Chapter 8
Biofuels Production from Renewable Feedstocks

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Abstract Predicted increases in greenhouse gas emissions, depleting fossil fuel supplies, global conflicts, and energy security are major factors driving the search for renewable energy supplies. Based on future energy demand projections, biofuels production is expected to increase. However, this increase represents a small fraction of this growing demand because the land area required to grow sufficient biofuels crops is unavailable. Hence, fulfilling the growing energy demand after attaining peak fossil fuel production will include using a combination of energy sources such as renewables, wind, geothermal, nuclear, hydroelectric, solar, and coal. Current and potential feedstocks include grains, grasses, root crops, oil seeds, algae, and lignocellulosics. Grains, sugar crops, and lignocellulosics are the main feedstocks used in full-scale first- and second-generation ethanol processes. While first-generation biodiesel is produced mainly from corn, soybeans, canola oil, rapeseed, palm oil, Jatropha, and coconut oil, second-generation fuels are produced from lignocellulosics. Third-generation technology employs several processes to produce a variety of biofuels from algae while fourth-generation technologies, a developing concept, is intended to employ genetically modified terrestrial or aquatic plants. In another concept, fourth-generation technologies can be configured with CO_2 sequestration and storage. First-generation biobutanol is produced from corn or molasses and from sugar beet as well as sugarcane, while second-generation production processes utilize lignocellulosics such as corn stover, rice straw, corn fiber, switchgrass, alfalfa, reed canary grass, sugarcane bagasse, *Miscanthus*, waste paper, dry distillers grain with solubles (DDGS), and soy molasses. A variety of technologies, based on the enzyme systems, are currently under investigation for producing biohydrogen. Biohydrogen production routes are divided into biophotolysis (direct/indirect), dark fermentation, and photofermentation. Increasing

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global demand is expected to drive increasing bioethanol and biobutanol production using food and nonfood feedstocks. At the same time, researchers are developing technologies to produce biohydrogen and biodiesel. Biohydrogen and biodiesel production technologies are in their developmental stages; however, with innovation, these technologies are expected to mature into economical processes.

Keywords Global energy supply and demand · Annual biofuel feedstock production · Biofuels production processes · first-, second-, third-, and fourth-generation processes

8.1 Introduction

Predicted increases in the global population to approximately 8.3 billion by 2030 is linked to issues such as climate change, depleting fossil fuel supplies, energy security, and affluence. Population growth and increasing wealth per capita are key drivers connected to growing energy demand. Developing renewable energy supplies offers a mechanism to reduce carbon emissions and combat issues associated with population growth. A primary driver for developing energy crops is the desire to decrease the quantity of greenhouse gases (GHG) associated with utilizing fossil fuels. Bioenergy production from renewable feedstocks could be a major mechanism in reducing carbon dioxide emissions.

Despite increasing energy efficiencies, consumption is increasing globally (Fig. 8.1). In 2012, the global biofuels industry was valued at approximately $95 billion U.S., a 14.4 % increase from 2010. The industry is expected to grow to $145.6 billion U.S. by 2023 [1]. Global primary energy consumption is projected to grow by 1.5 % per year from 2012 to 2035. This increase is expected to add 41 % to the global energy consumption by 2035. Renewables (including biofuels) are the fastest-growing fuels with growth averaging 6.4 % per year from 2012 to 2035. Nuclear (2.6 % per year) and hydro (2.0 % per year) are both expected to grow more than the total energy consumption [2]. As fossil fuel demand peaks around 2030, biofuels, hydroelectric, solar, wind, geothermal, and nuclear are expected to fill the gap created by depleting fossil fuel supplies (Fig. 8.1).

The deployment of bioenergy technologies, if carefully and strategically managed in a sustainable manner, could produce the following advantages [3]:

- provide a large contribution to the global energy supply;
- contribute to reducing GHG emissions;
- improve energy security and trade balances, by substituting imported fossil fuels with domestic biomass;
- provide opportunities for economic and social development in rural communities; and,
- allow for the utilization of wastes and residues which subsequently result in reducing waste disposal problems and allow for efficient utilization of global resources.
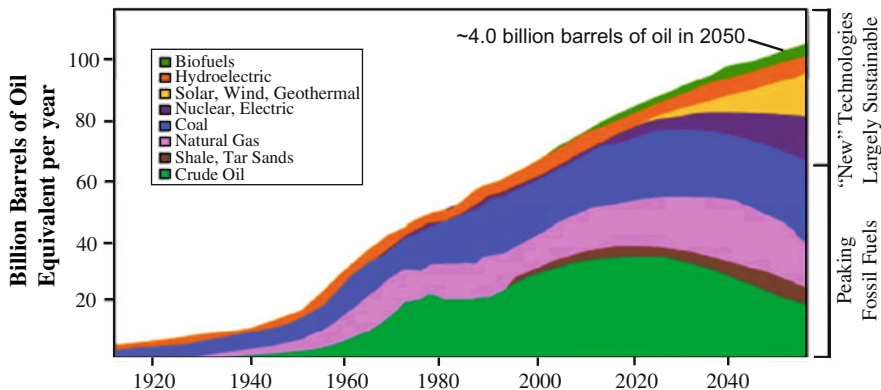
Fig. 8.1 World energy demand—long-term energy reserves. Data from Edwards [4] and Orr [5]

8.2 Biomass Feedstocks

Biomass generally refers to organic materials derived from living and nonliving matter. After coal, oil, and natural gas, biomass is the fourth largest energy source. Cultivation of terrestrial renewable energy crops across the globe is shown in Fig. 8.2. The global map accounts for crop cultivated on lands suitable and poorly suitable for first, second, and third-generation feedstocks.

First-generation biofuels are classified based on using commercially available technologies and conventional feedstocks such as oil seeds and grains [6]. Corn, sugarcane, wheat, and other grains plus rapeseed and palm oil are categorized as first-generation feedstocks because they are readily fermentable. Second-generation biofuels production processes utilize lignocellulosic materials feedstocks such as wheat stalks, corn stover, wood, and energy crops such as *Miscanthus* and switchgrass. Second-generation feedstocks (often referred to as lignocellulosics) require pretreatment including the use of complex enzyme mixtures prior to fermentation [6]. Second-generation biofuel technologies are used to produce hydrogen, ethanol, dimethylfuran (DMF), dimethyl ether (DME), Fischer–Tropsch (FT) diesel, and mixed alcohols. These technologies, including both biological and thermochemical, are not cost competitive with first-generation biofuels production. Second-generation technologies with substantial energy/environment benefits when compared to most first-generation biofuels is due primarily to greater biomass usability per unit land area. However, these technologies are characterized by greater capital intensity and lower feedstock costs when compared to first-generation technologies. Third-generation biofuels are a new category for classifying biofuels. Third-generation feedstocks include materials such as
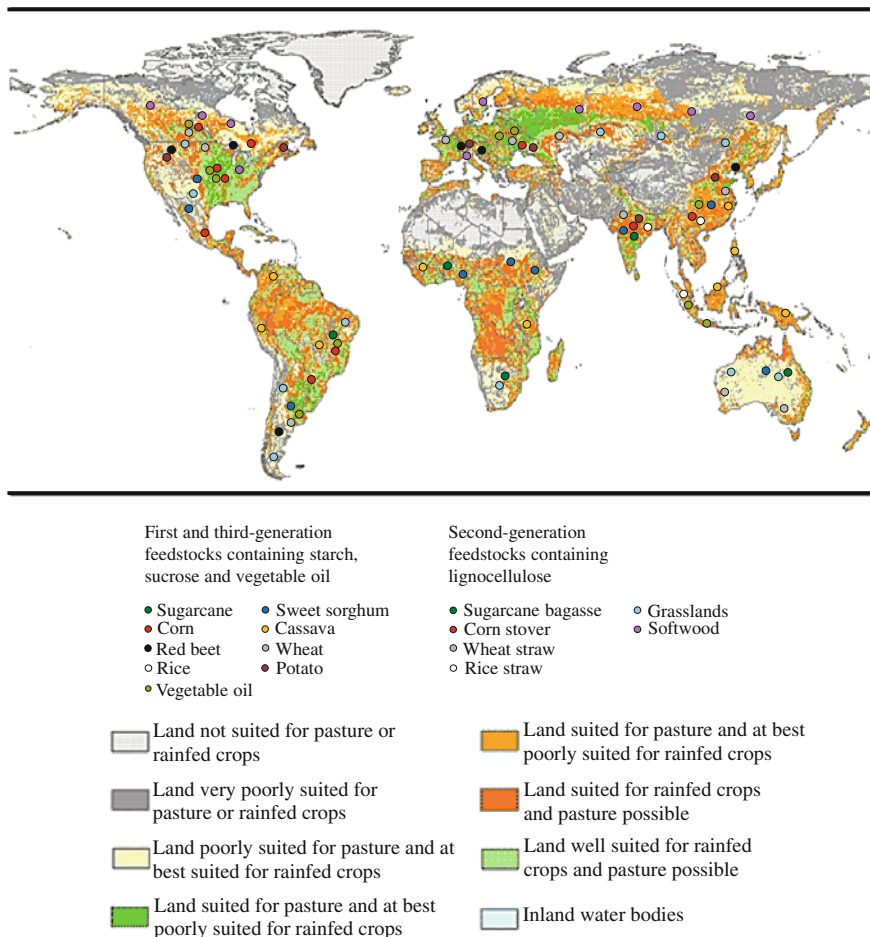
Fig. 8.2 Land suitability for pasture and rainfed crops. *Notes* Land suitability data map adapted from van Velthuizen et al. [7]. Crop cultivation data adapted from Stöcker and Tschentscher [8]. Vegetable oil production data accessed from http://www.indexmundi.com/agriculture/?commodity=soybean-oil&graph=production [9]. General cultivation locations are shown. The circle size is not representative of quantity produced

microalgae do not compete for land area [6]. Algae, the most significant feedstock for this technology, is cultivated to produce biodiesel from triglycerides, a metabolic product. Fourth-generation fuels have been classified based on synthetic biology of algae and cyanobacteria [10–12]. Synthetic biology includes the design and manufacture of biological components, devices and systems, and the reengineering of existing, natural biological systems for producing biofuels [13]. In an opposing concept, fourth-generation biofuel systems are proposed to be comprised of processing methods such as thermochemical coupled to carbon capture and

storage technologies which divert the CO_2 generated into geological formations or mineral storage as carbonates [13]. In the opposing concept, the technology ability to sequester and store CO_2 leads to the carbon negative concept.

Crop cultivation in various areas is dependent on factors such as irradiation time and intensity, temperatures, rainfall, season length, and soil quality. Temperate regions are associated with the cultivation of softwood while in arid regions, sweet sorghum, and switchgrass are preferred crops due to the low water demand. The annual global energy consumption is expected to increase with population and economic growth. In 2013, approximately 4185 million tonnes of fuel was consumed globally. Based on this consumption and assuming varying biomass yields of 5–50 tonne biomass (ha year)$^{-1}$ [14] and conversion efficiencies ranging from 25 to 75 % tonne biomass per tonne fuel, the land area requirement is expected to range from approximately 110-3350 Mha (Table 8.1). Using biomass to produce biofuels will partially meet this demand; however, the exorbitant area required to grow sufficient terrestrial as well as aquatic plants is unavailable (Table 8.1). Hence, fulfilling this global growing energy demand after attaining peak fossil fuels production will include utilizing a combination of other energy sources such as renewables, wind, geothermal, nuclear, hydroelectric, solar, and coal (Fig. 8.1).

Biomass feedstocks are the largest renewable energy option available for producing energy and chemicals [15]. Major biomass feedstocks categories are shown in Table 8.2 [16]. Climate change is attributed as the leading cause for varying biomass yields. Depending on the models and input climate scenario as well as assumptions, many global areas may experience significant decreases as well as significant increases in crop yields [17]. The global primary biomass potential forecast by numerous studies estimate annually over a 100-year timeframe is

Table 8.1 Estimated biomass conversion and land area requirement [14]

Yield (tonne biomass (ha year)$^{-1}$)	Proportion of biomass converted to biofuel (%)	Land area (Mha)
5	25	3348
	50	1674
	75	1116
10	25	1674
	50	837
	75	558
25	25	837
	50	419
	75	279
50	25	335
	50	167
	75	112

1 Mha = million hectare
2 Based upon 4185 million tonnes ∕ year fuel consumption as of 2013 [14]

Table 8.2 Major biomass feedstock categories [16]

Biomass category	Biomass feedstock
Forest products	Wood, logging residues, trees, shrubs, and wood residues, sawdust, bark, etc.
Biorenewable wastes	Agricultural wastes, mill wood wastes, urban wood wastes, urban organic wastes
Energy crops	Short-rotation woody crops, herbaceous woody crops, grasses, forage crops
Food crops	Residue from grains and oil crops
Sugar crops	Sugarcane, sugar beets, sorghum
Landfill	Municipal solid wastes
Industrial wastes	Food wastes, organic acid wastes, and vegetable oil wastes
Algae, kelps, lichens, and mosses	Water hyacinth, mushrooms, etc.
Aquatic plants	Algae, water weed, water hyacinth, reed, and rushes

expected to range from 50 to 1550 EJ [18] (equivalent to 8.2–253 billion barrels of oil equivalent (Bboe) per annum). Other studies have reported an annual global production potential of 30 EJ from forest and agricultural residues [19]. According to Demirbas [20], the global biomass production is estimated at 146 giga tonnes (Gt) per year. Klass [21] and Hall et al. [22] reported annual biomass yields range from 170 to 200 Gt (equivalent to 500–599 Bboe assuming an energy yield of 18 GJ per tonne biomass).

The annual global production of selected crops is shown in Table 8.3. Corn, sugarcane, and oilseeds are the major contributors for producing biofuels with corn and sugarcane accounting for approximately 76 % of the total bioethanol produced [23].

Table 8.3 Annual production of selected crops

Crop	Annual production (Million tonnes year^{-1})
Wheat	725[a]
Rice, milled	480[a]
Corn	1000[a]
Barley	145[a]
Oats	23[a]
Rye	13[a]
Cassava	250[b]
Sorghum	70[a]
Sugar beet	160[a]
Sugarcane	1880[c]
Soybeans	280[b]
Oilseed	530[a], 425[d]

[a]USDA [24]; [b]FAO [25]; [c]Koo and Taylor [26]; [d]OECD/FAO Agriculture Outlook [27]

The global total crop biomass annual production is estimated at approximately 8950 million tonnes, of which 5570 million tonnes (62 %) is categorized as crops and 3380 million tonnes (38 %) as above ground residues. Crops are produced for food (69 %), feed (19 %), and energy and materials (7 %). A small fraction is used for seed while another portion is waste (5 %). Of the estimated residues, 10 % is used for feed (corn and straw) and 6 % for bedding (in developed countries) [28]. Most of the residues remaining in the field are burned or grazed by livestock.

Approximately 1000 million tonnes of corn is produced annually (Table 8.3 and Fig. 8.3) with the U.S. and China accounting for approximately 60 % in 2014 [24]. Corn is utilized for feed (55 %), food (20 %), and also for producing biofuels while corn stover is used for livestock feed. Oil is extracted from corn kernels for consumption, cooking, and nonfood products. The average quantity of oil extracted is approximately 15 % of the total crop. The leaves and straw are recycled into the soil. Sugar beet is produced for food and biofuels. Annual wheat production as a major food source is estimated at 725 million tonnes. Cassava is produced (250 million tonnes year^{-1}) in tropical climates and mainly used for food. Global beet production, mainly in the European Union, is approximately 160 million tonnes year^{-1}. Brazil and India account for approximately 60 % of the global sugarcane production of 1880 million tonnes year^{-1} (Table 8.3). Sugarcane is cultivated for sugar (sucrose) and ethanol production. Brazil is the largest producer, followed by India and China. Sugarcane is a diversified crop used for producing food (sucrose, alcohol, molasses), energy, and biofuels (ethanol) [29]. Approximately 50 % of the
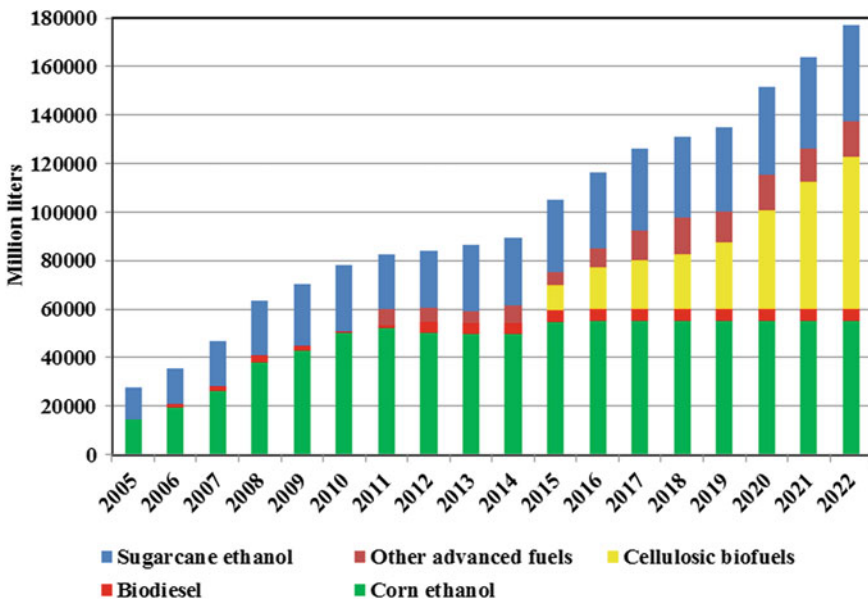

Fig. 8.3 Global biofuels production. *Source*: OECD/FAO [27]. United States Environmental Protection Agency [30]. United States Energy Information Administration [31]

Table 8.4 Chemical composition of selected agricultural grains, residues, and brown kelp

Feedstock	Cellulose	Hemicellulose	Mannitol	Algin	Starch	Fat	Ash	Protein	Lignin
Corn[a]	2.0	7.6			76.0	5.7	1.6	11.4	1.0
Soyabean[a]	2.0	5.0				18.8	5.5	42.8	
Wheat[a]	8.0	4.0			70.0	2.2	1.6	12.3	2.0
Sorghum[b]					73.0	4.6	1.2	10.9	
Switchgrass[a]	33.5	26.5					6.4	5.3	18.1
Brown rice[a]	1.0	2.0			74.4	2.6	1.6	8.5	
Giant brown kelp[c]	4.8		18.7	14.2			45.8	15.9	
Bermuda grass[c]	31.7	40.2					5.0	12.3	4.1
Poplar[c]	41.3	32.9					1.0	2.1	25.6

All data given in %w w^{-1}
[a]Abbas et al. [32]; [b]Léder [33]; [c]Klass [34]

bagasse produced is used for energy production and the rest remains unused in the environment [35]. Vegetable oils are produced (910 million tonnes year^{-1}) mainly for food products.

Biomass residues from fruits and vegetables, roots and tubers, and sugar beets are limited in quantity but have potential for bioenergy production when available in sufficient quantities. Their relatively high economic value makes these crops less favorable for uses other than food. Sugar beet is comparable to sugarcane, and the high sugar content makes the crop suitable for food, fuel, and energy.

Biomass sources include crops such as beet and sugarcane, woody and herbaceous species, wood wastes, agricultural residues, waste paper, municipal solid waste, biosolids, food processing waste, animal wastes, aquatic plants, bacteria, and algae. Cellulose, hemicelluloses, lignin, proteins, and fats are the major organic constituents of biomass. In the case of lignocellulosics biomass, the main constituents are cellulose (35–50 %), hemicellulose (20–35 %), and lignin (10–25 %) (Table 8.4).
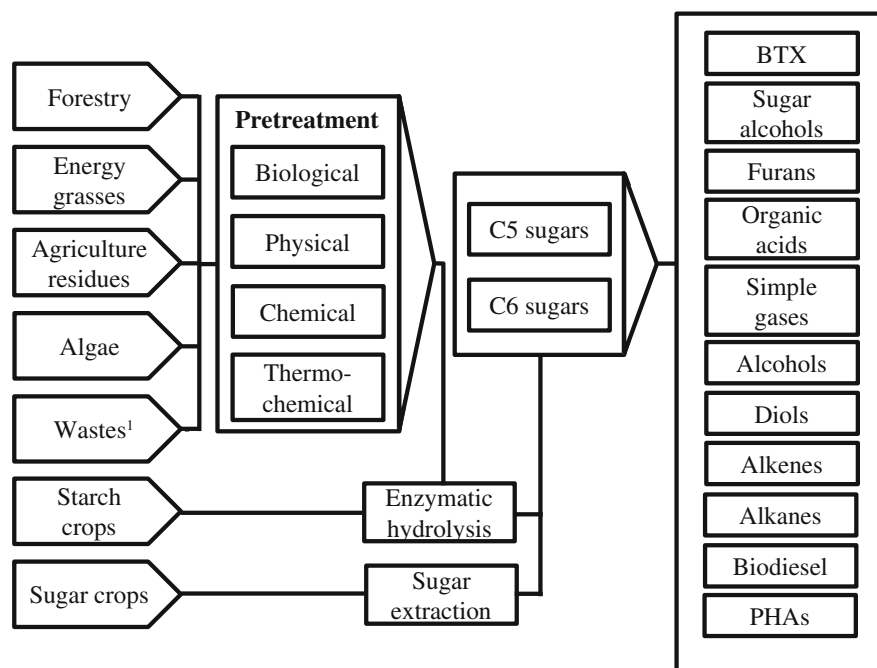
8.3 Biofuels Production

8.3.1 Overview

On a global scale, biofuel production from renewable biomass is projected to continue increasing over the next decade [36]. Corn, sugarcane, beet and ligno-cellulosics are major feedstocks for producing bioethanol while vegetable oil plus oilseeds are utilized to produce biodiesel. The U.S., Brazil, the EU, and Argentina are the largest biofuel producers while the world's largest biofuel exporters include Argentina, Brazil, and the U.S., with Argentina, Brazil, and the U.S. specialize in producing soybean oil-based biodiesel, sugarcane-based ethanol, and corn-based ethanol, respectively [36].

Currently, the EU remains the world's largest biofuels importer over a projected period until 2024. Biodiesel accounts for the majority of the EU's biofuel imports with Brazil supplying a large fraction of the EU's ethanol imports. The EU is also projected to import, oilseeds and vegetable oils for biodiesel feedstocks mainly from Ukraine, Russia, and Indonesia. Global trade for wheat, coarse grains plus soybeans, and soybean products is expected to reach 175, 175, and 235 million tonnes, respectively, by 2024 [36].

Wheat, coarse grains, soybeans, sugarcane, and beet feedstocks are employed to produce a variety of chemical and fuels utilizing biological, physical, thermal, and thermochemical processes. Currently, the major biofuels produced include methane, ethanol, and biodiesel (Fig. 8.3). Other chemicals produced from biomass include benzene/toluene/xylene (BTX), furans, organic acids, diols, alkenes, alkanes, and polyhydroxyalkanoates (PHAs) (Fig. 8.4). Producing biofuels and chemicals from renewable crops and residues is important from an energy security and environmental perspectives. However, approximately 43 % of the total crop produced annually is used for food and only 5 % is converted into energy producing chemicals [28]. The small fraction of the total global annual crop produced which is converted into energy is due to limited factors such as the total annual production, crop yield, climatic conditions, and the quantity used to produce food products.

Fig. 8.4 Biofuels production pathways (adapted from European Commission [37]). [1]Municipal and industrial

8.3.2   Biofuels Production Technologies

Biomethane, bioethanol, and biodiesel are produced in large quantities from a variety of feedstocks. Production processes for these fuels are described in subsequent sections.

8.3.2.1   First- and Second-Generation Biomethane Production

Biomethane, a useful energy carrier, is derived from renewable feedstocks. Biomethane under the first-generation category is produced by anaerobic digestion while the second-generation production process is configured with biomass gasification, purification, and catalytic methanation. According to the European biogas association (EBA), the 2010 total biogas production in Europe was estimated at 14.7 billion m^3 [93.8 million boe (barrel of oil equivalent) or 20.6 billion m^3 biogas] based on natural gas equivalents. The EBA projects the level of biogas production will reach 28 billion m^3 (based on natural gas equivalents) in 2020 [38]. Contradictory data by EurObserv'ER [39] reported the quantity of biogas produced in 2013 reached approximately 25.7 billion m^3. Major biomethane producing countries in Europe include Germany, Sweden, the Netherlands, Austria, Finland and the UK [39]. Germany is Europe's largest biogas producer [40] with a total capacity from biomass of 12.8 billion kWh [85.8 million boe (barrel of oil equivalent)] in 2010 [41]. In the U.S., methane biogas from cow manure is sufficient to produce 100 billion kilowatt hours (equivalent to 16.7 billion m^3 biogas or 61.4 Mboe or 11.3 billion m^3 natural gas equivalent). Methane biogas can reduce 99 ± 59 million tonnes of GHG emissions or approximately 3.9 ± 2.3 % of the GHGs produced by the U.S. [42].

A vast selection of crops has been evaluated for their potential to produce methane. The methane yield per hectare of selected sugar and starch crops are shown in Table 8.5. Methane can be produced from lignocellulosic crops; however, the methane yield from these crops is lower than that obtained from sugar and starch containing crops. Even though the conversion of lignocellulosics into methane faces an initial barrier related to the enzyme access to readily biodegradable components, the process is more environmentally sound and sustainable option for renewable energy production because lignocellulosic crops can be cultivated on marginal and set-aside lands [43].

Converting agriculture feedstock into methane is accomplished sequentially by various microbial populations during anaerobic digestion. These organisms which include hydrolytic degraders, acidogens, acetogens, and methanogens, produce monomers, organic acids, acetic acid, and eventually methane, respectively. Sugars are easily degraded to methane by anaerobic microorganisms; however, the process reaction rate is impaired significantly when the feed contains substrates such as lignocellulosics and lipids.

Table 8.5 Biomethane yield in function of methane production and crop field yield [43]

| Crops	Yield (m^3 STP CH_4 ha^{-1})
Cocksfoot	2390
Corn	5300–12,390
Festlolium	2800
Giant knotweed	3800
Hemp	2840
Jerusalem artichoke	3100–5400
Reed canary grass	3800–4200
Rhubarb	800–1700
Sugarbeets	5400
Sunflower	4695
Tall fescue	2749
Timothy	1840–2335
Timothy clover grass	2900–4000
Triticale	1112–6600

Biomethane production from a H_2 plus CO synthesis is classified as a second-generation biofuel. The production process involves four stages. In the first gasification stage, lignocellulosics are converted into a synthesis gas which is rich in CO and H_2. The synthesis gas is purified to eliminate tars and inorganic compounds in the second stage. Next, the synthesis gas is converted into biomethane using a heterogeneous catalytic conversion process. Finally, the biomethane stream is conditioned using gas separation processes in order to be compliant with standard specifications for natural gas [44].

8.3.2.2 First- and Second-Generation Bioethanol Production

First-Generation Ethanol Production from Starch- and Sucrose-Based Crops

Bioethanol production in 2015 from sugarcane and corn was estimated at approximately 84 billion liters (Fig. 8.3). By 2022, the global ethanol production is projected to reach approximately 157.2 billion liters (Fig. 8.1). Based on the 2022 data, corn, sugarcane, and lignocellulosics account for 35, 25, and 40 %, respectively, of the total first-generation biofuels produced. The 2022 ethanol production (157.2 billion liters) accounts for approximately less than 1 % of the total annual global energy utilized (Fig. 8.1). The 2022 data excludes production data for wheat, beet, and cassava because of the low annual ethanol production levels for these three feedstocks. Sugar beet bioethanol production accounted for approximately 0.83 billion liters in 2015 [45–47]. The annual low levels of bioethanol produced from wheat and cassava is due to the small fraction available for processing. In the

Fig. 8.5 Percent ethanol production based on countries [23]
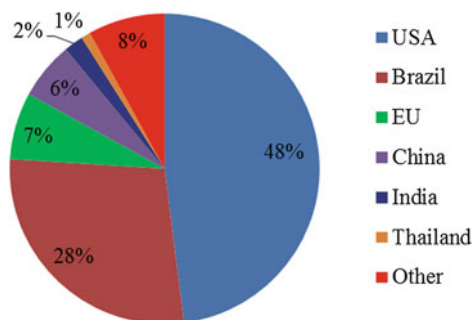
case of wheat, only 1.0 % of global wheat production is available while for cassava, only 0.6 % is available for producing ethanol [46].

Approximately 76 % of the ethanol produced globally is derived from sugarcane and corn with the remaining produced from beet, wheat, and other crops (Fig. 8.3). The U.S. and Brazil are major ethanol producers with a market share of approximately 75 % in 2012 (Fig. 8.5). Ethanol yields for selected crops are shown in Table 8.6. Sugarcane and coarse grains are the largest yielding ethanol producing crops with lower yields derived from oats and cassava. Ethanol production based on crop type is shown in Fig. 8.6. Sugarcane to ethanol production facilities are located in Brazil while corn to ethanol are situated in North America and Asia. Beet to ethanol production facilities are stationed in Europe.

Hydrolysis, the first reaction step in producing ethanol from cereal grains, involves converting starch to glucose monomers using hydrolyzing enzymes. In the second step, glucose and other sugar monomers are converted into ethanol using

Table 8.6 First-generation ethanol yields for sucrose and starch with grains, terrestrial, and root crops

Feedstock	Moisture (% wt)	Starch (% wt)	Sugar (% wt)	Crop yield (tonnes ha^{-1})	Ethanol yield (L dry tonne^{-1})
Sucrose					480[g] actual
Starch		100[a]			720[a]
Barley	9.7[a]	67.1[a]			399[a]
Beet	75[b]		17–18[b,f]		375[c]
Cassava	32[d]	35[d]			150[d]
Corn	13.8[a]	71.8[a]			407[a,c]
Oats	10.9[a]	44.7[a]			262[a]
Sweet Sorghum	70[e]		13[e]		400[g,] 520[g]
Sugarcane	82[f]		15–16[f]	74[g]	460–654[a,c]
Wheat	10.9[a]	63.8[a]			375[a]

[a]Saskatchewan Agriculture and Food [47]; [b]Asadim [48]; [c]Shapouri et al. [49]; [d]Kuiper et al. [50]; [e]Höfer [51]; [f]Cardona et al. [52]; [g]Bonin et al. [53]

Fig. 8.6 Percent ethanol production based on crop type [23]
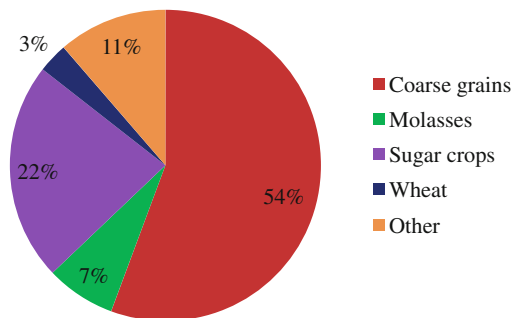
yeast. The fraction of biomass converted into fuels and chemicals depends on the availability of easily degradable sugars (Table 8.6). Starch, grain crops, root crops, and grasses are easily fermented into ethanol with less pretreatment when compared to ethanol production from lignocellulosics.

Ethanol production from grain crop such as corn and other starch rich grains is classified as wet or dry milling. Major differences between the two processes are the byproducts produced and the initial capital cost. In the wet milling process, corn is converted into fuel ethanol and dry distillers grain with solubles (DDGS). DDGS contains primarily protein and is sold as animal feed. The unit processes are configured in the following sequence: [54] 1. Grain grinding into a meal using hammer or roller mills; 2. Liquefying the meal using α-amylase at a 90 °C reaction temperature; 3. The liquefied mash is cooled and pH adjusted to 4–5. Glucoamylase is added to convert dextrins and oligosaccharides into glucose and maltose. Sugar monomers are fermented at approximately 30 °C for 40–60 h to produce ethanol and CO_2; and 4. The fermented mash is distilled to separate the ethanol from solids and water. After distillation, the residues are centrifuged into solid (grain residue) and liquid (thin stillage) fractions. The liquid fraction is further concentrated by evaporation to produce wet distillers grain (WDG). The WDG is sold directly as animal feed or concentrated to produce DDGS [16]. Almost all the industrially produced ethanol fermentation processes utilizes *Saccharomyces cerevisiae*. Other microorganisms include *S. uvarum*, *Schizosaccharomyces pombe*, and *Kluyveromyces* [55].

The wet milling process configuration is more complicated than the dry milling process. The wet milling of grains such as corn and wheat are different because of the gluten protein content. In general, the wet milling process consists of steeping, degerming, defibring, starch/gluten separation, liquefaction, saccharification and fermentation, distillation and dehydration [56]. Steeping involves a combination of biochemical, chemical, and mechanical processes. Maize kernels are conditioned to separate the germ, fiber, and gluten from starch. Separation is achieved by conditioning the kernels at 50–52 °C with 0.12–0.2 % sulfurous acid for 24–28 h [57]. Steeping water is concentrated to a liquor containing 35–45 % proteins and sold as fermentation nutrients or used to produce a gluten feed. During degerming, the steeped maize kernels are broken apart to produce a mixture containing maize germ

plus a starchy slurry. The maize germs, which are separated from the starch slurry, are washed, dewatered, and dried. Oil is extracted from the maize germs and subsequently, the spent germs is processed into germ meal or used to produce a gluten feed. The starchy slurry from the degerming process undergoes washing, grinding, and screening to produce a mixture containing fibers, starch plus gluten. The fibers are separated and dried to produce a gluten feed. The stream containing the remaining starch plus gluten is processed to produce a gluten-rich stream which is concentrated to a gluten meal. After removing the gluten, the starch-rich process stream is used to produce a series of starch products which are used to produce ethanol [16].

Ethanol yields from corn fermentation are estimated at approximately 400–425 L tonne[-1] for first-generation production technologies [48, 58, 59] while for lignocellusoics, the yield is approximately 300 L tonne[-1] of sulfite pretreated Douglas-fir forest residue (Table 8.6) [60]. The ethanol yield is not only feedstock dependent but it is also affected by the process design configuration. For instance, the yields for dry and wet corn milling processes are approximately 460 and 440 L tonne[-1], respectively [61].

The sugarcane to ethanol industry in Brazil evolved out of the 1970s global energy crisis. Sugarcane cultivation in Brazil's economy generates 2.5 % of its gross domestic product with the ethanol industry contributing a further 1.1 % [62] or $60 billion U.S. [63]. The sugarcane to ethanol first-generation process is configured with a series of unit operations which involve physical and biochemical processes [64]. In the first step, crushing and pressing releases the juice while heating and clarification unit processes separate solids from the liquid fraction. Evaporation, crystallization, centrifugation are used to concentrate and purify the sugar stream. After producing ethanol by yeast fermentation, the liquid stream is distilled and dried. The bagasse byproduct is used as an energy source. Alternatively, after pretreating bagasse, glucose is recovered and subsequently used to produce ethanol. The solids fraction from pretreating bagasse is utilized to produce power and heat.

Beet sugar production facilities are configured with unit processes to produce sugar which is subsequently converted to ethanol. Screening and washing are employed to remove rocks and other unwanted fractions such as leaves and small roots. The beet roots are chopped into 3 mm size fractions and processed to extract the sugar using hot water fed to rotary drum screens, followed by dewatering. The remaining solids are sold as animal feed. Liquid from the hot water treatment and dewatering processes are combined for further processing. The liquid sugar stream is clarified before fermentation to ethanol. Typical ethanol yield for beet is approximately 375 L dry tonne[-1] (Table 8.6).

Second-Generation Ethanol Production from Lignocellulosics

Currently, corn stover, cereal straws, and sugarcane bagasse are the primary feedstocks for producing second-generation lignocellulosic ethanol (Table 8.7).

Table 8.7 Lignocellulosic biomass composition and ethanol yield

Crop	Cellulose plus hemicellulose content	Lignin	Ash	Ethanol yield (L dry tonne^{-1})
	dry wt%			
Bagasse	59–76[1], 70.8[2]	19–24[1,2]	4.5–9.0[1,2]	300[3]
Corn stover	63[4]	17.5[4]	6.6[4]	300[3],220–255[5,10], 238[6]
Wheat straw	59[4]	25[4]	6[4]	340[7]
Miscanthus	69[8]	13[8]	3[8]	165–295[9]
Switchgrass	59[8]	18[8]	5[8]	225[10]

[1]Soccol et al. [65]; [2]Canikha e al [66]; [3]Somerville et al. [67]; [4]Abbas et al. [32]; [5]Tumbala et al. [68]; [6]Aden et al. [69]; [7]Talebina [70]; [8]Abramson et al. [71]; [9]Lee and Kuan [72]; [10]Ewanick and Bura [73]

However, energy crops, such as *Miscanthus*, a relative of sugarcane which can grow in cooler climates and switchgrass are considered as potential future lignocellulosic feedstocks. *Miscanthus* yields in various European countries typically range from 4 to 44 tonne ha^{-1} while in the U.S., the yield (tonne ha^{-1}) is typically 11–14.5 [74–76]. Typical switchgrass yields in the U.S. range from 5 to 11 tonne ha^{-1} [77].

The process design configuration for second-generation lignocellulosic ethanol production generally includes pretreatment followed by fermentation [78]. The initial pretreatment step involves deconstruction of the biomass using physical, physicochemical, chemical, or biological treatments to render the complex carbohydrates accessible to hydrolysing enzymes. These complex polysaccharides (cellulose and hemicellulose) are then treated with enzyme cocktails which include cellulases, xylanases, ferulic acid esterases, etc., to produce both hexose and pentose sugars. The sugars are fermented to ethanol by a range of microorganisms [79]. Recent pretreatments methodologies have focused on the separation of the hemicellulose fraction prior to enzymic digestion enabling a harsher treatment to be used on the cellulose fraction. Following fermentation, the ethanol stream is concentrated by distillation while lignin is recovered and used for energy production. Typical second-generation lignocellulosic ethanol yields are shown in Table 8.7.

A lignocellulosic to ethanol process developed by Iogen was recently licensed to Raízen Energia Participacoes S/A, a major sugarcane processor, in Brazil. The Iogen process, which uses a bagasse feedstock, is configured with pretreatment, enzymatic hydrolysis, lignin separation, and processing plus fermentation and distillation. The high temperature pretreatment process is designed with a short residence time and mild acid hydrolysis. Acid hydrolysis prepares the feedstock for enzymatic hydrolysis. During enzymatic hydrolysis, cellulose is converted into six-carbon sugars. The hydrolysis products are divided into solid and liquid fractions. The solid portion is primarily lignin while the liquid fraction containing sugars is converted to ethanol by fermentation. Five- and six-carbon sugars are converted to ethanol using genetically modified yeasts. The dilute ethanol stream is

concentrated into commercial-grade fuel ethanol. Other cellulosic ethanol facilities operating in the U.S. include Abengoa BioEnergy (Hugoton, Kansas) and Ineos Bio (Vero Beach, Florida) [80]. Facilities operational in Europe include Abengoa (Spain), Chempolis (Finland), Clariant/Sud-Chemie (Germany), Inbicon (Denmark), Mossi and Ghisolfi (Chemtex) (Italy), and St1 Biofuels (Finland) [81].

Saccharomyces cerevisiae and *Zymomonas mobilis*, genetically modified microorganisms are useful ethanologens for converting biomass into ethanol. These microorganisms have been used extensively in industry for producing ethanol using starch or sugar-based feedstocks [82, 83]. However, they only utilize hexose monomers and cannot consume pentose sugars [82, 83]. Bacteria such as *Escherichia coli* and *Klebsiella oxytoca* can consume a wide range of substrates including hexose and pentose sugars in cellulosic biomass hydrolysate. These excellent microorganisms have been genetically modified to ferment sugars in a hydrolysate from cellulosic biomass [82, 84, 85].

Second-Generation Ethanol Production Using a Hybrid Thermal/Fermentation Process

Thermal treatment of biomass to biofuels is divided between gasification and pyrolysis technologies. The Fischer–Tropsch three-step process combines coal gasification or natural gas reforming in the first step to produce a CO plus H_2 synthesis gas with a second-step heterogeneous catalytic step to produce a wide range of gaseous and liquid fuels. In the third step, longer chain, waxy synthetic hydrocarbons are hydrocracked to fuel grade fractions [86]. Coal gasification or alternatively methane reforming or partial oxidation produces a CO and H_2 rich gas under limited oxygen conditions [87, 88]. The technology was initially developed by Germany during World War II. The process was subsequently adopted by SASOL, a South African company, after the 1970s global energy crisis. The gasification and heterogenous catalytic processes are designed to operate under typical conditions of 2–20 MPa [89] plus 125–1600 °C [89–90] and 0.2–1.5 MPa [91] plus 125–325 °C [87], respectively.

Utilizing synthesis gas to produce bioethanol is a second-generation process under development. The process configuration for producing ethanol from biomass is simpler when compared to natural gas or coal processing to produce a CO plus H_2 rich synthesis gas. The hybrid biomass gasification plus fermentation process produces ethanol from synthesis gas. The fermentation reaction is mediated by anaerobic micoorganisms such as *Clostridium ljungdahlii* and *C. autoethanogenum* [92, 93]. The technology is licensed to Coskata Warrenville, Illinois. In a typical design configuration, the hybrid gasification fermentation pilot-scale technology is configured with a Westinghouse plasma gasifier [94].

8.3.2.3 Second-Generation Biofuel Production Using Thermal Processing of Lignocellulosics

Biomass pyrolysis is an evolving second-generation technology used to produce bio-oils, char, and gas. Pyrolysis is the thermal degradation of wood in the absence of oxygen. The technology is generally categorized as "fast" or "slow" depending on the reaction time for processing into byproducts. During fast pyrolysis, bio-oil yield can reach 80 % of the product on a dry fuel basis. Bio-oil can be used as a liquid fuel or as a feedstock for producing other chemicals. Biomass pyrolysis is typically performed at a relatively low temperature range (300–650 °C). During slow pyrolysis, the biomass is heated at a moderate rate to approximately 600 °C with a residence time 5–30 min. Typically for fast pyrolysis, the residence time is <2 s and the heating rate is high with a final temperature at 500 °C [95].

8.3.2.4 First-Generation Biodiesel Production from Vegetable Oils

Biodiesel production is mainly concentrated in the EU and the U.S. Approximately 60 % of the global total is produced in the EU. Biodiesel production is also emerging in Brazil China, India, Indonesia, and Malaysia. In 2007, the total biodiesel produced was estimated at approximately 10 billion liters [96].

Acid Hydrolysis

First-generation biodiesel production technology is well developed with feedstocks derived from corn, soybeans, canola oil, rapeseed, palm oil, Jatropha, waste frying oil, and coconut oil. Biodiesel (long-chain fatty acid methyl esters (LCFAME)) is produced by combining a vegetable oil with an alcohol (ethanol or methanol) and a catalyst (usually NaOH or KOH). The transesterification reaction involves converting the vegetable oil molecule into three LCFAME molecules plus one glycerol molecule [97]. The reaction mixture process stream, after mixing the catalyst, alcohol plus vegetable oil, is separated by centrifugation into methyl esters plus glycerol. In the next stage, fatty acid esters are neutralized with acid and glycerol is removed due to its low solubility. The centrate stream containing glycerol (50 %), fatty acid soaps, and methanol, is acidified and subsequently, the free fatty acids are phase separated and removed. Methanol is also removed and the glycerol stream is concentrated to 85 %. Methanol removed from the neutralization and acidification stages is combined and vacuum flash evaporated to separate methanol from water. The LCFAME stream is washed and subsequently dried to produce the biodiesel product [98].

Enzymatic Hydrolysis

Lipase-catalyzed hydrolysis of triacylglycerol is utilized to produce free fatty acids (FFA) plus glycerol. The enzymatic reaction is advantageous because glycerol is easily recovered without complex processing. The FFA are completely converted to methyl esters and wastewater treatment is not required [99]. Lipase-catalyzed transesterification is performed at low temperature and ambient pressure and hence, less energy intensive when compared to chemically catalyzed reactions. The technology is underdeveloped because of constraints such as enzyme cost and enzyme inhibition by methanol beyond a threshold level [99–102].

8.3.2.5   Third- and Fourth-Generation Biodiesel Production Using Algae and Yeast

Algae have been considered as third- and fourth-generation biofuel feedstock because existing processing routes can be designed to produce biodiesel. However, microalgae can be potentially processed into other fuels such as methane, alcohols, and distillate fuels [103]. Microalgae, which are high yielding, do not compete with land use and as food crops and hence, they are excellent feedstocks. Cultivation of any biomass requires water as well as nutrients. Terrestrial biomass cultivation generally requires water sources with relatively low salt levels because of problems associated with salt accumulation. Nutrients for terrestrial crop cultivation can be supplied from fertilizers, treated effluents as well as stabilized microbial cultures produced from wastewater treatment. In the case of algae cultivation, growth can be accomplished in seawater and nutrients supplied from wastewater streams.

Oleaginous yeast is another feasible source of third-generation feedstock. Glucose is the primary sugar used by yeast such as *Saccharomyces cerevisiae*. However, using glucose as a carbon source is not economically feasible and alternate electron donor carbon sources, especially waste material have received more attention to produce microbial lipid. A comprehensive review summarizing lipid analyses for 480 yeast strains has also reported 46 strains belonging to 14 species were oleaginous with yields reaching up to approximately 70 % oil (w w^{-1}) [104]. Many major species studied to date include *Yarrowia lipolytica, Rhodotorula glutinis, Rhodotorula graminis, Cryptococcus curvatus, Cryptococcus albidus,* and *Rhodosporidium toruloides* [105].

In the U.S., many algae strains have been identified by the Department of Energy (DOE) Aquatic Species Program (ASP). Several promising algal species such as *Botryococcus braunni, Chaetoceros calcitrans,* several *Chlorella* species, *Isochrysis galbana, Nanochloropsis, Schizochytrium limacinum,* and *Scenedesmus* species have been examined as potential biofuel feedstock sources [103, 106, 107]. The U.S. and Europe are the largest producers of algae biodiesel with the U.S. accounting for 87 % of the total global industrial production [103]. Typical lipid yields for a variety of algae and yeast species are provided in Tables 8.8 and 8.9, respectively.

Table 8.8 Biomass composition of microalgae expressed on a dry matter basis [108, 109]

Strain	Protein	Carbohydrates	Lipid
	% dry w w^{-1}		
Anabaena cylindrica	43–56	25–30	4–7
Botryococcus braunii	40	2	33
Chlamydomonas rheinhardii	48	17	21
Chlorella vulgaris	41–58	12–17	10–22
Dunaliella salina	57	32	6
Euglena gracilis	39–61	14–18	14–20
Porphyridium cruentum	28–39	40–57	9–14
Prymnesium parvum	28–45	25–33	22–39
Scenedesmus dimorphus	8–18	21–52	16–40
Spirogyra sp.	6–20	33–64	11–21

Table 8.9 Typical lipid composition for yeasts [104]

Species	Lipid content (% dry w w^{-1})	TG	FA	Sterol	SE	PL
		Percent composition				
Debaryomyces hanseni	7	27	4	6	1	60
Hansenula anomala	13	77	Trace	3	15	17
Lipomyces starkeyi	16	60	22	3	1	9
Saccharomyces cerevisiae (agar plate)	7	7	4	4	22	62
Saccharomyces cerevisiae (batch culture)	9	40	6	–	20	30
Yarrowia lipolytica (Candida lipolytica)	36	52	5	–	4	9
Candida utilis	11	55	1	2	1	38
Rhodotorula rubra	15	63	6	2	1	25

TG = triacylglycerols, FA = nonesterified fatty acids, SE = sterol esters, PL = phospholipids

Research and development activities as well as pilot-scale facilities development for third-generation algae to biodiesel facilities are primarily located in the U.S., Europe, and China. The U.S. DOE has invested heavily in developing the technology [110]. Many U.S. companies as well as research institutions are major players leading the technology development efforts.

The third-generation technology employs several processes to produce a variety of biofuels from algae. The unit process configuration utilizes oil extraction, transesterification, and subsequently, distillation. It is envisaged that future new fourth-generation technologies will be developed that advances the process design of third-generation technologies using a genetically modified feedstock, namely those terrestrial or aquatic plants which can capture CO_2 more efficiently. In

addition, genetically modifying algae may be employed to increase CO_2 utilization with a subsequent increase in lipid production [103].

### 8.3.2.6 First- and Second-Generation Biobutanol Production

Microbially produced butanol can be utilized without blending with other fuels or at any blend ratio in combustion engines. Butanol is produced together with other solvents by Clostridia [111–114]. Acetone, butanol, and ethanol (ABE) are produced by fermentation of hexoses. *C. acetobutylicum*, *C. beijerinckii, C. saccharobutylicum,* and *C. saccharoperbutylacetonicum* are mainly utilized in industrial production processes [115–119]. These microorganisms utilize mainly starch or sugars. Corn (starch) or molasses from sugar beet and sugarcane (sugar) are used for industrial ABE fermentations [112]. In addition, other substrates in wastes such as microalgae-based biodiesel residues have been used with varying success [120]. Microbial butanol yield is affected by the cost for substrates such as glucose, corn, sugarcane molasses, and whey permeate. An alternate approach to produce second-generation biobutanol is reducing the production cost by utilizing lignocellulosics such as corn stover, rice straws, corn fiber, switchgrass, alfalfa, reed canary grass, sugarcane bagasse, *Miscanthus*, waste paper, DDGS, and soy molasses [121]. Waste agriculture residues and lignocellulosics are complex structures containing a mixture of cellulose, hemicellulose, and lignin. Because the structure complexity does not permit direct fermentative microbial activity, pretreatment and coupled with hydrolysis are required prior to fermentation. During pretreatment, inhibitor chemicals impair the reaction rates and hence, purifying the hydrolysate is necessary before fermentation [121]. Microbial cultures such as C. *sacchrobutylicum* P262 and *C. beijerinckii* P260 have been utilized to produce hydrolysates containing toxic chemicals. Strains capable of withstanding chemical toxicity will accelerate development of the technology [121]. Butanol is commercially produced by companies such as GreenBiologics Ltd in the UK.

8.3.2.7 Biohydrogen Production

A variety of technologies have been under investigation for producing biohydrogen. The technology type is based on the enzyme systems used to produce hydrogen. Biohydrogen production routes are divided into biophotolysis (direct/indirect), dark fermentation, and photofermentation. In the direct biophotolysis process, water is converted into hydrogen plus oxygen via photosynthetic reactions in the presence of solar energy (Eq. 1). A major disadvantage is that the Fe-hydrogenase activity is oxygen sensitive. *Chlamydomonas reinhardtii*, a green algae, has been shown to deplete the oxygen level during the oxidative respiration [122]. However, the reaction is short-lived and the hydrogen production rate is approximately one-tenth of other photosynthetic reactions [123].

$$2H_2O + \text{light energy} \rightarrow 2H_2 + O_2 \tag{1}$$
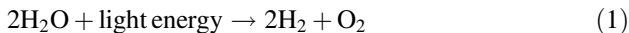
In the indirect process, enzymatic inhibition caused by O_2 is resolved by separating O_2 and H_2 evolution (Eqs. 2 and 3) [123]. Carbon dioxide is fixed and serves as the electron carrier between the O_2 producing (water splitting) reaction and the O_2 sensitive hydrogenase reactions. Many green algae and cyanobacteria are able to fix CO_2 via photosynthesis (Eq. 3) and they also have the ability to fix nitrogen and use enzymes which are able to catalyze the second H_2 generation step (Eq. 4) [123, 124].

$$12H_2O + 6CO_2 \rightarrow C_6H_{12}O_6 + 6O_2 \tag{2}$$

$$C_6H_{12}O_6 + 12H_2O \rightarrow 12H_2 + 6CO_2 \tag{3}$$
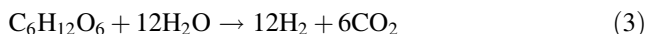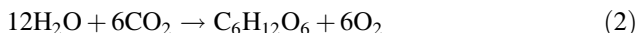
In the photofermentaton process, H_2 production by purple non-sulfur bacteria is attributed to nitrogenases under O_2 deficient conditions using light energy and electron donors (organic acids). *Rhodopseudomonas palustris* is able to oxidize organic electron donors in the presence of light energy to produce H_2 [125].

$$C_6H_{12}O_6 + 12H_2O + \text{light energy} \rightarrow 12H_2 + 6CO_2 \tag{4}$$
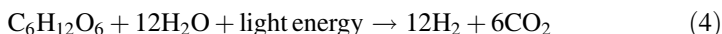
Dark fermentation is mediated by a consortium of microorganisms consisting of hydrolytic degraders, acetogens, acidogen plus methanogens. Carbohydrates, mainly glucose, are the preferred carbon sources used to produce acetic and butyric acids together with H_2 (Eqs. 5 and 6) [124].

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \tag{5}$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow CH_3CH_2COOH + 2CO_2 + 2H_2 \tag{6}$$

Clostridiales and *Enterobacteriaceae* are recognized H_2-producers during dark fermentation. However, H_2-consumers such as hydrogenotrophic methanogens and homoacetogens reduce the H_2 yield by producing methane and acetic acid, respectively. In addition to environmental and engineering factors, chemical inhibition of H_2 consumers is able to increase the H_2 yield. In general, factor are selected to promote the growth of H_2 producers and reduce the growth of H_2 consumers. Heat, pH adjustment, ethylene, and 2-bromoethanesulfonate (BES) have been used to inhibit H_2 consumers in mixed anaerobic cultures [126, 127]. Even though BES and ethylene are effective inhibitors, storage as well as toxicity are major issues if these chemicals are discharged into the environment. Long chain fatty acids (LCFAs) are renewable chemicals and relative nontoxic because they are degradable. LCFAs have been used effectively to inhibit H_2 consumers and subsequently, increase the H_2 yield in mixed anaerobic cultures [125].

Researchers have also employed genetic modification of pure cultures to control the production of reduced products such as alcohols and selected organic acids [128]. Kumar et al. [128] demonstrated that improving the H_2 yield can be achieved through redirecting the metabolic fluxes by blocking formation of alcohol and some organic acids in *Enterobacter cloacae* IIT-BT 08. The double mutant with defects in both alcohol and organic acid formation pathways was shown to yield 3.8 H_2 mol mol^{-1} of glucose. This yield is close to the theoretical H_2 yield of 4 mol mol^{-1} glucose.

Microbial technologies for producing biohydrogen can be classified based on substrate utilization and genetic modification. A large amount of work has focused on optimizing the H_2 yield using hexoses and pentoses feedstocks fed to mixed microbial cultures. However, low H_2 yields coupled with the production of reduced carbon products (alcohols plus organic acids) and high substrate cost are major factors preventing the development of utilizing carbohydrate feedstocks. Employing lignocellulosics have been used to produce H_2 using pure and mixed cultures [129–132].

8.4 Conclusions and Perspectives

Ethanol, diesel, butanol, and methane are the major biofuels accounting for a large fraction of the current renewable energy market. Currently, biofuels are produced mainly from food-based crops such as corn, wheat, sugarcane, sugar beet, palm oil, rapeseed, and soy. "Nonfood" feedstocks available globally for biofuel production include energy crops (*Miscanthus*, switchgrass, Jatropha), wastes (waste oils, food processing wastes), agricultural residues (straw, corn stover), forestry residues as well as emerging feedstocks such as algae. Further technology development includes converting lignocellulosics to ethanol, butanol, methane, and hydrogen and algae to biodiesel and developing cost-competitive technologies is a large component of this effort.

Although biofuels offer numerous benefits to society, a global debate over the past several years has critically evaluated the impact on food production and prices. Increasing global population growth is linked to increasing competition for land and water, for woody biomass (e.g., timber for construction), and for bioenergy (heat and power) as well as liquid biofuels. Biofuels are part of a growing global industry which is driven by issues such as reducing our dependence on fossil fuels, decelerate climate change, and increase fuel security. However, growth of the industry will be limited by the availability of suitable land and water resources.

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