Clean Energy Production Technologies

Series Editors: Neha Srivastava · P. K. Mishra

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Biofuel Production Technologies: Critical Analysis for Sustainability

Springer

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The consumption of fossil fuels has been continuously increasing around the globe and simultaneously becoming the primary cause of global warming as well as environmental pollution. Due to limited life span of fossil fuels and limited alternate energy options, energy crises is important concern faced by the world. Amidst these complex environmental and economic scenarios, renewable energy alternates such as biodiesel, hydrogen, wind, solar and bioenergy sources, which can produce energy with zero carbon residue are emerging as excellent clean energy source. For maximizing the efficiency and productivity of clean fuels via green & renewable methods, it's crucial to understand the configuration, sustainability and techno-economic feasibility of these promising energy alternates. The book series presents a comprehensive coverage combining the domains of exploring clean sources of energy and ensuring its production in an economical as well as ecologically feasible fashion. Series involves renowned experts and academicians as volume-editors and authors, from all the regions of the world. Series brings forth latest research, approaches and perspectives on clean energy production from both developed and developing parts of world under one umbrella. It is curated and developed by authoritative institutions and experts to serves global readership on this theme.

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Foreword

Rising human population and growing emphasis on improving the quality of human life have increased the demand of food and energy. Efforts to provide food for all have yielded results through the use of agrochemicals and fertilizers and increase in the area of cultivable land. The current agricultural practices have become energy intensive. Direct energy needs of people in all countries have also increased. The energy availability and security has thus become an important priority for all countries and more so for developing countries. The currently used conventional energy sources are finite in nature, and their extensive use causes pollution. Scientists now have come to a unanimous conclusion that global increase in carbon dioxide and other gases and deforestation is responsible for increasing the stress on the global environment. More efficient use of energy through appropriate policies and demand management, implementation of better energy-conservation technologies, and the intensive development of renewable energy sources are being talked about.

Various renewable energy options are biomass, geothermal, hydro, ocean current, solar, tidal, and wind. It is estimated that the developed countries are meeting around 3–4% of their energy needs through renewable energy resources as against 18–19% of developing countries. Out of the various renewable energy options, biomass is a quite versatile resource as it can be used for supporting both energetic and non-energetic requirements of human society. The diversified nature of biomass resources is quite often expressed in terms of 6-F concept, namely, food, feed, fuel, fiber, fertilizer, and feedstock, the essential requirements of modern human society. Thus, it is amply clear that there are several competitive areas that will be controlling the demand for biomass and energy is one of these.

Lignocellulosic biomass can be used for producing biogas, bio-hydrogen, hythane, bio-butanol, and ethanol. Algal biomass and sewage sludge are being considered as suitable feedstocks for producing biodiesel and bio-oil. Out of all the candidate biomasses, lignocellulosic biomass has the greatest potential for use as feedstock for producing chemicals and fuels. This however requires selection of the candidate biomass and a suitable pretreatment technology to make the selected biomass as a suitable substrate for bioconversion to a fuel. Consistent research efforts in the past two decades have resulted in considerable improvement in the pretreatment and bioconversion processes, having high productivity, high titer value, and high yield as well as inexpensive downstream processing. However, consistent efforts are still required to make biomass-based chemicals and biofuel production routes economically comparable to petrochemical-based routes.

The book entitled ***Biofuel Production Technologies: Critical Analysis for Sustainability*** edited by Dr. Neha Srivastava, Dr. Manish Srivastava, Prof. P. K. Mishra, and Dr. Vijai Kumar Gupta is focused on the different biofuels, including biogas, bio-alcohols (butanol, ethanol), biohydrogen, and biodiesel. It makes an attempt to present a summary of the state of the art as it exists today. Various factors that control the nature of biofuel production technologies and their scale are also included as and where required. The 12 intensive chapters comprising this book focus on various available production technologies together with the strategies required for economical production of various biofuels. The current bottlenecks impeding the wide-scale exploitation of available technologies are also discussed together with future perspectives in each case. The book is likely to be a valuable reference for academicians, researchers, students, and professionals interested in the area of biofuel production.

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The editors are thankful to all the academicians and scientists whose contributions have enriched this volume. We also express our deep sense of gratitude to our parents whose blessings have always prompted us to pursue academic activities deeply. It is quite possible that in a work of this nature, some mistakes might have crept in text inadvertently, and for these, we owe undiluted responsibility. We are grateful to all the authors for their contribution to present this book. We are also thankful to Springer Nature for giving this opportunity to editors and the Department of Chemical Engineering & Technology, IIT (BHU), Varanasi, UP, India, for all their technical support. We thank them from the core of our heart. Editor Manish Srivastava acknowledges the Department of Science and Technology (DST), Government of India, for awarding the DST-INSPIRE Faculty Award [IFA13-MS-02] 2014, and also Science and Engineering Research Board for SERB-Research Scientist Award-2019.

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Award, for his advanced research achievements in the field of fungal biology and biotechnology. He is the editor of few leading scientific journals of high repute, having many publications in his hands with h-index 21. He has edited many books for publishers of international renown such as CRC Press; Taylor & Francis, USA; Springer, USA; Elsevier Press, the Netherlands; Nova Science Publishers, USA; Walter de Gruyter, Germany; and CABI, UK.

Biofuels: Types and Process Overview

1

Pietro Bartocci, Roman Tschentscher, Yunjun Yan, Haiping Yang,
Gianni Bidini, and Francesco Fantozzi

Abstract

The term biofuels refer mainly to fuels derived from biomass, which can be considered as plants and organic residues. In this chapter attention will be focused on liquid biofuels that can be used mainly for transportation. As reported in the IEA Technology Road Map for biofuels, presented in 2011, they can be divided in two main categories, based on the type of technologies used: conventional biofuels (sugar- and starch-based ethanol, conventional biodiesel, biogas) and advanced biofuels (cellulosic ethanol, hydrotreated vegetable oil, biomass-to-liquids, biosynthetic syngas, etc.). The production of these biofuels is object of big research efforts directed through process intensification and increase of the efficiency of biomass conversion into an energy vector. For this reason this chapter takes into account the production of first-generation biodiesel, first-generation bioethanol, second-generation biodiesel, second-generation bioethanol, and hydrotreated vegetable oils focusing on their market and the most importantly production techniques.

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Biofuels · Biodiesel · Bioethanol · Vegetable oils · BTL · Fischer-Tropsch

1.1 Introduction to Biofuels

Compared to gasoline, diesel, and natural gas, alternative liquid biofuels derived from biomasses have one main selling point: they are renewable. While there are significant differences among liquid biofuels with regard to production, all are argued to have a lower environmental impact at both the extraction and consumption stages (Renewable Fuels Association 2015; Skutsch et al. 2011; Slade and Bauen 2013). Thus, while biofuels are economically marginal in the marketplace, they are socially and politically useful (Solomon et al. 2007).

The major benefits of biofuels by an economic, environmental, and energetic point of view are shown in Table 1.1.

Biomasses, based on their composition, can be divided into three main categories: sugar/starch crops, lignocellulosic biomass, and oil plants. The composition and main characteristics of these feedstocks will be better explained in the next paragraph. Figure 1.1 shows the most important conversion processes to produce biofuels from biomass. From sugar/starch crops, bioethanol can be produced through milling, hydrolysis, fermentation, and refining. Bioethanol can be also produced with similar processes from lignocellulosic materials. Lignocellulosic biomass can

Table 1.1 Benefits linked with the use of biofuels (Demirbas 2009a)

Economic impacts	Sustainability
	Fuel diversity
	Increased number of rural manufacturing jobs
	Increased income taxes
	Increased investments in plant and equipment
	Agricultural development
	International competitiveness
	Reducing the dependency on imported petroleum
Environmental impacts	Greenhouse gas reductions
	Reducing of air pollution
	Biodegradability
	Higher combustion efficiency
	Improved land and water use
	Carbon sequestration
Energy security	Domestic targets
	Supply reliability
	Reducing use of fossil fuels
	Ready availability
	Domestic distribution
	Renewability

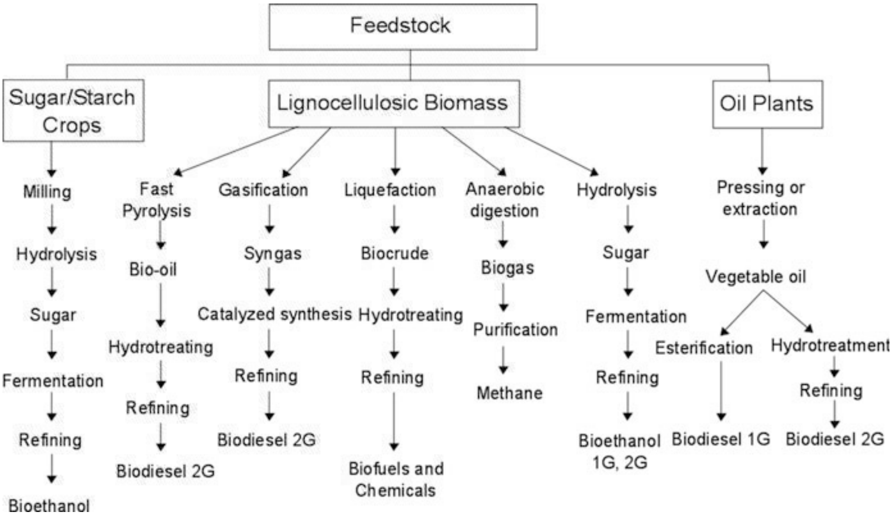

Fig. 1.1 Most important conversion processes to produce biofuels from biomass (Demirbas 2009b)

be converted also through pyrolysis, gasification, hydrothermal liquefaction, and anaerobic digestion. Vegetable oils can be converted through transesterification but also through hydrotreating, producing hydrotreated vegetable oils. This chapter will take into consideration the following biofuels:

- Biodiesel
- Bioethanol
- BTL (Biomass to Liquids)
- HVO (Hydrotreated Vegetable Oils)

These have been selected among the existing ones because they are believed to have higher market potential.

As it is reported in the World Energy Outlook 2018 of the International Energy Agency (IEA), transport accounts for a fifth of global energy demand and is responsible for a quarter of energy-related CO_2 emissions. More than 95% of today's transport sector emissions are from oil (IEA 2018) and the demand for the transport of people and of goods is projected to increase significantly through to 2040.

Global transport biofuel consumption has increased by more than 5% in 2017 and has reached 150 billion liters, of which three-quarters is ethanol. In energy terms, biofuel consumption is about 86 Mtoe, of which two-thirds is ethanol. Biofuel promotion policies are now in place in 68 countries. While large volumes of advanced biofuels could be produced sustainably, their development has been slowed by their costs. In fact, producing a barrel of second-generation biodiesel can cost around $140/barrel today (IEA 2018). Assuming that advanced biofuels are not responsible of net CO_2 emissions, a carbon tax above $150 per ton of CO_2 would

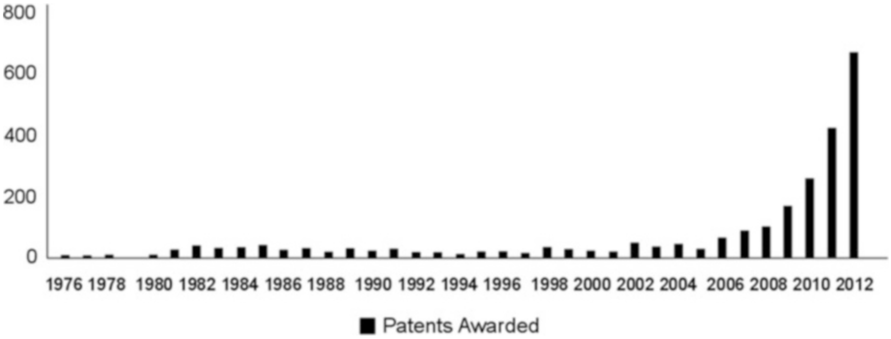

Fig. 1.2 Patents awarded for all biofuels technologies, N = 2587 (Arnold et al. 2019)

be required for them, to be cost-competitive with fossil ones (IEA 2018). Production costs have to be reduced through technological innovation. Continuous innovation must provide constant or increasing returns to innovative efforts, but complexity can increase the costs of those efforts (Costantini et al. 2013, 2015a). In the analysis of (Arnold et al. 2019), an innovation is considered to be a technical novelty that earns a patent. Using the data provided by the United States Patent and Trademark Office (USPTO), a database of liquid biofuel technologies patented since 1976 has been constructed (Arnold et al. 2019).

Figure 1.2 shows that biofuel technologies of all generations show a low level of innovation from the start of the data series through 2005, while from 2006 the level of innovation has risen and continues to rise consistently. This rise in patenting parallels the results seen in other international studies. In fact, biofuel patents rose first in Japan, in the period 1994–2002, and then increased in Europe in 2004 and in the United States in 2005 (Albers et al. 2016). The reasons for this increase can be found in market forces, concerns over supply, price, and air quality.

From 1976 through 2012, the number of patents per author has declined from 0.64 patents per author in 1976 to 0.33 patents per author in 2012. Thus it can be concluded that the productivity of innovation in biofuels has also declined. Besides, the increase in patenting from 2006 on did not affect the trends in patents productivity. The decline of productivity of innovation is evident in both newer technological areas (such as information technology, biotechnology, and nanotechnology) and in older sectors (Strumsky et al. 2010; Tainter et al. 2018). This appears to be the result of increasing complexity in the research process (Strumsky et al. 2010; Tainter et al. 2018). As Kessler and Sperling (Kessler and Sperling 2016) noted, second-generation biofuel technologies are surely more complex than those first-generation ones (Himmel et al. 2007). This implies that nowadays biofuel innovation requires increasing diversity of technical knowledge and a multidisciplinary approach. It is now difficult for a single researcher to master all of the technologies that make up a biofuel patent (Costantini et al. 2015b). As a result, it requires the collaboration of increasing numbers of researchers to develop a patent, who work in interdisciplinary teams (Albers et al. 2016).

1.2 Feedstock

1.2.1 Vegetable Oils

The main feedstock for first-generation biodiesel production worldwide includes oils from energy crops (such as soybean, rapeseed, canola, sunflower, corn, palm kernels, animal fats) and recycled oil. *Jatropha curcas L.* oil has also been used for biodiesel production in tropical areas such as India and Africa.

Vegetable oils from energy crops (which are also often commercialized in the food sector) are considered high-quality materials for biodiesel production because they have a high triglyceride content (92–99%) and low FFA content (<2%). Vegetable oils produced from soybean and rapeseed are the most commonly used feedstock for biodiesel production in the United States and Europe, respectively.

Waste oil is recycled cooking oil used in restaurants, food industry, and households. It contains usually more free fatty acids and water and less triglycerides than fresh vegetable oils. The typical composition of waste oil includes linoleic acid (53%), oleic acid (28%), and palmitic acid (11.73%) (Shah et al. 2007). Because of its high FFA concentration and water content, waste oil usually needs a pretreatment to remove water and transform FFAs to esters. The production of waste oils worldwide is significant; in 2007, in fact more than 15 million tons have been generated in the world (Gui et al. 2008). Vegetable oils composition and main characteristics are proposed in Table 1.2 (Leung et al. 2010).

1.2.2 Starch and Sugars

Ethanol derived from biomass has the potential to be a sustainable transportation fuel that can replace gasoline (Wang 2000; Kim and Dale 2004). Ethanol can be produced from sugar- or starch-containing crops (see Table 1.3) and lignocellulosic biomass (such as agricultural residues, herbaceous crops, forestry wastes, wastepaper, and other wastes) (Wyman 1996). The production of bioethanol from lignocellulosic biomasses is still under development. The composition of lignocellulosic biomasses is presented in the next paragraph.

1.2.3 Lignocellulosic Biomass

Lignocellulosic biomass composition derives directly from the composition of the plant cell wall (Caffall and Mohnen 2009). The lignocellulosic feedstock is represented by the agricultural and forest residuals, which are mainly composed by the cell wall tissue, which remains after the plants have died. Plant cell wall biomass contains mainly cellulose, hemicellulose, and lignin. Different species of plants have significant differences in the proportions of the main components and important differences in the types of hemicellulose which are contained and the ratios of

Table 1.2 Feedstock for biodiesel production (Leung et al. 2010)

Type of oil	Species	Fatty acids composition (wt. %)	Kinematic viscosity (cst. at 40 °C)	Acid value (mg KOH/g)
Edible oil	Soybean	C16:0, C18:1, C18:2	32.9	0.2
	Rapeseed	C16:0, C18:0, C18:1, C18:2	35.1	2.92
	Sunflower	C16:0, C18:0, C18:1, C18:2	32.6	–
	Palm	C16:0, C18:0, C18:1, C18:2	39.6[a]	0.1
	Corn	C16:0, C18:0, C18:1, C18:2, C18:3	34.9[a]	–
	Canola	C16:0, C18:0, C18:1, C18:2, C18:3	38.2	0.4
Nonedible oil	Jatropha curcas	C16:0, C16:1, C18:0, C18:1, C18:2	29.4	28
Other	Used cooking oil	Depends on fresh cooking oil	44.7	2.5

[a] Kinematic viscosity at 38 °C, mm^2/s

Table 1.3 Starch content in energy crops used for 1st generation bioethanol (Zabed et al. 2017)

Crop	Scientific name	Starch content (%)[a]
Corn	*Zea mays*	70–72
Sorghum	*Sorghum bicolor*	68–70.7
Wheat	*Triticum aestivum*	65.3–76
Rice	*Oryza sativa*	87.5
Oat	*Avena sativa*	65.6
Potato	*Solanum tuberosum*	73

[a] Dry weight

monomers in lignin (Pauly and Keegstra 2010). The composition in terms of main components of the most important lignocellulosic feedstocks is shown in Table 1.4.

Woody biomass contains more cellulose and lignin, whereas grass biomass has higher content of hemicellulose (mainly xylan), extractives, and ashes.

Cellulose is a polysaccharide consisting of a linear chain of D-glucose units.

Hemicellulose has a backbone composed of 1, 4-linked β-D-hexosyl residues and may contain pentoses, hexoses, and/or uronic acids. Other sugars, such as rhamnose and fucose, may also be present, and the hydroxyl groups of sugars can be partially substituted with acetyl groups (Gírio et al. 2010). Unlike cellulose, hemicellulose composition varies depending on cell tissue and plant species (Chundawat et al. 2011). In fact it can be noted that:

- The principal hemicellulose of hardwoods is an O-acetyl-4-O-methylglucuronoxylans.
- The main hemicellulose of soft woods is an O-acetylgalactoglucomannan.

Table 1.4 Main chemical composition of some lignocellulosic feedstocks (Zhao et al. 2012)

Feedstock	Cellulose (%)	Xylan (%)	Galactan (%)	Araban (%)	Lignin (%)	Mannan (%)	Extractives (%)	Ash (%)
Hybrid poplar	48.6	14.6	0.3	0.3	21.8	0.5	NA*	0.7
White oak	43.6	18.0	0.4	2.4	23.2	2.9	NA	0.6
Red oak	43.4	18.9	NA*	1.9	25.8	2.7	NA	NA
Walnut	46.2	16.5	NA	1.8	21.9	2.6	NA	NA
Maple	44.9	17.3	NA	2.8	20.7	2.9	NA	0.4
Corn stover	40.9	18.0	1.0	3.0	16.6	0.6	7.3	9.7
Wheat straw	38.2	21.2	0.7	2.5	23.4	0.3	13.0	10.3
Rice straw	34.2	24.5	NA	NA	11.9	NA	17.9	16.1
Switchgrass	31.0	20.4	0.9	2.8	17.6	0.3	17.0	5.8

*NA: data not available

- The main hemicellulose in Gramineae (such as cereal straws) is arabinoxylans, which are similar to harwoods xylan, but the amount of L-arabinose is higher (Peng et al. 2011).
- Lignin is the organic substance which is responsible of binding the cells (Sticklen 2008). The three basic monomeric units constitute lignin: p-Hydroxyphenyls (H); Guaicyls (G); Syringyls (S).

Hardwood lignins are predominantly G and S monolignols with trace amounts of H units. Soft wood lignins are composed of mostly G units. Herbaceous plants contain all three units in significant amounts (Chundawat et al. 2011; Buranov and Mazza 2008).

1.3 First-Generation Biodiesel

1.3.1 Transesterification Reaction

The transesterification reaction with alcohol is represented by the general equation shown in Fig. 1.3a which consists of a number of consecutive, reversible reactions. These are shown in Fig. 1.3b. The first step is the conversion of triglycerides into diglycerides, and then diglycerides are converted into monoglycerides and monoglycerides into FFAs and glycerol. Each step yields one methyl ester molecule (Freedman et al. 1986; Noureddini and Zhu 1997). The transesterification can be both catalyzed by acid and alkali.

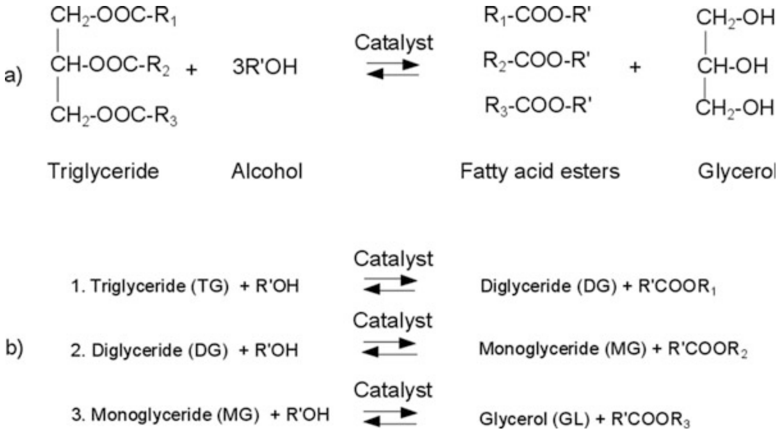

Fig. 1.3 Transesterification reaction (Eckey 1956)

Different types of catalyzed transesterification can be adopted (Lam et al. 2010):

1. Homogeneous base catalyst
2. Heterogeneous base catalyst
3. Homogeneous acid catalyst
4. Heterogeneous acid catalyst
5. Enzymes

State-of-the-art biodiesel production usually is done using base catalyst (e.g., KOH or NaOH). In that case reaction time can vary between 0.33 and 2 hours and yields are between 88% and 98% (Lam et al. 2010; Liu et al. 2010). Catalyst loading is between 1 and 6%wt, while methanol excess is between 7:1 and 9:1, expressed in molar ratio. Temperature can range between 60 and 87 °C (Lam et al. 2010). Also two-step catalysis can be a solution: first acid catalyst, then followed by basic catalysis.

Homogeneous acid catalyst usually can use H_2SO_4 or HCl. Heterogeneous basic catalysis can be performed using basic zeolites, alkaline earth metal oxides (e.g., CaO), and hydrotalcites. Heterogeneous acid catalyst can be zirconium oxide (ZrO_2), titanium oxide (TiO_2), tin oxide (SnO2), zeolites, sulfonic ion-exchange resin, sulfonated carbon-based catalyst, and heteropoly acids (HPAs) (Lam et al. 2010).

Enzyme catalysts lipases can be produced from several microorganisms, such as *Mucor miehei* (Lipozyme IM 60), *Pseudomonas cepacia* (PS 30), *C. antarctica* (Novozyme 435), *Bacillus subtilis*, *Rhizopus oryzae*, and *Penicillium expansum* (Lam et al. 2010; Liu et al. 2010, 2011a, b; Yan et al. 2014; Fan et al. 2016, 2017; Su et al. 2016; Li et al. 2017).

1.3.2 Biodiesel Production Process Diagram

Figure 1.4 shows the flow sheet of the production processes used for biodiesel.

Based on Fig. 1.4 scheme, it is assumed that alcohol, catalyst, and oil are inserted in the reactor and agitated for approximately 1 h at 60°C. Small plants often use batch reactors (Stidham et al. 2000), while larger plants (higher than 4 million liters/year) use continuous stirred-tank reactors (CSTR) or plug flow reactors operated in continuous mode (Assman et al. 1996).

Once methyl ester has been produced, it must be separated from the glycerol (through phase separation because glycerol is much heavier). Methyl esters undergo a neutralization step and then pass through a methanol stripper. A vacuum flash process or a falling film evaporator can be used for this purpose. Before washing with water, acid is added to the biodiesel to neutralize any residual catalyst and to split any soap that may have formed during the reaction. Soaps react with the acid to form water-soluble salts and FFAs. The salts are removed during the water washing step. The water washing step removes traces of catalyst, soap, salts, methanol, or free glycerol remained in the biodiesel. After the wash process, remaining water is removed from the biodiesel by flash-vacuum distillation.

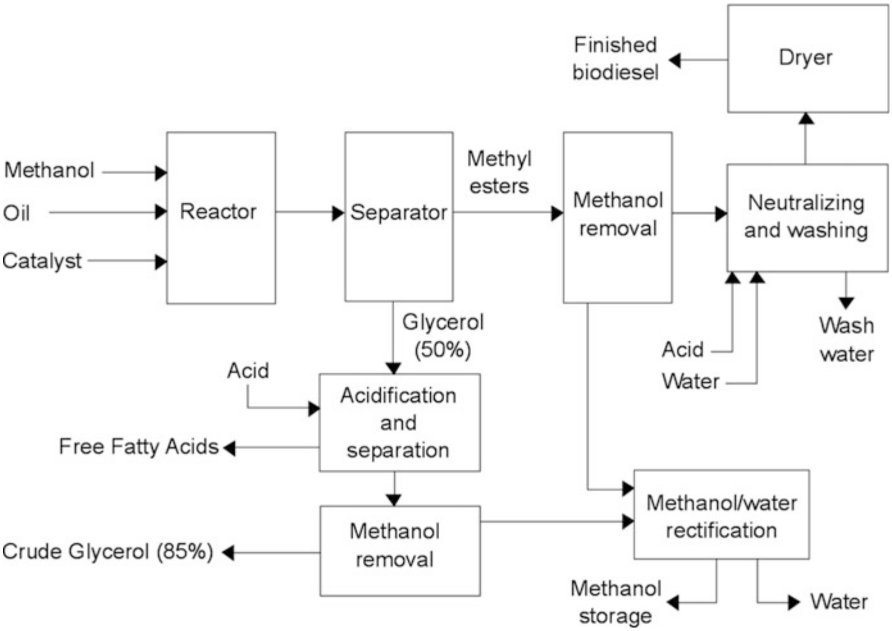

Fig. 1.4 First-generation biodiesel production flow sheet (Van Gerpen 2005)

The glycerol stream leaving the separator is composed only by about 50%wt glycerol. It contains also methanol, catalyst, and soap. The first step in glycerol refining is to add acid to split the soaps into FFAs and salts. The free fatty acids are not soluble in the glycerol and will rise to the top, so that they can be removed and recycled. The salts generally remain with the glycerol. The methanol mixed with the glycerol is removed by flash-vacuum distillation or conventional distillation. A purity of approximately 85% is reached; this allows to sell the glycerol to a refiner. Glycerol refining can be performed using vacuum distillation or ion exchange processes. A purity comprised between 99.5%wt and 99.7%wt is achieved.

The methanol that is removed from the methyl ester and from glycerol is mixed with water after separation has been performed. This water should be removed in a distillation column before the methanol is recycled into the process.

1.4 Bioethanol

1.4.1 Production of Ethanol from Sucrose

Sugar cane, sugar beet, and sweet sorghum are crops which contain sugars, which can be used as feedstock for ethanol production. Their main advantages are high yield of sugar per hectare and low conversion costs.

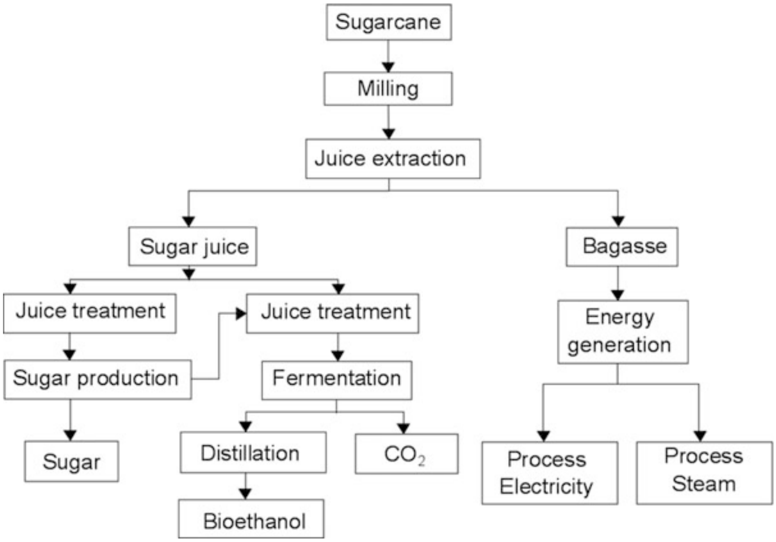

Fig. 1.5 Bioethanol production from sugar juice (Vohra et al. 2014)

Sugarcane has become a very effective source of biofuel, given that:

1. Bagasse can be used to generate process steam and electricity.
2. Vinasse (the liquid effluent) can be used as a fertilizer and irrigation supply to the cane fields (Kojima and Johnson 2005).

Sugar cane must be processed within 24–72 h after being harvested. Sugar is first extracted by crushing the stalks, to release the juice (Fig. 1.5). Calcium hydroxide is then added to precipitate the fiber and the sludge, and the mixture is then filtered. The filtrate solution is evaporated to concentrate and crystallize the sugar. The sugar is removed by centrifugation.

The sugar which is not crystallized and the accompanying salts are concentrated to form a syrup called molasses. These are used to produce ethanol (Kojima and Johnson 2005). To achieve the optimum fermentation efficiency of yeast *Saccharomyces cerevisiae*, the sugar content in the molasses has to be adjusted in the range of 14–18%wt. The typical temperature of the fermentation process is about 33–35 °C, while cell density is about 8–17% (v/v). Cell recycle system can be used to concentrate yeasts and recycle them into the process, obtaining high cell densities, which shorten fermentations to 6–10 h (Wyman 2004). Fermentation is interrupted at concentration of approximately 10% (v/v) ethanol. Fermentation reaction is the following:

$$\mathrm{C6H12O6} \rightarrow \mathrm{2C2H6O} + \mathrm{2CO2} \tag{1.1}$$

The next step is represented by distillation and rectification. An azeotropic solution of 95% (v/v) ethanol is obtained. Further concentration to absolute ethanol is finally achieved by molecular sieves or azeotropic distillation (using benzene or cyclohexane) (Chiaramonti 2007).

1.4.2 Bioethanol Production from Starch

As reported in Table 1.3, grains (corn, wheat, or barley) mainly provide starch. This is made up of long chains of glucose units. The amylose structure contains 1000 monomeric units, while the amylopectin structure contains 1000–6000 units. Starch is the most utilized for ethanol production in North America and Europe. To produce ethanol it is necessary to hydrolyze the starch into monomers. The hydrolytic reaction is catalyzed by glucoamylase enzyme. D-glucose, which is an isomer of glucose, is obtained as final hydrolysis product. Enzymatic hydrolysis is then followed by fermentation, distillation, and dehydration to yield anhydrous ethanol (Kumar et al. 2010).

There are two distinct methods for processing corn: wet milling and dry milling. Dry mills are usually smaller in size and are built primarily to produce only ethanol. Wet mill facilities also produce a list of high-valued co-products such as high-fructose corn syrup, corn oil, and corn gluten.

Corn dry-milling process is carried out in five steps (Vohra et al. 2014):

(i) Biomass handling (milling)
(ii) Liquefaction
(iii) Hydrolysis (saccharification)
(iv) Fermentation
(v) Distillation and recovery

In dry-grind process, the corns are milled to a powder and heated with water at 85°C (Kojima and Johnson 2005). Then hot water and alpha-amylase enzymes are added and the mixture is heated at 110–150 °C for an hour. This causes the liquefaction of starch. When liquefaction is completed, the mixture is cooled down and glucoamylases are added to produce dextrose. In dry-grind milling plants, often the glucoamylases are directly added into the fermentor. The process is known as "simultaneous saccharification and fermentation" (SSF) (Fig. 1.6).

In the fermentation process, yeasts convert glucose into ethanol and carbon dioxide. The process is completed in about 40–50 h. During fermentation, the mash is continuously mixed and it is cooled down. The beer obtained from fermentation is transferred to the distillation columns where ethanol is separated from the stillage (Singh et al. 2001). The stillage contains protein, oil, and fiber and are dried to obtain dried grains with solubles (DDGS) or just distillers dried grains (DDG). DDGS contain the process syrup combined with the solids, while DDG don't contain it.

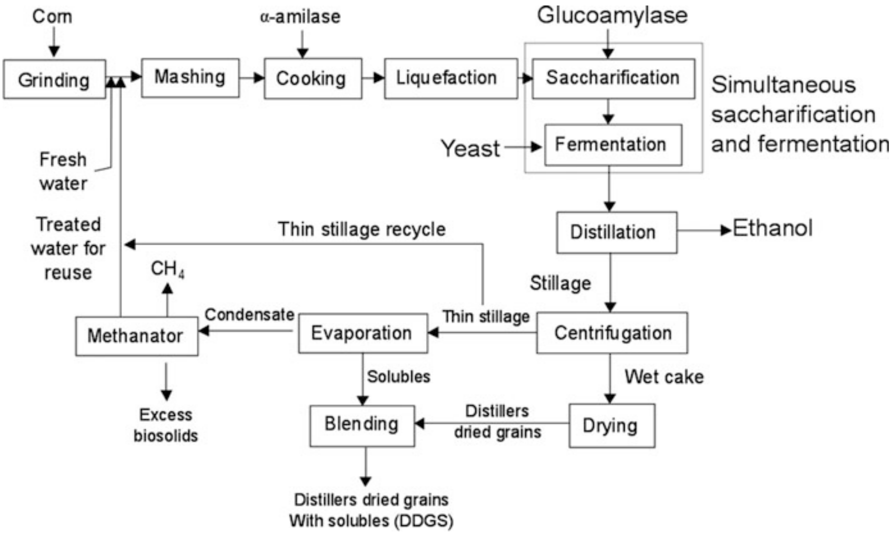

Fig. 1.6 Corn dry milling process flow diagram (Vohra et al. 2014)

In wet milling the shelled corns pass through mechanical cleaners designed to remove unwanted material, such as pieces of cobs, sticks, husks, meal, and stones. The cleaned corns are then fed into “steep” tanks, where they are soaked in dilute sulfuric acid and remain for 24 to 48 h at a temperature of about 52°C. Steeping softens the kernel and helps to break down the protein holding the starch particles. Generally, water drained from the steep tank, called “light steep water” contains about 6% of the original dry weight of the grains and is discharged to multiple-effect evaporators. The solids from steep water are rich in protein and are concentrated to 30–55% solids. The resulting steeping liquor can be sold as animal feed (May 1994) (Fig. 1.7).

The germ is removed from the steeped corn in the degerminating mills, which break the kernel to free the germ, the starch, and the gluten. The germ is separated in liquid cyclones from the mixture of fiber, starch, and gluten. It is then washed, dewatered, dried, and further processed to extract corn oil (Bothast and Schlicher 2005).

The starch and gluten are separated from the fiber by further washing, grinding, and screening operations. The solids and the fiber are used as a feed. The starch is separated from the gluten by centrifugation (May 1994; Bothast and Schlicher 2005). Once the pure starch slurry is obtained, the wet-mill process is similar to that of dry milling. First, the pH of the slurry is adjusted to 5.8–6.2 with calcium hydroxide, and then alpha-amylase is added to convert the starch into soluble short-chain dextrins (liquefaction). Calcium is often added (20–100 ppm) to enhance enzyme stability.

The slurry from the liquefaction stage is mixed with heat-sterilized steep water and sent for saccharification. The steep water provides both the fermentation

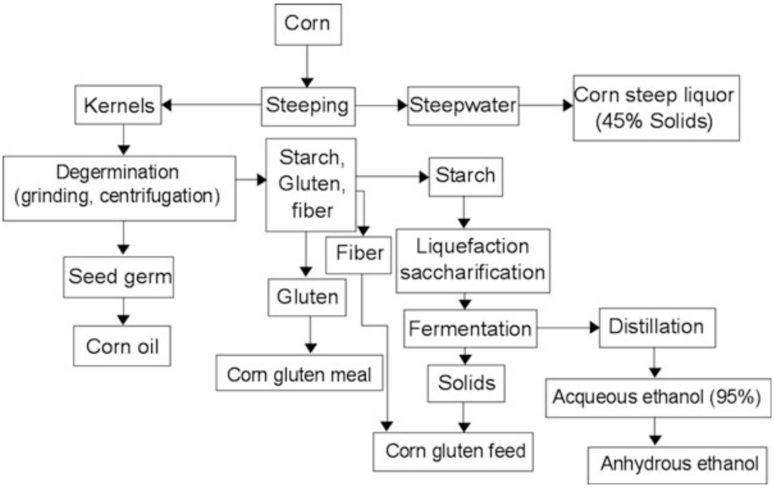

Fig. 1.7 Corn wet milling process flow diagram (Vohra et al. 2014)

nutrients and pH adjustment for saccharification, in which the glucoamylase converts the dextrins to glucose at a pH of 4.5 and a temperature of 65 °C. Then *S. cerevisiae* is added to ferment the sugars to ethanol and CO_2. The total fermentation time varies from 20 to 60 h. The final product from a continuous process will have an ethanol content of 8–10%v (Kojima and Johnson 2005; Bothast and Schlicher 2005).

1.4.3 Bioethanol Production From Lignocellulosic Feedstock

Bioethanol produced from lignocellulosic materials is commonly known as second-generation bioethanol. There have been huge research efforts in developing economically feasible advanced technologies for ethanol production; however, some challenges are still remaining (Cheng and Timilsina 2011). Chemical composition of lignocellulosic materials is the key factor affecting efficiency of biofuel production. Cellulose and hemicellulose are more present in hardwoods (78.8%) than softwoods (70.3%), while lignin is more present in softwoods (29.2%) than hardwoods (21.7%) (Balat 2011). According to (Vohra et al. 2014), the technologies for the conversion of lignocellulosic feedstocks to ethanol can be grouped into two broad macrocategories:

- The sugar platform (biochemical conversion)
- The syngas platform (thermochemical conversion)

The sugar platform uses enzymes to convert lignocellulosic biomass materials into sugars, while the syngas platform gasifies biomass and converts syngas into ethanol (Datta et al. 2011).

The biochemical platform consists of three main processes (Cotana et al. 2015; Barbanera et al. 2018; Buratti et al. 2015, 2018; Cavalaglio et al. 2016):

- Pretreatment
- Enzymatic hydrolysis
- Fermentation

1.4.3.1 Pretreatment

The pretreatment process significantly affects all the downstream processes and ultimately influences the overall biofuel yield and cost.

Pretreatment step can be performed through biological, physical, and chemical processes or a combination of them. Chemical methods use dilute acids (such as sulfuric or hydrochloric acid), alkalis (such as calcium hydroxide), and liquid ammonia (the ammonia fiber explosion pretreatment), while a physical method is represented by steam explosion (Ruane et al. 2010).

Pretreatment with dilute acid and intermediate temperatures is generally considered quite cost-effective. It loosens the cell wall matrix through degradation of hemicelluloses. Lignin is unaffected by this process. Accessibility to cellulose microfibrils is increased to provide a higher yield of sugars for fermentation. Acid treatment will result in other high-value products like furfural, hydroxyl-methyl furfural (HMF), phenolics, aldehydes, and aliphatic compounds. These products have to be removed before using the residues for further biochemical treatments. Acid pretreatment processes have to be followed by neutralization and detoxification (Kurian et al. 2013).

Steam explosion is the physical treatment where the lignocellulosic biomass is subjected to high pressures and temperatures for short duration, followed by the rapid decrease to atmospheric pressure, which will break the polymeric bonds in the substrate. Temperatures can range between 180 and 250 °C, pressures can range between 1 and 5 MPa (Jacquet et al. 2011).

Steam explosion has the following advantages:

- Lower capital investment
- Significantly lower environmental impact
- More potential for energy efficiency
- Less hazardous process conditions
- Complete sugar recovery

To compare steam explosion conditions, the severity factor has to be taken into account, defined as (Li et al. 2005)

$$\mathrm{S}_0 = \log\{\exp[(\mathrm{T} - 100)/14.75]\mathrm{t}\} \tag{1.2}$$

where T is the temperature (°C) and t is the duration of treatment (min).

Steam explosion is considered the most cost-effective option for hardwood and agriculture residues, while it is less effective for softwood. Acid catalysis can be used also within the steam explosion treatment and is found to reduce the temperature and the retention time. Another advantage is that complete hydrolysis of hemicellulose can be achieved (Mood et al. 2013).

1.4.3.2 Hydrolysis

During the hydrolysis, polysaccharides are broken down to simple sugars. Two examples of hydrolysis methods of cellulose into glucose are (Lynd et al. 2002):

1. Concentrated acid (H_2SO_4 30–70%, 40 °C, a few hours to achieve >90% glucose yields)
2. Enzymatic hydrolysis (cellulase mixture, 50 °C several days to reach 75–95% glucose yields)

The current trend is to use enzymatic hydrolysis to avoid costly recovery and wastewater treatment requirements, resulting from the use of acid hydrolysis. Enzymatic hydrolysis is attractive because it produces better yields than acid-catalyzed hydrolysis and enzyme producers have recently reduced their cost using biotechnology (Ruane et al. 2010). The conversion of cellulose and hemicellulose is catalyzed by cellulase and hemicellulase enzymes, respectively.

1.4.3.3 Fermentation

The ability to use the hemicellulose component in biomass feedstock is critical for any bio-ethanol plant. *Saccharomyces cerevisiae* and *Zymomonas mobilis*, the commonly employed organisms in alcohol fermentation, are not able to ferment hemicellulose-derived pentose (C5) sugars. There are organisms that can ferment C5 sugars (e.g., *Pichia stipitis*, *Pachysolen tannophilus*, *Candida shehatae*), but their efficiencies are low. They also need microaerophilic conditions. This implies that for more than 20 years research activities have focused on the development of improved microorganisms for the fermentation of pentose sugars (Hahn-hägerdal et al. 2007). Besides this, currently there are not known natural organisms that have the ability to convert both these C6 and C5 sugars at high yields. While pentose fermentation has been achieved on ideal substrates, (i.e., laboratory preparations of sugars designed to imitate a perfectly pretreated feedstock), significant work remains to apply this to real lignocellulosic feedstocks (Sims et al. 2008). Lignocellulosic biomass conversion into bioethanol flow diagram is shown in Fig. 1.8.

A typical process for making cellulosic ethanol starts with pretreatment and separation of the insolubles. The insoluble fraction is then hydrolyzed with cellulase and glycosidases to release glucose, which is fermented to produce ethanol. The residual insoluble material, mostly lignin, is burned to generate energy (Ruane et al. 2010). If the fermentation process is performed after the hydrolysis, this is called separate hydrolysis and fermentation (SHF). The fermentation process produces wastewaters which can be used to recover a nutrient-rich microbial cell mass (Kurian et al. 2013). Pentose fermentation, when it is carried out, is accomplished in an independent unit. The advantage of SHF is the ability to carry out each step under

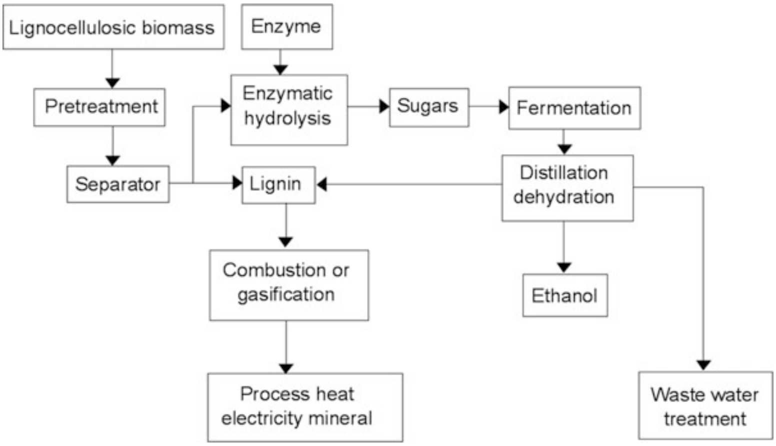

Fig. 1.8 Lignocellulosic biomass conversion into bioethanol process flow diagram (Vohra et al. 2014)

optimal conditions, i.e., enzymatic hydrolysis at 45–50 °C and fermentation at about 35 °C (Cardona and Sanchez 2007; Kurian et al. 2013). Hydrolysis and fermentation can also be performed through integrated techniques, such as simultaneous saccharification and fermentation (SSF), simultaneous saccharification and co-fermentation (SSCF), and consolidated bioprocessing (CBP) (Vohra et al. 2014).

1.4.3.4 Bioethanol Production Through Syngas Fermentation

Syngas conversion using microbial catalysts offers three main advantages:

- It requires significantly lower temperature and pressure conditions (usually atmospheric conditions).
- It is less susceptible to varying feed gas compositions.
- Chemical catalysts are more susceptible to poisoning, compared to microbial processes (Köpke et al. 2011).

After biomass gasification has been performed, cleaned gas is cooled to the normal ambient temperature and stored at a high pressure. The gas is then fed into an ethanol conversion chamber, where microbes ferment it into ethanol and acetic acid. After fermentation is completed, the liquid is distilled to separate ethanol from other products. Then ethanol is dehydrated (Dwivedi et al. 2009); see Fig. 1.9.

A large number of bacterial strains have been isolated that have the ability to ferment producer gas (composed by CO, CO2, and H2) to ethanol, acetic acid, and other useful liquid products; see, for example, Clostridium ljungdahlii (Henstra et al. 2007), *Butyribacterium methylotrophicum*, and *Clostridium autoethanogenum* (Abubackar et al. 2011).