The Global Scenario of Biofuel Production and Development

Mingxin Guo

Abstract Bioenergy has been ranking number one among all forms of renewable energy consumed by human beings. Over the past two decades, tremendous investment has been made in biofuel development and production. This chapter reviews the global research, refinery, and utilization of biomass-based liquid biofuels as transportation petro-fuel substitutes. There are four major types of liquid biofuels: bioethanol, biodiesel, pyrolysis bio-oil, and drop-in transportation fuels. Bioethanol has been commercially produced from lignocellulosic materials since 2013, supplementing the annual 25.7 billion gallons from food crops. Biodiesel from oilseeds and animal fats reached the 8.3 billion gallons/yr production capacity, with further increases depending on new feedstock development. Pyrolysis bio-oil and most drop-in transportation fuel candidates are still in the development stage, facing cost-effective conversion and upgrading challenges. Commercial production of two drop-in biofuels, hydrotreated vegetable oil (HVO), and Fischer–Tropsch liquids has just started or is starting. Overall, the global development and consumption of bioenergy and biofuels are steadily advancing, particularly in the cellulosic bioethanol and HVO sectors. By 2050, biofuels will likely account for 27% of the world's liquid transportation fuel supply.

Keywords Bioenergy · Biofuel · Bioethanol · Biodiesel · Drop-in fuel · Fischer–Tropsch liquids · Hydrotreated vegetable oil · Lignocellulosic biomass · Pyrolysis bio-oil

1 Introduction

In physics, energy is defined as "the capacity of a physical system to perform work," and work is "to move a physical object against a force over a distance." Energy exists in various forms that can be classified into two broad categories: kinetic

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energy (electric energy, thermal energy, radiant energy, and motion energy) and potential energy (chemical energy, nuclear energy, mechanical energy, and gravitational energy) (Aubrecht 2005). The energy stored in biomass is termed "**bioenergy**," a chemical energy in the potential energy category. The First Law of Thermodynamics states that energy can be converted from one form into another, or transferred from one object to another, but it cannot be created or destroyed (Hasse 1971). When biomass is combusted, bioenergy is transformed into thermal energy (heat) and radiant energy (light) and released into the environment.

Bioenergy originates from solar energy. Plants, algae, and cyanobacteria utilize solar energy (predominantly 400–700 nm radiation) to synthesize organic matter from CO_2 through photosynthesis. To produce 1 g of biomass carbon, approximately 833 kJ of solar energy are absorbed but less than 5% of it (~39 kJ) is transformed to chemical energy and stored in the synthesized carbohydrates (Klass 1998). Globally soil-grown plants produce around 120×10^{15} g of dry biomass (equivalent to ~56×10^{15} g organic carbon) each year (Broadmeadow and Matthews 2003, Beer et al. 2010), storing 2.2×10^{18} kJ of bioenergy. The annual bioenergy generation through terrestrial plant photosynthesis nearly quadruples the present global energy need (~5.6×10^{17} kJ; Enerdata 2015). However, not all land is accessible and can be used to produce bioenergy for human purposes. Cropland, remote areas, wildlife habitats, and domestic facilities occupy a significant portion of the world's total land surface. The practical bioenergy potential of the Earth's terrestrial ecosystem is predicted at 1.9×10^{17} kJ yr^{-1} (Haberl et al. 2013), deliverable to meet one-third (~34%) of the global energy consumption at the present level (Enerdata 2015).

When biomass and its processed products are combusted, the inherent bioenergy is released in heat and light. If used for energy purposes (except for food consumption), the biomass materials are termed "**biofuels**." Broadly, biofuels can be of solid, liquid, and gaseous forms, all combustible and carbon-rich. Starting from the discovery of fire at the dawn of human history, biofuels have been utilized to provide energy in numerous civic activities. Wood was the primary fuel worldwide before the twentieth century. Wide exploitation and use of coal, petroleum, and natural gas for energy did not start until the early nineteenth century (Hulse 1999). It was in 1881 that the USA began to consume more fossil energy than bioenergy. Today 87% of the US energy demand comes from fossil fuels (EIA 2013a). Worldwide, fossil energy shares nearly 80% of the global energy consumption (IEA 2013a). The intensive mining and consumption of fossil fuels, however, have generated disastrous environmental impacts. The uneven distribution and dwindling supply of fossil fuels further pose threats to modern energy independence and security (IEA 2013b). In the past two decades, tremendous endeavors have been made to develop and utilize renewable energy including bioenergy, hydropower, solar energy, wind electricity, and geothermal heat.

The world transportation relies on liquid fuels. Petroleum is refined to produce gasoline, diesel, aviation fuel, bunker fuel, and other liquid fuels to power vehicles, aircrafts, and ships. The global daily consumption of petroleum mounted to 93.2 million barrels (1 barrel = 42 gallons) in 2014 (EIA 2015a). Every day 930 million gallons of gasoline are being used worldwide by more than 600 million traveling passenger cars. The US daily consumption of gasoline was 384.7 million gallons in 2015 (EIA 2016a). To produce liquid fuels, biomass is the sole **renewable** feedstock. More important, biomass is extensively available from well-established production systems, engendering the practicality of manufacturing renewable liquid biofuels. Tremendous research has been carried out to develop efficient techniques for converting biomass into liquid fuels such as bioethanol, biodiesel, pyrolysis bio-oil, and drop-in transportation fuels. Bioethanol and biodiesel have been increasingly produced in many countries since 1980 to supplement the petro-gasoline and diesel supply. For example, 6% of the global crop grains went to biofuel production in 2014 (REA 2015); in the same year, 37% of the US corn grain was used to generate 14.3 billion gallons of bioethanol (IAState 2015). The European Union (EU) has established the goal to meet 10% of its liquid transportation fuel demand with biofuels by 2020 (USDA 2015). As such, biofuels mostly refer to biomass-based liquid fuel products, though there are solid biofuels (e.g., firewood) and gaseous biofuels (e.g., biomethane). This chapter adopts the narrow meaning of "biofuel." It reviews the development and production of various liquid biofuels from different biomass materials in the global scenario, helping envisage the future of biofuels. Perspectives of other solid and gaseous biofuels can be found in Guo et al. (2015).

2 Development and Production of Bioethanol

Most four-wheeled passenger automobiles are powered by a four-stroke, spark-ignition internal combustion engine that runs on gasoline, a liquid (density ~0.745 g cm^{-3} at 15 °C) of C_4–C_{12} hydrocarbon mixture (higher heating value 46.5 kJ g^{-1}) refined from petroleum by fractional distillation (1 barrel of crude oil yields 19 gallons of gasoline). Today, gasoline engine vehicles and gasoline supply infrastructure are all over the world and become a critical component of the modern economy.

The supply of gasoline depends solely on the availability of petroleum, the so-called crude oil formed from the remains of ancient marine organisms under specific geologic conditions (e.g., high temperature and high pressure) over millions of years (NGS 2013). Petroleum exists only in underground pockets of certain geographic locations, and therefore, reliance on crude oil for gasoline poses threats to the energy independence and security of many nations. The energy crisis in the 1970s during which the USA, Western Europe, Japan, and other industrial countries suffered from extraordinarily high crude oil price and severe gasoline shortage, for example, was caused by the petroleum export embargo from Organization of the Petroleum Exporting Countries (OPEC) and the Islamic Revolution-induced social chaos in Iran (a major crude oil exporting country) (Lifset 2014). Moreover, petroleum is non-renewable; its limited reserve can only maintain the supply of crude oil at the current trading flow into the future 50 years (IEA 2013b). In addition, extraction of crude oil and consumption of gasoline have engendered enormous environmental impacts such as water pollution, wildlife habitat destruction, and climate change.

Renewable fuels alternative to gasoline have been intensively researched, especially in the recent fifteen years.

Biomass-derived ethanol or **bioethanol** is such a candidate. Ethanol, a 2-C alcohol with the chemical formula CH_3CH_2OH, is a clear, volatile, and combustible liquid at room temperature. Bioethanol is typically generated by alcoholic fermentation of plant sugars (e.g., the hexoses glucose, fructose, mannose, and galactose and the pentoses xylose, arabinose, and ribose) and used as a fuel. If used as a beverage, the liquid is called "alcohol." Alcoholic fermentation is activated by zymase-producing yeast and can be described by the following reactions:

$$C_6H_{12}O_6 \text{ (glucose, fructose, mannose, etc.)} \overset{\text{yeast}}{\rightarrow} 2C_2H_5OH \text{ (ethanol)} + 2CO_2 \quad (1)$$

$$3C_5H_{10}O_5 \text{ (xylose, arabinose, ribose, etc.)} \overset{\text{yeast}}{\rightarrow} 5C_2H_5OH \text{ (ethanol)} + 5CO_2 \quad (2)$$

Plant tissues are composed predominantly of cellulose, hemicellulose, and lignin (Table 1). Of these three backbone construction compounds, cellulose and hemicellulose are polysaccharides and can be hydrolyzed into simple sugar molecules. These two constituents account for up to 70% of dry plant matter (Table 1). Cereal grains (e.g., corn, wheat, and rice) and tuberous roots (e.g., yam, potato, and cassava) are rich in starch (a polysaccharide). Sugar beets, sugarcane, and sweet sorghum are abundant in sugar (sucrose, a disaccharide). Cellulose, hemicellulose, starch, sucrose, and simple sugars (monosaccharides or sugar monomers such as glucose, fructose, mannose, galactose, xylose, and arabinose) are carbohydrates, consisting solely of C, H, and O following the formula $(CH_2O)_n$, where $n \geq 3$. Through hydrolytic decomposition as shown in Eqs. 3, 4, and 5, polysaccharides and disaccharides can be transformed into simple sugars ready for alcoholic fermentation (Eqs. 1 and 2).

$$(C_6H_{10}O_5)_n \text{ (cellulose, starch)} + nH_2O \rightarrow nC_6H_{12}O_6 \text{ (glucose)} \quad (3)$$

Table 1 General biomass composition (% of dry weight) of lignocellulosic plant materials (Lee et al. 2007; Sannigrahi et al. 2010; Limayem and Ricke 2012; Serapiglia et al. 2013)

Raw material	Cellulose	Hemicellulose	Lignin	Ash
Crop residues	30–50	15–40	10–20	3–9
Hardwood	40–50	25–35	20–25	0.80
Softwood	40–45	25–30	25–35	0.50
Herbaceous plants	25–45	15–35	10–20	3–12
Newspaper	40–55	25–40	18–30	0–2
Switchgrass	30–45	25–30	15–20	4–9
Shrub willow	39–45	31–35	20–23	0.5–2.2
Hybrid poplar	42–49	17–23	21–30	0.6–2.0

$$C_{12}H_{20}O_{10}\text{ (sucrose)} + 2H_2O \rightarrow C_6H_{12}O_6\text{ (glucose)} + C_6H_{12}O_6\text{ (fructose)} \quad (4)$$

$$C_m(H_2O)_n\text{ (hemicellulose)} + H_2O \rightarrow C_6H_{12}O_6\text{ (hexoses)} + C_5H_{10}O_5\text{ (pentoses)} \quad (5)$$

Considering the dominant presence of cellulose and hemicellulose in plant tissues (Table 1), all vegetative materials are potential feedstocks for simple sugars (Eqs. 3, 4, and 5) and bioethanol (Eqs. 1 and 2). In plants, however, cellulose, hemicellulose, and lignin are interwoven with one another to form a recalcitrant structure of cell walls (Fig. 1). It is rather difficult to separate cellulose and hemicellulose from lignin in twisted fibrils and decompose the polysaccharides into sugar monomers. All the currently designed procedures for the purpose are inadequate in rate and efficiency, requiring stringent conditions and specialized enzymes. Even worse, the resulting

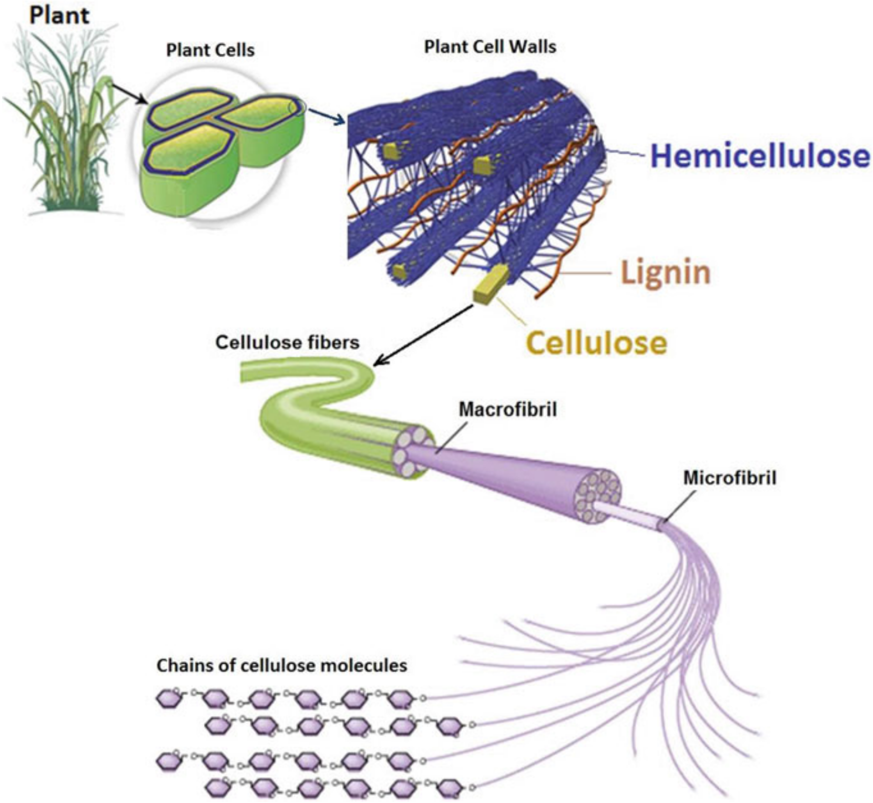


Fig. 1 Interwoven structure of lignocellulosic plant materials

sugars are generally unstable in rigorous environments, degrading to other compounds prior to alcoholic fermentation. Further research is needed to develop practical "pretreatment" methods for efficiently extracting sugars from lignocellulosic materials.

2.1 Food Crop-Derived Bioethanol

Figure 2 illustrates the common procedure for generating bioethanol from starch- and sugar-based feedstocks. The procedure covers three major phases: (1) conversion of starch in food crops to simple sugars or extraction of sugar from sugarcane/beets, (2) fermentation of sugars to ethanol, and 3) refinery of ethanol from the fermentation beer. In a dry-milling corn ethanol plant, for example, pre-cleaned dry corn grains (moisture ≤14%) are milled to <4 mm flour (the milling step) and added with water to form cornmeal slurry. The slurry is conditioned in a cooker at 40–60 °C for 12 h and then cooked (with heat from steam) at 110–120 °C for 2 h to prepare a corn mash (the cooking step). Prior to cooking, corn germ can be recovered by flotation and skimming for oil extraction (Singh and Eckhoff 1999). The mash, with pH 6.0–6.5, is then cooled by settling to 80–90 °C, added with the enzyme α-amylase, and liquefied for at least 30 min (the liquefaction step). The liquefied corn mash is further cooled to 30 °C, added with another enzyme glucoamylase, and settled for 30 min to allow conversion of starch to glucose (the saccharification step). The corn mash is transferred to a fermenter, where yeast is added to start ethanol generation at 32 °C for 48 h (the fermentation step). In fact, continuing saccharification concurs with

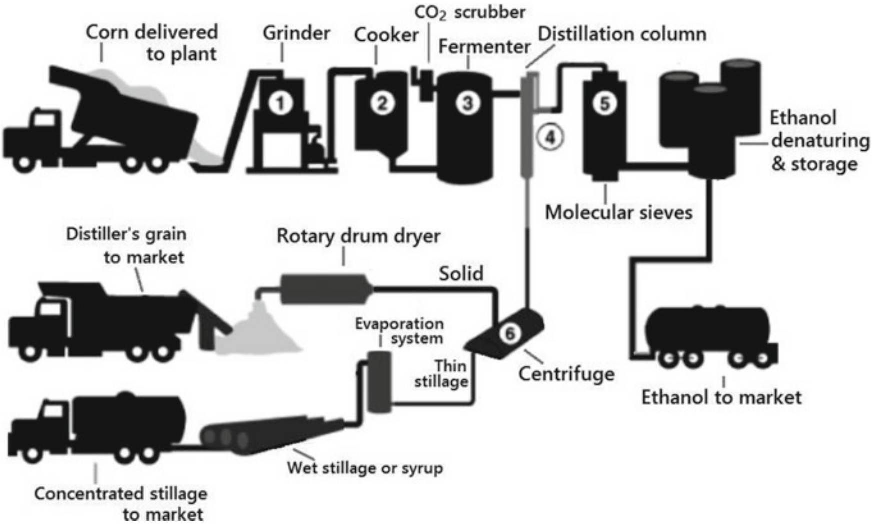


Fig. 2 Technical flow chart of bioethanol production from corn in the USA

fermentation in the fermenter. The fermented “beer” containing 8–12% ethanol by weight is then distilled to recover ethanol (the distillation step). The ethanol is passed through molecular sieves to remove water (the drying step), and gasoline is added at 2–5 vol% to denature its beverage function (the denaturing step) (Purdue Extension 2006). The stillage can be separated by centrifugation into the solid portion (dried distiller’s grain, DDG) and the liquid portion (thin stillage) and used as animal feed. Corn oil can be recovered from the thin stillage if it is not extracted before the “cooking” process. The entire corn ethanol process takes 55–60 h, with the average productivity of 2.7 gallons of ethanol per bushel (25.4 kg) grain. Different from dry-milling, the wet-milling corn ethanol technique starts with soaking corn kernels in dilute SO_2 solution for 48 h (steeping). The softened grains are then milled, removed of germ, bran fiber, and gluten protein, and the resulting starch slurry is further processed for ethanol (AMG 2013).

Currently, food crops are the predominant feedstock for commercial production of bioethanol. These food crops are high in starch or sugar content, exemplified as corn, wheat, barley, sugarcane, sugar beet, sweet sorghum, potato, yam, and cassava. In 2015, the world annual bioethanol production reached 25.7 billion gallons, of which merely 11.8 million gallons were from nonfood crops. The top five bioethanol production countries were the USA, Brazil, China, Canada, and France, contributing 57.7%, 27.6%, 3.2%, 1.8%, and 1.2% to the world 2015 bioethanol output, respectively (AFDC 2016a). The feedstocks used in these countries for bioethanol were corn, sugarcane, corn/wheat/cassava, corn/wheat/barley, and sugar beet/wheat/corn, respectively. In the past five years, the USA invested its 37–42% of annually harvested corn grains (~125 million tons) in bioethanol production, targeting on 10% replacement of the nation’s demanded gasoline (IAState 2015). Overall, the global commercial bioethanol production has been expanding rapidly, in particular since the beginning of the twenty-first century (Fig. 3). In 1980, the annual bioethanol production was 1.15 billion gallons. The number increased to 4.02 billion gallons in 1990 and to 4.52 billion gallons in 2000. In 2005, the annually produced bioethanol amounted to 8.23 billion gallons. The volume was abruptly raised to 23.31 billion gallons in 2010. It was further increased to 25.68 billion gallons in 2015 (Fig. 3). The USA has been the world’s largest bioethanol producer since 2000. Especially in the past six years, the USA produced more than 13.2 billion gallons of bioethanol each year, accounting for >55% of the global production (Fig. 3). When food crops are used as the feedstock, bioethanol competes with human food and animal feed for natural resources and, therefore, influences the global food security. As such, the EU has set up the 7% cap for investing its food crops in biofuels (EurActiv 2015). Indeed, the present food crops-based bioethanol production has nearly reached its practical potential.

Bioethanol has been used in gasoline blends. In the USA, E10 (blends consisting of 10 vol% ethanol and 90 vol% gasoline) is being supplied through all gas stations across the nation, E15 (blends containing 10.5–15 vol% ethanol) is fueling the 2001 and newer light duty cars, while E85 (blends containing 51–83 vol% ethanol) only applies to flexible fuel vehicles (FFVs) (AFDC 2016b). In the EU, supply of 5 vol% ethanol gasoline blends (E5) is mandatory; the ethanol blending rate will be elevated

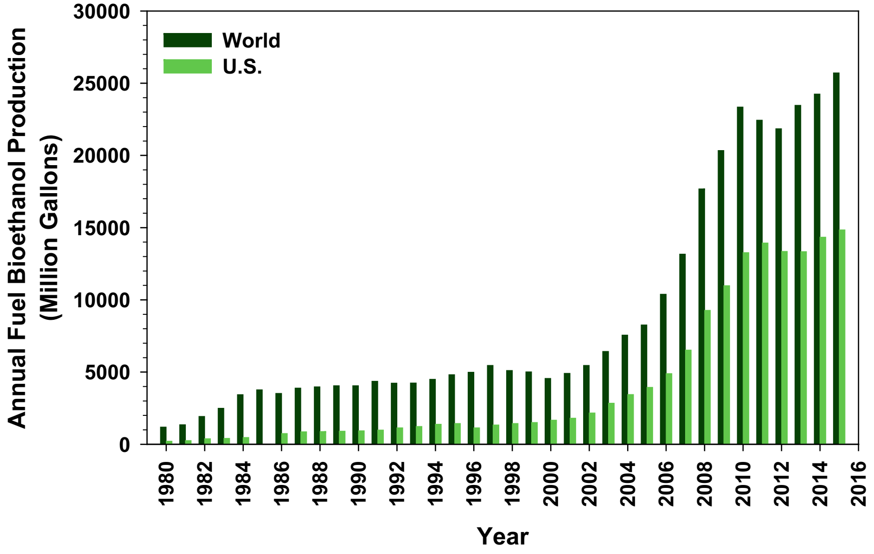


Fig. 3 The world and US fuel bioethanol production from 1980 to 2015. *Data sources* Licht (2012); RFA (2016); EIA (2014)

to 10 vol% in the soon future (EBTP 2015a). In Brazil, E25 (blends containing 25 vol% ethanol) is the fuel norm at gasoline stations (EBTP 2015a).

2.2 Nonfood Crop-Derived Bioethanol

Starch- and sugar-based bioethanol is categorized as one of the "**first-generation biofuels**," which source from food crops and, therefore, compete with human food and animal feed. Production of bioethanol from nonfood materials such as plant debris and algae has been enthusiastically explored, attempting to manufacture the "**second-generation biofuels**." Indeed, relative to food crops, lignocellulosic biomass is much more available, with wild grasses, forest thinnings, crop residues, yard trimmings, and food processing waste nearly everywhere. The US annual generation of vegetative residues is estimated at 1.02 billion tons, including 500 million tons of crop residues, 240 million tons of forestry debris, 210 million tons of municipal organic waste, and 65 million tons of animal manure (USDA 2006; McKeever 2004; EPA 2014). Globally, 3.76 billion tons of crop residues and 11.81 billion tons of forestry debris are generated each year (Lal 2005; FAO 2010). Furthermore, intensive research has been conducted to develop dedicated energy crops excelling in biomass yield, soil fertility and water requirements, climatic adaptation, and handleability. The promising candidates include switchgrass, miscanthus, shrub willow, and hybrid poplar (Bomgardner 2013). Typical annual biomass yields of these plants are demonstrated

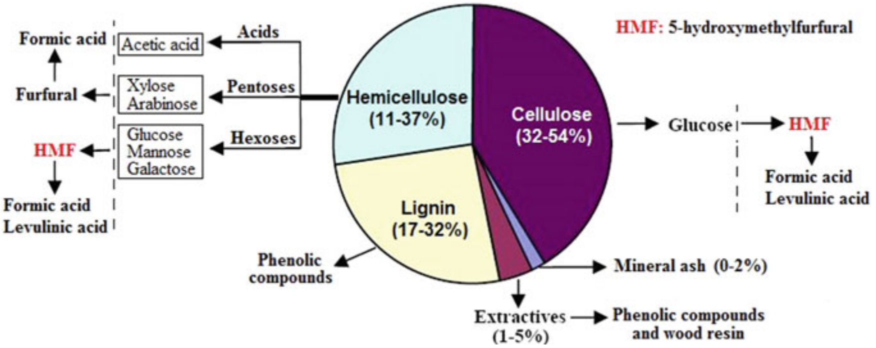


Fig. 4 Hydrolysis products of lignocellulosic materials and their further degradation compounds (chemicals behind the dashed line). *Source* Taherzadeh and Karimi (2007)

at 10–15, 13–25, 10–12, and 9–11 dry tons ha^{-1}, respectively (Fuentes and Taliaferro 2002; Pyter et al. 2007; Sannigrahi et al. 2010; Volk et al. 2011).

Based on their (hemi)cellulose contents (Table 1), lignocellulosic materials possess the ethanol potential of 97–113 gallons ton^{-1} (AFDC 2013a). The practical ethanol yields, however, are substantially lower. The major challenge is to effectively extract simple sugars from lignocellulosic materials and conserve the sugars from rapid degradation prior to fermentation (Fig. 4). Over the past two decades, breakthrough progress has been achieved in developing feasible cellulosic ethanol production systems. However, further technological and economic optimization of the system in feedstock supply, sugar extraction, and alcoholic fermentation remains necessary. Especially the technical efficiency and the involved cost for extracting sugars from lignocellulosic materials have not met the requirements of commercial-scale cellulosic ethanol production. To date, two extraction methods have been intensively tested for recovering sugars from lignocellulosic materials: acid treatment and enzyme treatment (Badger 2002). Acid treatment (acid-catalyzed hydrolysis) is to soak plant materials in an acid solution (e.g., sulfuric acid) to promote (hemi)cellulose hydrolysis for releasing sugars. If dilute acids (e.g., 1–10% H_2SO_4) are used, the treatment is typically carried out under high temperature (e.g., 237 °C) and high pressure (e.g., 13 atm) conditions. In such stringent environment, sugars can be rapidly transformed to furfural and other chemicals (Fig. 4), leading to the overall low sugar recovery (i.e., ~50% of the theoretical level assuming complete hydrolysis of feedstock (hemi)cellulose. The process, however, is prompt (i.e., <15 s) and can be conducted in a continuous feedstock flow. Trials with sawdust showed an ethanol productivity of 38 gallons/ton feedstock following the dilute acid treatment method (Badger 2002). Considering that pentoses (5-carbon sugars) are more susceptible than hexoses (6-carbon sugars) to a high temperature and high pressure environment, the acid treatment can be separated into two stages to improve the sugar recovery: in the initial stage, cellulosic materials are subject to mild conditions (e.g., 100 °C) for 2–6 h to allow hemicellulose to hydrolyze and release pentoses; the residual feedstock is then water rinsed, press-drained, and conveyed to the second stage hydrolysis in a rigorous environment (e.g., 230 °C) to recover hexoses (Lenihan et al. 2010). By the two-stage treatment method, the sawdust ethanol productivity was elevated to 55 gallons/ton feedstock (Badger 2002). Alternatively, concentrated acids (e.g., 30–40% H_2SO_4) could be used in the second stage to facilitate cellulose hydrolysis. In this case, the residual feedstock is typically soaked in the concentrated acid for 2–4 h at 100 °C. The resulting sugar/acid solution is then neutralized by lime and fermented for ethanol. The strong acid treatment takes longer time, but the sugar recovery can be increased up to 80%. Following this treatment method, corn stover demonstrated an ethanol productivity of 65 gallons/ton feedstock (Badger 2002). Enzyme treatment (or enzymatic hydrolysis) is to use active enzymes in place of inorganic acids to facilitate the hydrolytic decomposition of lignocellulosic feedstock. To prepare favorable substrate for enzymes to work efficiently, appropriate pre-processing of the feedstock becomes essential. Lignocellulosic materials are commonly pretreated by hydrothermal softening, ammonia fiber explosion, and dilute acid hydrolysis to help “unbraid” plant microfibrils (Kumar et al. 2009; Talebnia et al. 2010; Conde-Mejia et al. 2012). Other pretreatment methods have also been explored, such as steam explosion, lime extraction, co-solvent fractionation, dilute sulfite pulping, and ionic liquid deconstruction (Conde-Mejia et al. 2012; Nguyen et al. 2016; Xu et al. 2016). All these pre-processing methods are effective to disintegrate the rigid lignocellulosic structure (Fig. 1) through providing a temperature-, pressure-, and pH-controlled environment, but the preferable ones are those using a high solid/water ratio, yielding highly digestible (hemi)cellulose, causing minimal sugar degradation, consuming low chemicals and electricity, requiring low infrastructure cost, and having low operational risks and downstream waste (Novozymes 2016). Once cellulose and hemicellulose are liberated from the interwoven fiber structure (Fig. 1), the polysaccharides can be readily transformed into simple sugars (hexoses and pentoses, Fig. 4) by cellulolytic enzymes such as glycoside hydrolases. Substantial research endeavors have also been invested in selecting highly efficient, low-cost cellulases and carbohydrate esterases. The identified enzyme candidates, however, remain marginally satisfactory for commercial applications. Today the relatively high enzyme preparation cost is still a major factor throttling industrial-scale cellulosic ethanol production (Gies 2014). To improve the cellulose-ethanol conversion, more efficient yeast strains used in alcoholic fermentation have continuously been explored (Bratis 2013). Integration of best feedstock pre-processing, enzymatic hydrolysis, and alcoholic fermentation technologies allowed pilot cellulosic ethanol plants to achieve the cellulose saccharification rate up to 80% and the ethanol yield up to 90 gallons/ton cellulosic biomass (Novozymes 2016).

Alternative to the biochemical fermentation pathway, the thermochemical pathway has also been investigated to produce ethanol from lignocellulosic materials, in which the feedstock is transformed by gasification in a 700–900 °C, O_2-controlled chamber to syngas (a mixture of CO and H_2) and then synthesized into ethanol using particular catalysts ($3CO + 3H_2 \rightarrow CH_3CH_2OH + CO_2$) (NREL 2007; Gonzalez et al. 2012). Synthesis of ethanol from syngas may also be realized by anaerobic fermentation in a specially designed fermenter with acetogenic bacteria capable of utilizing CO and H_2 as the carbon and energy substrates (Liu et al. 2014).

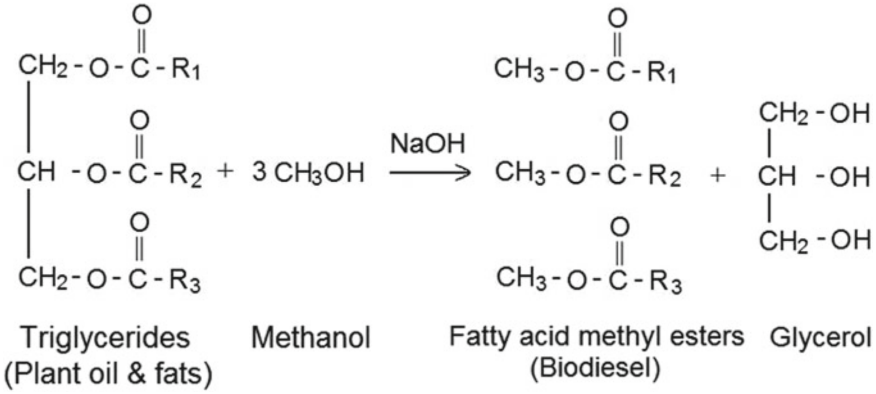
Practically, 75 gallons of ethanol would be generated per dry ton of lignocellulosic biomass (containing ~65 mass% carbohydrates), assuming an 80% (hemi)cellulose-sugar conversion rate (Johnson 2016). The 2015 commercial cellulosic ethanol production cost ranged from $2.63 to $3.16 per gallon (IEA 2015). Preparation of the required cellulase using lignocellulosic materials instead of glucose would reduce the cost to $2.36 per gallon (Johnson 2016). However, at above $2.15/gallon cellulosic ethanol is not cost competitive (NREL 2016). Even at the competitive cost level, cellulosic ethanol production could not be economically viable if the crude oil market price was below $80/barrel (IEA 2015). In fact, commercial production of cellulosic ethanol just started in October 2013 by the Crescentino Biorefinery (Crescentino, Italy), in which rice/wheat straw and giant reed were processed by dilute acid hydrothermal softening, enzymatic hydrolysis, and alcoholic fermentation to generate bioethanol. To date, there are nine operational commercial-scale cellulosic ethanol plants worldwide, with a total production capacity of 156.2 million gallons per year (MMGY): **Crescentino Biorefinery** at 20 million gallons per year (MMGY), **Enerkem Alberta Biofuels** (Edmonton, Canada) with thermochemical production of methanol and ethanol from municipal organic waste at 10 MMGY, **GranBio** (Alagoas, Brazil) with biochemical production of ethanol from sugarcane bagasse at 21.6 MMGY, **Raizen** (Piracicaba, Brazil) with biochemical production of ethanol from sugarcane bagasse and straw at 10.6 MMGY, **Abengoa Bioenergy** (Hugoton, KS, USA) with biochemical production of ethanol from corn stalk/grass/switchgrass at 25 MMGY, **DuPont Cellulosic Ethanol** (Nevada, IA, USA) with biochemical production of ethanol from corn stover at 30 MMGY, **Fiberight of Blairstown** (Blairstown, IA, USA) with biochemical production of ethanol from municipal vegetative waste at 6 MMGY, **INEOS-Indian River Bioenergy Center** (Vero Beach, FL, USA) with thermochemical production (gasification and anaerobic fermentation) of ethanol from municipal solid waste at 8 MMGY, and **Poet-DSM Advanced Biofuels** (Emmetsburg, IA, USA) with biochemical production of ethanol from corn stover/cobs at 25 MMGY (EPM 2016). Due to the high production cost, cellulosic ethanol has shared <0.05% of the overall bioethanol market since its emergence. In 2013, 2014, and 2015, for example, the US actual cellulosic ethanol volumes were 0.22, 0.73, and 2.2 MMGY, respectively, though the nation's cellulosic ethanol capacity (including demonstration, pilot, and commercial-scale plants) was above 100 MMGY (EPM 2016). Worldwide, the number of commercial cellulosic ethanol plants and the total production capacity has been slowly yet steadily increasing, indicating the thriving future of this nonfood renewable liquid fuel (Novozymes 2015).

The biomass of carbohydrate-rich algae such as the strains *Euglena gracilis*, *Prymnesium parvum*, *Sargassum horneri*, and *Gracilaria edulis* also serves as the potential feedstock for "second-generation bioethanol." Productive cultivation of target algae, however, is not cost-competitive. Currently, algal ethanol remains at the research stage (Oilgae 2016; Opposingviews 2016).

3 Development and Production of Biodiesel

Different from gasoline engine-powered passenger cars, heavy vehicles such as trucks and tractors are typically driven by mightier diesel engines. The ignition mechanism of diesel engines is different, and therefore, only diesel fuel can be used to run the engines. Slightly denser than gasoline, diesel is another refinery product of petroleum. One barrel of crude oil yields approximately 10 gallons of diesel by fractional distillation at 200–350 °C. In chemical nature, diesel is a C_8–C_{25} liquid hydrocarbon mixture that possesses a density of 0.835 g cm^{-3} (15 °C) and a higher heating value of 45.8 kJ g^{-1} (EIA 2013b; AFDC 2013b). The global annual diesel consumption is around 385 billion gallons, of which nearly 10% occurs in the USA (EIA 2013c; American Fuels 2014). Biomass-based liquid fuels have been developed to supplement the petro-diesel supply.

Biodiesel, a renewable biofuel produced from natural lipids via basic chemical transformation, is a substitute for petro-diesel. In the presence of an alkaline catalyst, the predominant component triglycerides of vegetable oil, animal fats, algal lipids, and waste grease react rapidly with methanol to form fatty acid methyl esters (FAME)—biodiesel. The reaction is termed transesterification and can be described as:



(6)

where R_1, R_2, and R_3 are aliphatic C_{11}–C_{24} hydrocarbon chains. Potassium hydroxide (KOH) can be used in place of NaOH as the catalyst if the resulting glycerol (glycerin) is disposed of by composting. The yield of biodiesel is dependent on the quality of the feedstock oil and fat (i.e., moisture, impurity, and free fatty acid contents), the reaction conditions (time, temperature, mixing, and airtightness), and the oil/methanol ratio. Under optimal conditions, up to 98% of the feedstock lipids can be transformed into biodiesel (Guo and Xiao 2012). The properties of biodiesel, however, vary with the lipid feedstock. In general, biodiesel is a mixture of numerous mono-alkyl fatty acid esters. It is a yellow-tinted, transparent liquid at room temperature, with density ranging from 0.873 to 0.884 g cm^{-3} and kinematic viscosity ranging from

3.8 to 4.8 mm s^{-2}. Compared with petro-diesel, biodiesel possesses a slightly lower energy density (38–45 kJ g^{-1}, ~90% of that of petro-diesel), a higher cloud point (−4 to 14 °C vs. −9.5 °C for No. 2 diesel), and a lower stability against oxidation (Hoekman et al. 2012). As a fuel, biodiesel low in cloud point but high in oxidation stability is more desirable. If feedstock oil contains high contents of long, saturated hydrocarbon chains, the derived biodiesel typically shows a higher cloud point and higher oxidation stability. Biodiesel generated from the oils rich in short, multi-unsaturated aliphatic carbon chains demonstrates a lower cloud point and lower stability (Hoekman et al. 2012). Evidently, the quality of biodiesel can be improved by manipulating the feedstock constitution.

Vegetable oil and animal fats have long been used in the human history as a fuel for lighting. It was until the 1900s that vegetable oils were tested for powering diesel engines (Knothe 2001). Due to its relatively high viscosity, however, raw vegetable oil failed to flow at desirable rates in the engine fueling system. An array of methods such as pre-heating, thermal cracking, and diesel mixing was attempted to reduce the viscosity of vegetable oil. The transesterification approach (Eq. 6) was discovered by George Chavanne, a Belgian scientist, who noticed that vegetable oils became much less viscous after reacting with methanol or ethanol. He patented the "Procedure for the transformation of vegetable oils for their uses as fuels" in 1937 (Knothe 2001). Forty years later, the Brazilian scientist Expedito Parente developed the first industrial biodiesel production process. In 1989, Austria established the first commercial biodiesel plant to produce diesel substitute from canola oil. Coming to the twenty-first century, the global production and demand for biodiesel have been progressively increasing, owing to the soaring crude oil price and the dwindling petroleum reserve.

Biodiesel feedstocks extend to plant oils, animal fats, and yellow grease (used cooking oil): theoretically all biomaterials that are rich in lipids. Many crops and trees have been intentionally cultivated for harvesting oilseeds to produce biodiesel, including canola, rapeseed, soybean, sunflower, camelina, castor bean, jatropha, tung, and palm (Table 2). The machinery and techniques for growing and harvesting soybean, peanut, sunflower and the oil food crops canola, rapeseed and camelina are existing, and therefore, biodiesel has been produced predominantly from these food crops. Food crop-based biodiesel belongs to the "first-generation biofuels." The biodiesel from nonfood crops such as jatropha, castor bean, tung, and algae is viewed as advanced biofuels or "second-generation (2G) biofuels." It is worthy to mention that significant research has been conducted to develop algal biodiesel. The algal strains with high body lipid accumulation have been screened, including *Chaetoceros calcitrans*, *Dunaliella teriolecta*, *Phaeodactylum tricornutum*, *Neochloris oleabundans,* and *Scenedesmus obliquus*. Commercial-scale algal cultivation and oil extraction, however, are not cost competitive at the current technological stage (Biofuels Digest 2014a; CleanTechnica 2015; DOE 2016a).

Figure 5 illustrates the general procedure for producing biodiesel from vegetable oil. The feedstock oil needs to be low in water and free fatty acids (FFA), with moisture <0.2% and the FFA value (amount of KOH required to neutralize one unit mass of oil) <5 mg/g. A measured volume of vegetable oil is transferred into the reactor.

Table 2 Average seed oil contents and typical seed yields of selected feedstock crops for biodiesel (AGMRC 2013)

Crop	Oil content (% dry mass)	Seed yield (kg ha^{-1})
Soybean	20.0	3363
Canola	43.8	2782
Rapeseed	40.0	2430
Camelina	35.0	1687
Sunflower	44.0	1697[a]
Peanut	48.5	4250[a]
Castor bean	50.5	2243
Jatropha seed	35.0	2500
Oil palm	35.0[b]	10,800[b]

[a] Include shell weight
[b] Fresh fruit

Methoxide (methanol + sodium hydroxide) is prepared by thoroughly dissolving NaOH at ~5 g L^{-1} oil in methanol (20% volume of the oil). The vegetable oil is heated to 50–60 °C, followed by addition of the prepared methoxide under stirring. The reactor is immediately closed and maintained at 50–60 °C to allow transesterification (Eq. 6) to carry out for 2 h under continuous agitation. The reacted mixture is then settled for 2–12 h at room temperature to separate crude biodiesel in the top layer from crude glycerin in the bottom layer. The crude glycerin containing excess methanol, the alkaline catalyst, and small amounts of soap and mono/di/triglycerides can be funnel-drained out of the reactor and refined to recover the methanol and purify the glycerin. The crude biodiesel containing excess methanol and trace quantities of soap and mono/di/triglycerides is typically purified by membrane refining or water washing to remove the impurities (Atadashi et al. 2011; Guo and Xiao 2012). Yellow grease usually contains high contents of FFA. If this material is used for biodiesel production, it needs to be pretreated by filtration and settling to remove solid particulates and water. Methanol and concentrated sulfuric acid are subsequently added to initiate "acid-catalyzed esterification" to transform FFA and part of the triglycerides into biodiesel. After removing the generated glycerin and the acid catalyst, the remaining mixtures are subject to transesterification reactions for further biodiesel production (Fig. 5).

The quality of biodiesel is regulated in the USA by the American Society for Testing and Materials (ASTM) standard D6751 and in Europe by EN14214, with specifications in flash point, cloud point, kinematic viscosity, cetane number, acid number, glycerin content, methanol content, water content, sulfur content, oxidation stability, and other parameters (eXtension 2012). Relative to petro-diesel, biodiesel demonstrates a cleaner emission profile and higher use safety. Biodiesel is normally distributed to end users in blends with petro-diesel. In the USA, the most common blend is labeled as B20, containing 6–20 vol% biodiesel. Low-level blends containing $\leq$5 vol% biodiesel do not carry distinct labels, while use of biodiesel as the sole fuel (B100) requires special handling and even equipment modifications and therefore, is

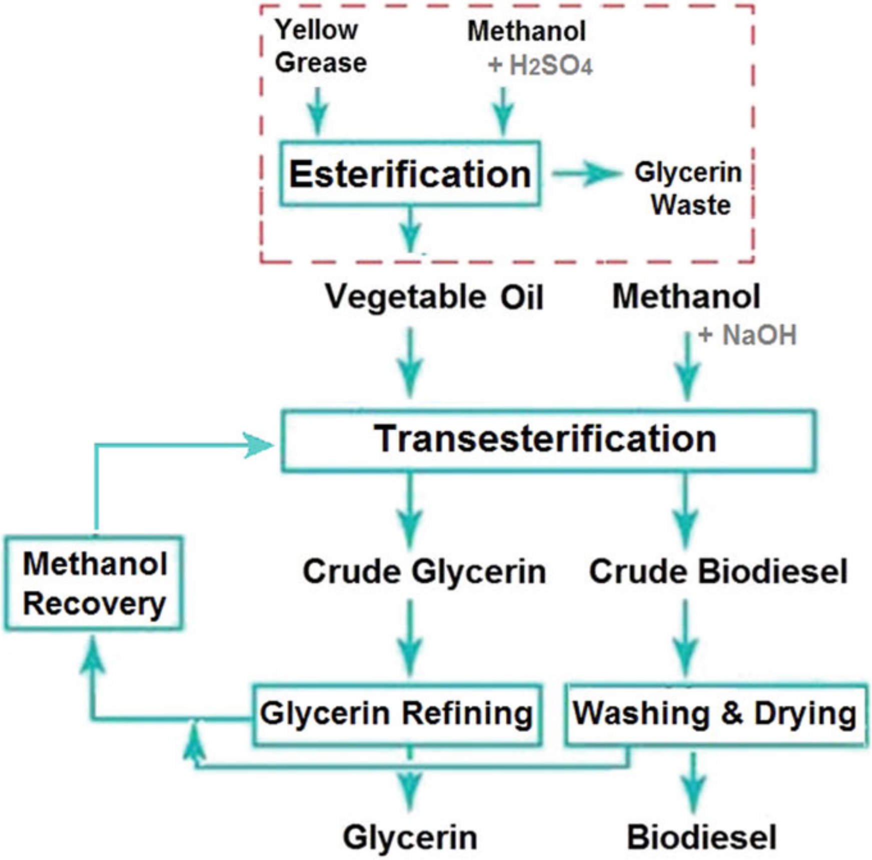


Fig. 5 Technical flow chart of biodiesel production from vegetable oil. If yellow grease (used cooking oil) is the feedstock, acid-catalyzed esterification (in the dashed square) is additionally needed at the beginning to remove excess free fatty acids

not encouraged (AFDC 2016c). In Argentina, use of B10 (10 vol% biodiesel blends) is mandatory. The EU and Brazil have adopted the B7 (containing 7 vol% biodiesel) and B5 (containing 5 vol% biodiesel) diesel blend forms, respectively (Biofuels Digest 2014b).

The global production and consumption of biodiesel have been progressively increasing. In 1991, merely 2.9 million gallons of biodiesel were produced; the annual production increased to 265 million gallons in 2001 and further to 5651 million gallons in 2011 (Fig. 6). In 2015, a total of 8331 million gallons of biodiesel were produced and consumed, of which 39.8% was produced in the EU (primarily in Germany, France, Spain, Italy, and Poland) from rapeseed oil, animal fats, and yellow grease, 15.2% in the USA solely from soybean oil, 12.7% in Brazil mainly from soybean, castor bean, and sunflower oils, 7.4% in Argentina from soybean oil and used vegetable oil, 3.6% in China predominantly from yellow grease, and the rest

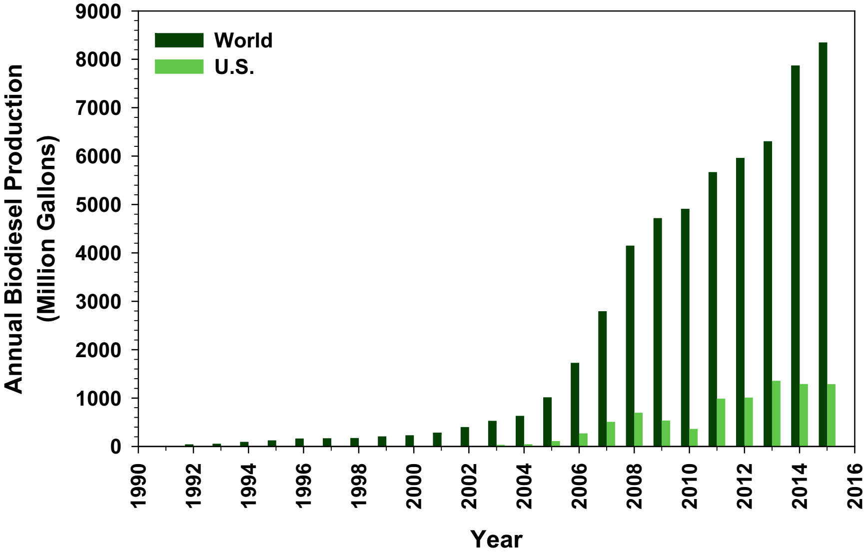


Fig. 6 The world and US biodiesel production from 1991 to 2015. *Data sources* Licht (2012); EIA (2014, 2016b)

in other countries from mixed feedstocks. With improvements in nonfood feedstock production such as cultivation of oily algae and oilseed trees, the global production and consumption of biodiesel will maintain a gradual increasing trend into the near future.

4 Development and Production of Pyrolysis Bio-Oil

A thermochemical pathway for generating liquid fuel from biomass is pyrolysis. The technology is to transform plant materials in a high temperature (300–900 °C), O_2-absent environment to charcoal (the black solid residue), bio-oil (the brown vapor condensate), and syngas (the uncondensable vapor, mainly CO and H_2) (Fig. 7; Vamvuka 2011). Pyrolysis has been practiced to produce wood charcoal since the beginning of human civilization. Depending on the heating rate of biomass in the reactor, pyrolysis can be implemented in two patterns: slow pyrolysis and fast pyrolysis. In slow pyrolysis, plant materials are placed in a batch reactor or a continuous flow bed and heated to 300–500 °C for a number of minutes or even days. Air is prevented from entering the reactor during the heating. Slow pyrolysis has a low yield of bio-oil, typically 30% of the feedstock dry mass (Guo et al. 2012). In fast pyrolysis, the feedstock is ground to <2 mm particles and delivered into a high-temperature (e.g., >900 °C) reactor, in which the fine biomass particles are heated to approximately 500 °C in 2 s, yielding bio-oil at 50–70% of the feedstock dry mass from

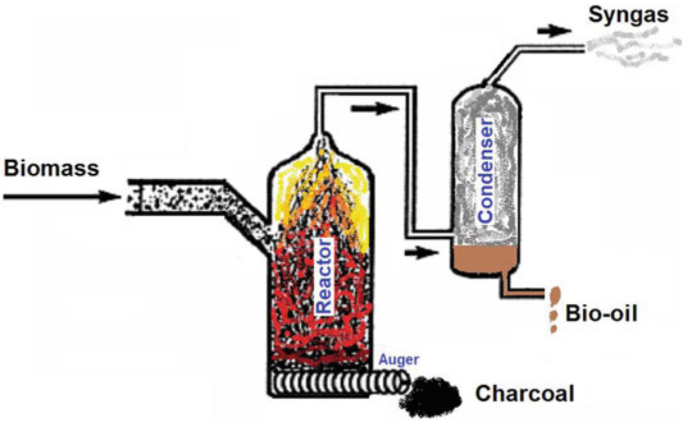


Fig. 7 Pyrolysis of plant biomass to generate char, bio-oil, and syngas

rapid vapor condensation (e.g., <2 s) (DOE 2016b). In fact, other thermal treatment techniques (e.g., incomplete combustion and gasification) also result in bio-oil, but it is fast pyrolysis that maximizes the bio-oil yield among the three products.

Theoretically, all solid biomass residues can serve as the feedstock for pyrolysis bio-oil. To avoid reactor clogging and to reduce pollutant emissions, however, wood is the preferred source material owing to its low mineral ash, nitrogen, and sulfur contents (Vamvuka 2011). Under optimized fast pyrolysis conditions, 60–75% of the ash-free feedstock mass (and the inherent energy) can be recovered in bio-oil (Chatham-Kent 2013; Carpenter et al. 2014).

Crude pyrolysis bio-oil is a blackish-brown fluid consisting of water, colloidal char particulates, and various organic compounds (Table 3). It is acidic (pH 2–3), corrosive (abundant in low molecular weight organic acids), instable (layer separation after settling), and inflammable. More than 300 organic compounds have been identified in bio-oil, including acids, alcohols, aldehydes, esters, ketones, phenols, alkenes, sugars, furans, and aromatics. The organic mixture, in general, contains 54–58 wt% C, 5–7 wt% H, 35–40 wt% O, and 0–0.2 wt% N (Ringer et al. 2006; Vamvuka 2011). Prior to being utilized as a petro-distillate alternative, pyrolysis bio-oil needs to be upgraded to reduce its moisture content, acid content, and viscosity and improve its energy density, ignitability, and storage stability (Czernik and Bridgwater 2004; Xu et al. 2008). A variety of upgrading methods have been developed, including hydrogen treatment, catalytic cracking, molecular distillation, supercritical fluidization, esterification, emulsification, steam reforming, Fischer–Tropsch process, and red mud processing (Zhang et al. 2013; Ruddy et al. 2014; Xiao 2014; Open Source Ecology 2016). Successful applications of upgraded bio-oil in place of heavy petro-distillates (e.g., diesel and No. 2 heating oil) to power diesel engines, furnaces, and electric generators have been reported (Lehto et al. 2013; WSU Extension 2014). Nevertheless, the available upgrading techniques are

Table 3 Properties of wood-derived pyrolysis bio-oil as compared with petroleum distillate fuels (Czernik and Bridgwater 2004)

Properties	Pyrolysis bio-oil	Petroleum distillate fuel
Water content (wt%)	15–30	0.1
pH	2–3	–
Density (kg m^{-3})	1.2	0.94
Elemental composition (wt%)		
C	54–58	85
H	5.5–7.0	11
O	35–40	1.0
N	0–0.2	0.3
Ash	0–0.2	0.1
High heating value (MJ kg^{-1})	16–19	40
Viscosity (50 °C) (cSt)	33–83	190
Solid particulates (wt%)	0.2–1	1
Distillation residue (wt%)	Up to 50	1

not cost-competitive at the industrial scale. Economically feasible upgrading protocols for transforming crude pyrolysis bio-oil into petroleum distillate fuel substitute are desperately warranted (Valle et al. 2014; Ciddor et al. 2015).

Currently, the European Committee for Standardization is developing quality specifications for pyrolysis bio-oil as a fuel substitute for heavy fuel oil, light fuel oil, and stationary combustion engine fuel (EBTP 2015b). Nevertheless, the production and application of bio-oil remain at the fledging stage. No industrial-scale manufacturing of bio-oil has existed. Worldwide, a few pilot plants are operating to produce bio-oil from wood at the 10–130-ton d^{-1} feedstock processing capacity. These plants are exemplified as Ensyn Technologies, Inc. (Canada and USA), DynaMotive Energy Systems (Canada and USA), Agri-Thermo (Canada), Fortum Co. (Finland), and BTG-BTL Empyro (The Netherlands) (Chatham-Kent 2013). The chief barrier to commercialization of bio-oil production is lack of cost-effective technologies for upgrading crude pyrolysis bio-oil into petro-distillate alternatives (Lehto 2012).

5 Development and Production of Drop-in Biofuels

Unlike petro-distillate hydrocarbon fuels that contain little oxygen in their componential molecules, the most popular biofuels bioethanol and biodiesel are relatively high in oxygen content. As a result, bioethanol and biodiesel possess moderate dissolution capability and are corrosive to elastomer and metallic apparatus (Kass et al. 2011). The existing fuel supply infrastructure is not fully compatible with these biofuels. It is not safe to use the current fueling system without modifications to distribute bioethanol and biodiesel. Even in gasoline and diesel blends at above 20 vol%, bioethanol and biodiesel can dissolve rubber gaskets and rust certain metal parts, causing damages to engines, storage tanks, and fuel dispensers (Kass et al. 2011; DOE 2016c).

It is desirable to produce “drop-in” biofuels that possess chemical composition, fuel characteristics, and energy density comparable to those of petro-distillate fuels and, thus, fully compatible with the existing distribution equipment. Drop-in biofuels can be directly distributed to end users through the available fuel supply system and used in fuel engines without any infrastructure modifications or petro-fuel blending. The promising drop-in biofuel candidates have been identified as hydrotreated vegetable oil, Fischer–Tropsch biofuels, butanol, liquefied biomass, sugar hydrocarbons, syngas complexes, and others (AFDC 2012; EIA 2015b). These drop-in biofuels vary in biomass feedstocks and refining techniques.

Hydrotreated vegetable oil (HVO), so-called green diesel or renewable diesel or Hydroprocessed esters and fatty acids (HEFA), is a diesel substitute produced from vegetable oils and animal fats by catalytic hydrogen processing (Fig. 8). The involved chemical reactions can be simplified as:

$$\begin{array}{l} CH_2\text{–}OCOR_1 \\ | \\ CH\text{–}OCOR_2 \\ | \\ CH_2\text{–}OCOR_3 \end{array} + H_2 \overset{\text{Catalyst}}{\underset{\Delta}{\rightleftharpoons}} \begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_3 \end{array} + \begin{array}{c} H_3C\text{–}R_1 \\ H\text{–}R_2 \\ H_3C\text{–}R_3 \end{array} + H_2O + CO_2 \tag{7}$$

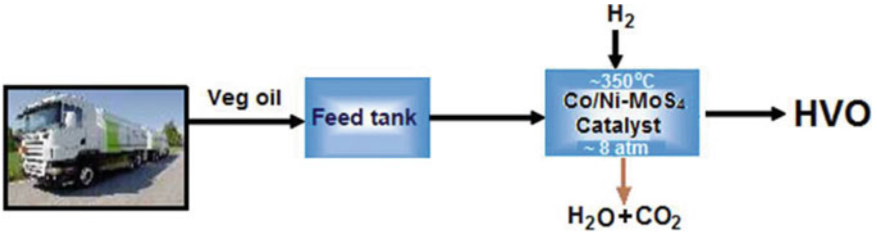


Fig. 8 Catalytic hydroprocessing of vegetable oil for a drop-in biofuel

where R_1, R_2, and R_3 are aliphatic hydrocarbon groups in the fatty acid moiety of oil molecules (triglycerides). The product HVO is a liquid mixture of straight chain aliphatic hydrocarbons free of oxygen, nitrogen, and sulfur. It possesses an energy density roughly identical to that of petro-diesel. In comparison with the latter, HVO is lower in lubricity, poorer in cold flow properties, and higher in cetane number (Lapuerta et al. 2011). Nevertheless, HVO has a much lower emission profile, higher storage stability, and lower cloud point (EBTP 2015c) than biodiesel.

Vegetable oils, animal fats, and yellow grease can be used as the source material to produce HVO. Commercial production of HVO started in 2010. There are a number of HVO biorefinery plants operational in Singapore, USA, The Netherlands, Italy, and Finland. The global capacity has been steadily growing, from 350 million gallons/yr in 2011 to nearly 1200 million gallons/yr in 2014 (EIA 2015b). Currently, HVO is being used as an aviation fuel in 50 vol% blends with petro-jet fuel. Depending on the market price of petroleum, production of HVO is technically feasible and may be economically feasible (Hilbers et al. 2015).

Fischer–Tropsch biofuels are liquid transportation fuels manufactured from biomaterials through the "biomass to liquid via Fischer–Tropsch synthesis" (BTL-FT) process, in which biomass is first converted to syngas via gasification, the syngas is then synthesized into a liquid mixture of gasoline (>70 wt%), diesel (15–20 wt%), middle and heavy distillate oils in the presence of cobalt-based catalysts at 180–200 °C and 5–15 atm, and the synthesized liquid fuels are eventually recovered by fractional distillation (Ail and Dasappa 2016). The BTL-FT process can be described as:

$$\text{Biomass} \overset{\text{gasification}}{\rightarrow} H_2 + CO(\text{syngas}) \tag{8}$$

$$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \tag{9}$$

$$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O \tag{10}$$

The composition of the synthesized liquid can be manipulated by controlling the H_2/CO ratio of the syngas. At a ratio of 2.0:1–2.3:1, the gasoline yield is maximized (Ail and Dasappa 2016). The gasoline generation can be further improved by using shape-selective zeolite catalysts instead of cobalt-based catalysts, as outlined in the syngas to gasoline plus (STG+) technique (Primus 2015):

$$2H_2 + CO \rightarrow CH_3OH\ (\text{methanol}) \tag{11}$$

$$2CH_3OH \rightarrow H_3COCH_3\ (\text{dimethyl ether}) + H_2O \tag{12}$$

$$nH_3COCH_3 \rightarrow C_6 - C_{10}\ \text{hydrocarbons (gasoline)} + nH_2O \tag{13}$$

Commercial production of liquid transportation fuels via FT process or STG + synthesis from coal-derived syngas (coal gasification) and natural gas-derived syngas (steam methane reforming) has been realized (e.g., the Sasol Synthetic Fuels, Ltd established in 1982 in Secunda with 85,000 barrels per day capacity and the Qatar Shell Service Company established in 2009 in Qatar with 14,000 barrels per day capacity). To date, however, there are no commercial scale BTL-FT plants operating to synthesize liquid transportation fuels from biomass, largely due to the high production cost. In 1996, CHOREN Industries installed a demonstration BTL-FT plant in Freiberg, Germany, with 1000 barrel per day capacity (Ail and Dasappa 2016).

Another drop-in biofuel candidate is biobutanol. Biomass-derived sugars can be converted to butanol (a drop-in fuel) through acetone-butanol-ethanol (ABE) fermentation by the anaerobic, spore-forming bacterium strains of *Clostridia* (Schiel-Bengelsdorf et al. 2013). The molar ratio of acetone, butanol, and ethanol in the fermented slurry is typically 3:6:1. The sugar to ABE conversion rate, however, is merely 8%. Furthermore, separation of butanol from the ABE mixture can be costly (Sreekumar et al. 2015). Biomass-derived sugars can also be synthesized into petroleum-like drop-in biofuels through a series of catalytic chemical transformations (catalysis) including dehydrogenation, deoxygenation, hydrogenolysis, and cyclization (Biddy and Jones 2013). Pyrolysis of plant and algal biomass in an H_2-abundant environment (hydropyrolysis) yields a black liquid (85% of feedstock mass) in addition to minor char and syngas; the liquid (hydropyrolysis oil) can be refined to recover quality transportation fuels (Duan et al. 2013). Biomass can also be processed by hydrothermal liquefaction, through which biomass/water slurry (5–35% dry solids) is treated under high temperature (e.g., 300–350 °C) and high pressure (e.g., 100–200 atm) conditions to form an organic liquid (biocrude). Biocrude is a complex mixture of organic acids, alcohols, ketones, phenols, naphthol, benzofurans, and others and can be upgraded in existing refineries to gasoline, diesel, and related distillate fuels (Biddy et al. 2013; Elliott et al. 2015). These drop-in biofuel technologies, however, are still at the research and development stage.

6 Summary and Conclusions

The global renewable energy utilization has been notably expanding over the past two decades. Bioenergy is the largest renewable energy sector, accounting for more than 65% of the global renewable energy consumption and contributing 10% to the world's primary energy supply (REN21 2015). Within twenty years, the world's bioenergy consumption increased by 34.8% to 69.1×10^{15} kJ in 2013. It is estimated that by 2050, the world's annual bioenergy consumption will reach 190×10^{15} kJ, and biofuels will provide up to 27% of the world transportation fuel (WEC 2013; IEA 2016).

Biomass is the sole renewable source for manufacturing liquid transportation fuels. Worldwide, tremendous efforts have been made to develop liquid biofuels as substitutes for petro-gasoline and petro-diesel. The liquid biofuels include bioethanol, biodiesel, pyrolysis bio-oil, and drop-in biofuels. The global annual bioethanol production increased from 8.2 billion gallons in 2005 to 25.7 billion gallons in 2015. At the same time, the world's annual biodiesel production increased from 1.0 billion gallons to 8.3 billion gallons. Nevertheless, these gigantic volumes of biofuels were sourced exclusively from food crops, imposing great pressure on human food and animal feed supply. Refining biofuels from nonfood biomaterials has been intensively explored. Breakthrough progress has been achieved in extracting simple sugars from lignocellulosic biomass for bioethanol production. With effective feedstock pretreatment techniques, efficient cellulosic enzymes, and improved fermentation yeast strains, commercial production of bioethanol from lignocellulosic materials has become technically feasible and economically viable. Starting from 2013, the global production of lignocellulosic ethanol has been gradually expanding. Development of new, nonfood source materials for biodiesel has been focusing on algal oil, but algal cultivation and oil extraction need further improvement to reduce the production cost. The fast pyrolysis technology has also been researched to convert solid biomass into liquid fuel. Refining the resulting pyrolysis bio-oil for liquid transportation fuels, however, has not been cost-competitive. In recent years, significant investments have been committed to developing drop-in biofuels that are compatible with the existing fuel supply infrastructure. A successful candidate is HVO, with the current global production capacity of 1.2 billion gallons/yr. Production of drop-in biofuels via BLT-FT synthesis is promising, yet the technology remains at pilot production stages. Other drop-in biofuel technologies are being investigated, such as hydropyrolysis, hydrothermal biomass liquefaction, ABE fermentation, and sugar catalysis.

Given the present renewable energy and climate change policies, it is evident that global production and consumption of liquid biofuels will continue to increase. Biofuel has been playing a major role in the emerging "green economy."

Review Questions

1. Globally, what is the bioenergy potential for meeting human fuel demands?
2. Give examples of lignocellulosic materials.
3. What is the technological bottleneck for producing bioethanol from lignocellulosic materials via alcohol fermentation?
4. Describe the advantages and challenges of second-generation biofuels.
5. What is transesterification?
6. Compare biodiesel with petrol diesel for differences in physical, chemical, and energy properties.
7. What is pyrolysis? What products can be obtained from fast pyrolysis of wood?
8. Pyrolysis bio-oil is comparable in fuel quality to commercial heating oil from petroleum. Is it true?
9. Name three candidates of drop-in transportation biofuels and briefly explain how they can be produced from plant biomass.

10. In the USA, what are currently the predominant feedstocks for bioethanol and biodiesel? Will these feedstocks be taken place of by other plant materials in the future?

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