (De Gioannis et al. 2013).

When the sugar concentration (organic load) is too high in the media, the pH decreases and more end products form resulting in inhibition of hydrogen-producing bacteria. This inhibition happens as a result of increase in ionic strength of the solution at low pH, which alters the metabolic pathway to solvent generation rather

than H_2 production. Indeed, non-polar dissociated acids penetrate into cell walls and release proton inside them where the internal pH is higher. This phenomenon would increase the energy requirement of cell for maintaining its pH at neutral level and consequently reduce the flux of glucose through glycolysis (Chong et al. 2009). Even at high pHs in which H_2 production is accelerated, inhibition may occur for hydrogen-producing bacteria since the rapid formation of acids can decrease the buffering capacity (Hay et al. 2013). The best approach for overcoming this hurdle is to adjust food-to-microorganism ratio (F/M) or design two-stage systems in which the first stage is used for H_2 production and the remaining organic biomass can be reconsumed by methanogens for methane generation in the second stage. This process would lead to biohythane production consisting of 10 % H_2 , 30 % CO_2 , and 60 % CH_4 which can be used in combustion engines as well with a higher thermal efficiency and power output (Cavinato et al. 2011). Simultaneous production of hydrogen and methane increases the total energy recovery by 100 and 30 % compared to single-stage hydrogen or methane production process, respectively (Liu et al. 2013). Cavinato et al. (2011) optimized a two-phase thermophilic biohydrogen production through reject water recirculation. They suggested that in order to prevent the methanogen activity, HRT should be low. However, it can cause a great decrease in pH, thanks to the high organic load. Therefore, instead of adding chemical agents to control pH, recirculation of the AD effluent to the dark fermentation reactor can buffer the system and maintain the pH at optimum level. The maximum hydrogen produced was 51 L H_2 /kg TVS at a low organic loading rate of 16 kg TVS/m³ d accounting for 37 % increase in H_2 generation. Chinellato et al. (2013) also obtained the maximum H_2 of 2,116 ml at organic loading rate of 30 kg TVS/m³ by recirculating the digestate for pH control.

Pan et al. (2008) adjusted F/M ratio of food wastes at both mesophilic (35 °C) and thermophilic (50 °C) conditions instead of pretreating the inoculum to enhance the hydrogen yield. They indicated that pretreatment is an expensive approach for full-scale purposes and it is not certified that the entire of hydrogen-consuming bacteria are dead. Additionally, only the spore-forming H_2 bacteria survive after thermal treatments. The maximum hydrogen obtained at F/M ratios of 6 and 7 under mesophilic and thermophilic modes was 39 and 57 ml H_2 /g VS, respectively.

The partial pressure of H_2 in the liquid phase is another crucial point that should be considered. The less the H_2 is dissolved in liquid phase, the more the H_2 is found in the form of gas. The hydrogenase enzyme can reversibly oxidize and reduce the ferredoxin. Oxidation of reduced ferredoxin will lead to oxidation of H_2 to proton which means a decrease in concentration of H_2 at gas phase. However, by nitrogen sparging, the concentration of hydrogen in liquid phase would decrease significantly (Chong et al. 2009).

The volumetric productivity is low in thermophilic mode ($T > 60$ °C), since the strains tend to grow in lower cell density in suspension media or switch their metabolic pathways to other reduced final products such as lactate, ethanol, and alanine rather than H_2 . However, it can provide better conditions for H_2 production in reactors compared to mesophilic mode. Furthermore, in thermophilic mode, less

by-products are formed, the H_2 tolerance is higher, and it is economically feasible and best (Pawar and van Niel 2013).

Long HRT usually leads to inhibition of hydrogen-producing bacteria and methanogen activity. In fact, when the HRT is short, which means that dilution rate is high, washout might happen to methanogens since their specific growth rate is lower than hydrogen-producing bacteria (Cavinato et al. 2011).

Addition of some nutrients (peptone or yeast extract) and trace elements such as iron which is a key factor in hydrogenase and other enzyme generation, vitamins, and growth factor may enhance the H_2 production (Hay et al. 2013). Pan et al. (2013) investigated effect of ammonia on biohydrogen production from food waste. They concluded that at F/M of 3.9 and 8, the hydrogen yield of 77.2 and 51 ml H_2 /g VS would increase to 121.4 and 60.9 ml H_2 /g VS by adding 3.5 and 1.5 g/L ammonia, respectively.

So far, different wastes and residues have been used for hydrogen production as well as other biofuels. Municipal solid wastes, wastewater sludge, lignocellulosic materials, and industrial wastes are of some examples. However, some of these feedstocks should be pretreated in order to increase the yield. It is usually preferred to pretreat the lignocellulose before digesting them in an AD process since they have a heterogeneous and crystalline structure. Lignocellulosic wastes account for 220 billion ton worldwide which is equal to 60–80 billion ton crude oil. In China, the annual production of lignocellulose is estimated as 1.4 billion ton which has the potential of hydrogen production of 100 billion kg. It is stated that 10.3 kg cellulose is required to produce 1 kg H_2 equating to the energy provided by 1 gallon of gasoline (Ren et al. 2009). During 1998–2001, in Western Europe, 0.7 billion ton of agricultural and forestry residues were generated. In France, for instance, this amount was estimated as 374 million ton in 2006. Therefore, there is a great potential for using lignocellulosic wastes as a feedstock for different biofuel productions. Guo et al. (2010) reviewed hydrogen production from agricultural wastes via dark fermentation. Jia et al. (2014) applied fruit–vegetable wastes by alkali and acid pretreatments followed by enzymatic hydrolysis and obtained the maximum hydrogen production of 10.11 ml/h after acid hydrolysis. In South Africa, 2.95 and 7.88 million ton agricultural and municipal wastes are produced, respectively, of which only 35 %, mainly MSW, are recycled and the rest are either incinerated or landfilled. Sekoai and Gueguim Kana (2013) compared bean husk (BH), cornstalk (CS), and OFMSW individually and as a mixture to produce hydrogen. Each of BH and CS could hardly produce H_2 since they need pretreatments. However, in combination of same ratio of OFMSW and BH, 41.16 ml H_2 /g TVS was produced, while the solo OFMSW produced 56.47 ml H_2 /g TVS. Li et al. (2012) indicated that 4 million tons of agricultural waste is produced as well as 69 m³ beverage wastewater per year which consisted of 74 % carbohydrate. They evaluated the techno-economic feasibility of hydrogen production from beverage wastewater and mushroom farm solid wastes (55 % cellulose) by considering two different pretreatment conditions for mushroom wastes with the aid of Aspen Plus software. The results showed the hydrogen production rate of 4.38 l/d/l with maximum annual

profit and return rate of 60 and 39 %, respectively, based on Aspen price. They concluded that the process is economically feasible.

In Korea, Japan, China, and Malaysia, food wastes are the major components of municipal solid wastes, about 20–54 %. In 2011, 930 tons of unconsumed food was wasted daily in Malaysia, which has been doubled over the past 3 years (Yasin et al. 2013). In Hong Kong, food wastes are estimated as 3,280 ton/year (36 % of MSW). Xiao et al. (2013) could achieve a hydrogen yield of 155.2 ml/g VS of food waste at 37 °C by adding 40 ppm $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

In India, 580 billion rupees of food items is wasted annually. Pasupuleti et al. (2014) studied the up-scaling of biohydrogen production in a semi-pilot biofilm reactor through optimizing organic load. They observed an inhibition at organic load as high as 66 g COD/l. However, they gained a maximum hydrogen production of 9.67 l/h. Gadhe et al. (2014) performed an ultrasonication on food waste at 20 kHz for 15 min at TS of 8 % to enhance the hydrogen yield and obtained 1,192 ml H_2 . Elbeshbishy et al. (2011) also compared the single and combined effects of different pretreatments on food wastes. The maximum and minimum H_2 production was obtained as 97 and 46 ml H_2 /g VS after single ultrasonication and alkaline treatment, respectively. Whereas the combination of ultrasonication and acidic pretreatment enhanced the hydrogen yield up to 118 ml/g VS, the combination of ultrasonic either with alkaline agents or with thermal methods had negative effect on hydrogen production.

Textile industries produce the most toxic wastewaters due to their need for applying different substances such as dyes, surfactants, and textile's additives. Since biological methods are not able to eliminate dye which is a structured polymer with low biodegradability, other methods including active carbon, cation exchange resin, solvent recovery, chemical catalysts, gold extraction, gas separation, and liquid adsorption are used to degrade it. The dark fermentation of textile wastewater at 37 °C, treated with active carbon and inoculated with municipal WWS having a sugar concentration of 20 g/L which was obtained after hydrolysis with amylase for 20 min at 70 °C, resulted in 1.37 mol H_2 /mol reducing sugar.

Benincasa hispida or *petha* sweet is a solid waste produced in a sugar syrup process. About 30–35 ton of *petha* is produced daily which can be used for hydrogen production. Singhal and Singh (2014) pretreated the inoculum (cow dung) using microwave at 320 W for 5 min and obtained 14 mmol H_2 /mol soluble sugar.

In developing countries, herbal medicines are popular and 80 % of world population tend to use it instead of chemicals. The wastewater produced after processing such kind of medicines contains a great amount of COD whose treatment is essential. Thus, it can be applied in AD process for biohydrogen production. At optimum pH and temperature of 6.5 and 50 °C, the maximum H_2 yield was 480 ml/g COD (Sivaramakrishna et al. 2014).

The liquid residue at the bottom of distillation tower of processing sugarcane to ethanol is called *vinass*. It is estimated that 12–15 L *vinass* is usually produced per one liter of ethanol. In Brazil, 25 billion liter ethanol was produced in 2012–2013, which resulted in production of 370 billion liter *vinass*. However, it is currently

used as a fertilizer, due to its low pH and high COD and potassium content that can contaminate soil and groundwater, and its application is limited. Therefore, it has the potential to be used as nutrient additives for carbon sources such as molasses and sugarcane juice for biohydrogen production. Adding *vinass* to sugarcane juice and molasses resulted in hydrogen generation of 7.14 and 3.66 mol/mol sucrose, respectively, with the aid of different microorganisms (Sydney et al. 2014).

In 2011, 80.3 million automobiles and vehicles were manufactured globally. An automobile industry with annual production rate of 400,000 cars is capable of producing 410,000 m³ wastewater which is rich in heavy metals, grease, oil, and dye. The produced wastewater is usually treated with chemicals, and after decantation, the effluent that is called DECA can be co-digested with municipal or industrial sludge and glucose for biohythane production. However, the presence of compounds containing zinc or other metal salts can inhibit methanogens. While the methane was completely inhibited at concentration of 75 mg/L of Zn, the hydrogen was produced as 2.4 mol/mol glucose. It was reported that the addition of glucose could prevent the zinc inhibitory effect and decrease the hydrogen yield instead (Bajaj and Winter 2013).

Biohydrogen production is explained in detail in Chap. 7.

2.3 Challenges Ahead

Due to the everyday increase in worldwide energy demand and the depletion of fossil fuels as well as growing concerns on environmental issues, the global attention has been dragged on biofuels which are mainly based on biomass resources. However, other renewable types of energy such as wind, solar and geothermal are being investigated likewise. It is predicted that by 2025, the global energy demand would increase by 50 % (Ragauskas et al. 2006). The transportation sector has a great share in energy consumption, comprising the 60 % of global oil uptake (Tsita and Pilavachi 2013). In 2011, 94 % of the required energy in this section was supplied from fossil fuels, indicating that it has a great share not only in energy consumption but also on GHG emissions (Menten et al. 2013). About 15–22 % of world's GHG emissions are related to transportation vehicles of which 70 % are originated from diesel and gasoline usage on roads (Soimakallio and Koponen 2011; Chin et al. 2013). Since a 40 % increase in transportation sector is expected by 2035 (Chin et al. 2013), expanding the biofuel's portion in engines is being considered by politicians. According to RED, a directive enacted by European Union on June 2009, the application of biofuels in transportation sector in EU was about 3.5 % in 2008 which should be enhanced to 10 % by 2020, provided that its GHG emission's share be reduced by 35, 50, and 60 % until 2016, 2017, and 2018, respectively (Soimakallio and Koponen 2011). On the other hand, the US Energy Independence and Security Act depicts a 136 billion liter rise in ethanol production by 2022 from the initial amount of 41.9 billion liter in 2009, of which 79.3 billion liter must be obtained from advanced biofuels (Menten et al. 2013).

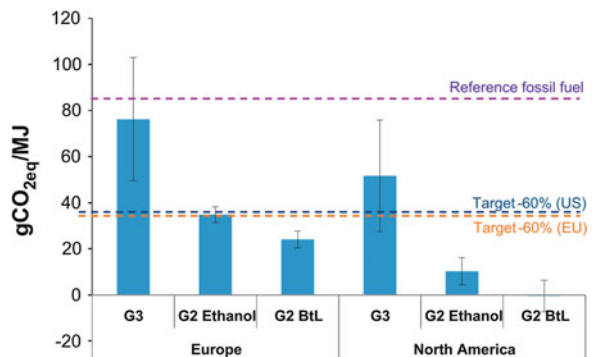
In 2009, the Europe exceeded the world on biodiesel production by achieving 65 % of its share. The global ethanol production was also 20 million gallon including the USA (54 %), Brazil (34 %), and EU (5 %) as the major manufacturers (Serra and Zilberman 2013). It is worthwhile to remind that these quantities are entirely supplied from first-generation biofuels. Even though there is a good potential for increasing the production rate of this sort of biofuels, some concerns, such as deforestation, devastation of biodiversity, and haze pollution, increase in GHG emissions, thanks to the change in land use, water shortage, loss of fertile lands, and “food versus fuel confliction” have taken it into criticism (Chin et al. 2013). In this case, advanced biofuels (second and third generations) might seem a good solution for some of these problems; however, they are somehow challenging as well.

Although 170 billion ton biomass is produced annually (Sivakumar et al. 2010), lignocellulosic materials such as straw that can balance the farmland fertility and organic carbon might be a challenge if be overharvested from fields (Lindorfer et al. 2014). Furthermore, the permanent availability of lignocellulosic feedstocks around all time of the year is under doubt.

From environmental point of view, GHG emissions of advanced biofuels should be calculated in order to prove its advantages. Many LCA studies have been carried out to figure out the GHG emissions of advanced biofuels. Recently, Menten et al. (2013) reviewed this issue by meta-regression analysis. They concluded that while the GHG emissions for third-generation biofuels produced from microalgae (G3) have the highest amount, cellulosic ethanol (G2 Ethanol) and biodiesel (G2 BtL) produced biologically and thermochemically, respectively, emitted lesser amounts. However, the measured values were higher in the USA than EU due to the selection of different approaches in the LCA study. Figure 2.3 displays a clearer comparison between the cases. Whereas fossil fuels as a reference index discharged 83.8 g CO₂/MJ in average, the G3, G2 Ethanol, and G2 BtL released 60, 19.7, and 19.5 g CO₂/MJ, respectively. Thus, the production of second-generation biofuels can reduce environmental concerns to some extent if only the proper method is applied.

According to Lee and Lavoie (2013), second-generation biofuels are supplied from homogenous, quasi-homogenous, and non-homogenous feedstocks which are mostly regarded as residues and wastes. Homogenous feedstocks like white wood

Fig. 2.3 Comparison of GHG emissions between advanced biofuels and fossil fuels in the North America and Europe (Menten et al. 2013)



chips cost about US\$ 100–120/ton, while agricultural and forest residues as well as low-value feedstocks such as municipal solid wastes have lower prices of US\$ 60–80/ton and US\$ 0–60/ton, respectively. In spite of low price that non-food feedstocks offer, technological challenges decelerate their development. In most cases, the application of pretreatment which is usually energy intensive and energy expensive as a result of requiring chemical agents and detoxification step is critical. In addition, the price of enzymes (cellulase) usually needed for enzymatic hydrolysis of pretreated lignocelluloses during ethanol and butanol fermentation is predicted to reach US\$ 0.12–0.2/L by 2015. Therefore, the amount of cellulose, hemicellulose, and lignin content of a biomass has a key role on the biofuel yield and costs. Furthermore, in order to make the process more economical, the conversion of hemicellulose or extraction of lignin has to be counted too. In North America, 45 % of the forestry biomass is made of glucan resulting in ethanol production of 313 L/ton with market and production price of US\$ 0.68/L and US\$ 0.3/L, respectively. Cellulosic ethanol has a value of US\$ 212/ton of biomass whose biomass costs around US\$ 60–80/ton. By taking the saccharification price into account as well, it would be revealed that this process is more expensive than the first-generation ones (Lee and Lavoie 2013).

Another technological challenge that put off the commercialization of second-generation biofuels is associated with genetic engineering progress in modifying high-tolerant and high-yield microorganisms. Besides, the development of more efficient and less energy-intensive pretreatment methodologies is still under investigation (Tsita and Pilavachi 2013). From another aspect, biofuel production from wastes postulates new stages of biorefineries (cluster biorefineries) where not only the wastes are collected and recycled but also value-added products are fabricated with the minimum to almost zero carbon emissions (Ragauskas et al. 2006; Chin et al. 2013). Moreover, integrated biorefineries would be more cost-effective if they are installed besides current petroleum refineries to benefit the existed infrastructures and pipelines (Yue et al. 2013). Since the spectrum of raw materials for second-generation biofuels are diverse, lack of experienced workers would also lead to some uncertainties in process yield such as causing errors in operation, production of unqualified products, and delay in order delivery (Yue et al. 2013).

Apart from mentioned technical hurdles, some social hindrances are also in the horizon. Although social acceptance is not a major obstacle, it can slow down the advancement of the process. The dispute of food versus fuel for the first-generation biofuels is a good example for lack of social acceptance in this issue. Furthermore, stakeholders and investors who have spent their money on first-generation industries are still waiting for the ball to drop, and naturally, they are less willing to start a new bargain. As a matter of fact, financial supports from governments and private investors or legislating new supportive policies could help the start-up of large scale second-generation biofuels. Additionally, local residents may prevent the establishment of new plants as a consequence of unawareness. In this case, developing ideas such as decentralized biorefineries or scattered small-scale plants which are more visible than a large plant may be restricted by more social groups (Chin et al. 2013; Yue et al. 2013).

As a more economical approach, it should be indicated that finding a new market for biofuels can also help its development. Conducting the airline and aircraft industries to utilize second-generation biofuels is a new gate for the market. Additionally, it has environmental benefits as well (Köhler et al. 2013).

In essence, it should be stated that the transition of first-generation biofuels to the newer versions does not mean to omit the primers. It is praiseworthy to mention that relying entirely on wastes and residues for continuous biofuel production is not possible since some of them are not abundant all the time. Hence, the integration of both first- and second-generation biofuels will be continued until achieving the most compatible technology to economics, environment, and society (Sims et al. 2008).

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