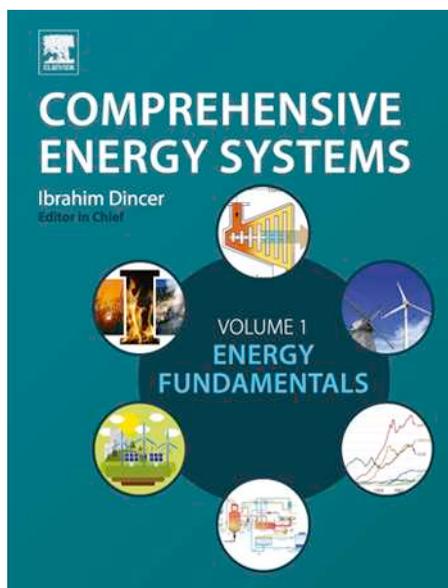


**Provided for non-commercial research and educational use.  
Not for reproduction, distribution or commercial use.**

This article was originally published in *Comprehensive Energy Systems* published by Elsevier, and the attached copy is provided by Elsevier for the author's benefit and for the benefit of the author's institution, for non-commercial research and educational use including without limitation use in instruction at your institution, sending it to specific colleagues who you know, and providing a copy to your institution's administrator.



All other uses, reproduction and distribution, including without limitation commercial reprints, selling or licensing copies or access, or posting on open internet sites, your personal or institution's website or repository, are prohibited.

For exceptions, permission may be sought for such use through Elsevier's permissions site at:

<http://www.elsevier.com/locate/permissionusematerial>

Yaşar Demirel. (2018) 1.22 Biofuels. In: Dincer, I. (ed.), *Comprehensive Energy Systems*. vol. 1, pp. 875–908. Oxford: Elsevier.

© 2018 Elsevier Inc. All rights reserved.

## 1.22 Biofuels

Yaşar Demirel, University of Nebraska Lincoln, Lincoln, NE, United States

© 2018 Elsevier Inc. All rights reserved.

<b>1.22.1</b>	<b>Introduction</b>	876
<b>1.22.2</b>	<b>Background and Fundamentals</b>	877
1.22.2.1	Biomass	877
1.22.2.2	Biofuel and Conversion Processes	877
<b>1.22.3</b>	<b>Biorefinery Systems</b>	878
<b>1.22.4</b>	<b>Conversion Processes</b>	880
1.22.4.1	Biochemical Processes	880
1.22.4.2	Chemical Processes	880
1.22.4.3	Thermochemical Processes	881
1.22.4.4	Hydrothermal Liquefaction	881
<b>1.22.5</b>	<b>Biofuels</b>	882
1.22.5.1	Biohydrogen	882
1.22.5.2	Bioethanol	883
1.22.5.2.1	First generation bioethanol	883
1.22.5.2.2	Second generation bioethanol	883
1.22.5.2.2.1	Second generation bioethanol by biochemical processes	883
1.22.5.2.2.2	Second generation bioethanol by thermochemical processes	884
1.22.5.3	Fischer–Tropsch Diesel	884
1.22.5.4	Biobutanol	885
1.22.5.5	Biomethanol	885
1.22.5.5.1	Biomethanol from sewage sludge	886
1.22.5.6	Biodimethyl Ether	886
1.22.5.7	Biodiesel	886
1.22.5.7.1	Biodiesel from plant oils	886
1.22.5.7.2	Green diesel	887
1.22.5.7.3	Biodiesel from algae	887
1.22.5.7.4	Nutrient recovery from municipal wastewater for algae-based biofuel production	888
1.22.5.7.5	Jet fuel from camelina	888
<b>1.22.6</b>	<b>Further Discussions</b>	889
1.22.6.1	Comparison of Biomass Used for Bioethanol Production	889
1.22.6.2	Chemical and Fuel Properties of Biofuels	890
1.22.6.3	Energy Efficiencies of Biofuels	890
1.22.6.4	Renewable Fuel Standard	892
1.22.6.4.1	Categories of renewable fuel	892
1.22.6.5	Biofuel Assessment Models	892
1.22.6.5.1	Life cycle assessment	893
1.22.6.5.2	Risk assessment for biofuels	893
1.22.6.6	Right Way to Use Biofuels	893
1.22.6.6.1	Safety of biofuels	893
1.22.6.6.2	Economic assessment of biofuels	893
1.22.6.6.3	BioBreak model for second generation biomass feedstock	894
1.22.6.6.3.1	Willingness-to-pay for lignocellulosic bioethanol production	895
1.22.6.6.3.2	Willingness-to-accept for lignocellulosic bioethanol production	895
1.22.6.6.4	Optimum cost of algae biomass	898
<b>1.22.7</b>	<b>Case Studies</b>	899
1.22.7.1	Biohydrogen Production	899
1.22.7.2	Biomethanol Production	900
1.22.7.3	Biodimethyl Ether Production	902
1.22.7.4	Methyl Dodecanoate (Biodiesel)	902
<b>1.22.8</b>	<b>Future Directions</b>	903
<b>1.22.9</b>	<b>Closing Remarks</b>	904
<b>References</b>		905
<b>Further Reading</b>		907
<b>Relevant Websites</b>		907

**Nomenclature**

$C_{\text{Algae}}$	The maximum acceptable cost of algae, US\$ t <sup>-1</sup>	$E_V$	Energy equivalent factor
$C_{\text{ES}}$	Establishing and seeding cost	$G$	Government incentives
$C_{\text{HM}}$	Harvest and maintenance cost, US\$	$M$	Mass of algae, t
$C_I$	Investment cost, US\$	$PG$	Price gap: WTA-WTP, US\$ t <sup>-1</sup>
$C_O$	Operating cost, US\$	$P_{\text{gas}}$	Price of gas US\$ L <sup>-1</sup>
$C_{\text{Opp}}$	Opportunity cost, US\$	$P_{\text{oil}}$	Price of oil US\$ barrel <sup>-1</sup>
$C_S$	Biomass storage cost, US\$ t <sup>-1</sup>	$Q$	Biogas volume produced by anaerobic digestion (400 m <sup>3</sup> t <sup>-1</sup> )
$D$	One-way transportation distance, km	$T$	Tax credit, US\$ t <sup>-1</sup>
$DFC$	Transportation fixed cost, US\$ km <sup>-1</sup>	$V_{\text{CP}}$	Coproduct production, t
$DVC$	Transportation variable cost, US\$ km <sup>-1</sup>	$V_O$	Octane benefit, US\$0.1 gal <sup>-1</sup>
$E_{\text{biodiesel}}$	Average energy content of biodiesel, MJ t <sup>-1</sup>	$w$	Oil content of algae biomass, %
$E_{\text{biogas}}$	Energy content of biogas MJ m <sup>-3</sup>	$Y_B$	Biomass yield, %
$E_{\text{petroleum}}$	Energy contained in a barrel of petroleum, MJ barrel <sup>-1</sup>	$Y_E$	Conversion ratio

**Abbreviations**

CHST	Cost of collection harvesting, storage and transportation, US\$ t <sup>-1</sup>	HHV	Higher heating value, MJ kg <sup>-1</sup>
CLSG	Chemical-looping steam gasification	ICI	Imperial chemical industries
CNR	Nutrient replacement cost, US\$ t <sup>-1</sup>	LCA	Life Cycle Assessment
DDGS	Dried distillers' grain solubles	LHV	Lower heating value, MJ kg <sup>-1</sup>
DMC	Dimethyl carbonate	LPG	Liquid petroleum gas
DME	Dimethyl ether	MeOH	Methanol
EROI	Energy Return on Investment, US\$ t <sup>-1</sup>	NREL	National Renewable Energy Lab
FAPRI	Food and Agricultural Policy Research Institute	POLYSYS	Policy Analysis System
FASOM	Forest and Agricultural Sector Optimization Model	RFS	Renewable fuel standard
FDA	Food and Drug Administration	RIN	Renewable identification number
F-T	Fischer-Tropsch	SRWC	Short rotation woody crops
GGE	Gallon of gasoline equivalent	TEA	Technoeconomic analysis
GHG	Greenhouse gas	TEAM	Tools for Environmental Analysis and Management
GTAP	Global Trade Analysis Project	USDA	United States Department of Agriculture
		WTA	Willingness-to-accept
		WTP	Willingness-to-pay

**1.22.1 Introduction**

Secure energy supplies drive technological developments for every nation. Because of the concerns of climate change, renewable energy is pursued as a secure and clean energy source [1,2]. Biofuels must contain over 80% renewable materials such as biomass, which is originally derived from the photosynthesis process. Biomass resources are mainly divided into four types, which are first, second, and third generations, and wastes. The first generation is food-based biomass such as corn, sugarcane, plant, vegetable oils, and fats. The second generation refers to nonfood-type biomass, which includes cellulose and hemicellulose, while third generation biomass mainly refers to algae and cyanobacteria. All these types of biomass can be converted to alcohols, biogas, biooil, biodiesel, and bioproducts by using biochemical, thermochemical, and hydrothermal processes [3,4].

Biofuels are promising alternatives to fossil fuels and are becoming part of sustainable development worldwide because they are produced predominantly from biomass feedstock. Biomass is a renewable resource with carbon sequestered and energy stored with very little sulfur content during the photosynthesis. Therefore, the biofuels have the capability of controlling the greenhouse gas (GHG) emissions and could have a positive impact on climate change. Bioethanol and biodiesel are the most widely used biofuels. Because of the demand for secure energy supplies and concerns of climate change due to the adverse impact of fossil fuels, biofuels are increasing their share in renewable energy usage worldwide as the conversion technologies of biomass to biofuels keep improving and biofuel costs are being reduced [4,5].

Biorefinery systems with multigeneration technology are advancing fast to integrate with the existing infrastructure of energy storage and distribution. This study highlights some recent developments and improvements in the biofuel production processes using various types of biomass feedstock. The main conversion processes including fermentation, transesterification, gasification, and Fischer-Tropsch (F-T) synthesis are analyzed together with economics and safety of biofuel production and usage.

## 1.22.2 Background and Fundamentals

Biofuels are biomass-based energy forms and this section summarizes what kinds of biomass and conversion processes are used to produce various biofuels.

### 1.22.2.1 Biomass

Biomass feedstock originates from diverse resources including naturally growing terrestrial and aquatic plants as well as natural or human-made wastes. Biomass also has diverse compositions of components including carbohydrates, lipids, lignin, and proteins. Based on this diversity, biomass feedstock is classified into first, second, and third generations, as well as wastes, as seen in [Table 1](#). Lignocellulosic biomass requires large land usage but does not compete with the food supply chain. On the other hand, aquatic biomass does not compete with the food supply chain and land usage either and its cultivation results in a higher yield.

[Table 2](#) shows the proximate and ultimate analyses of second generation biomass. The ultimate analysis indicates that the biomass contains between 40% and 53% of carbon and 5% and 6% of hydrogen, while the percentage of ash varies between 0.25% and 12%. Lignocellulosic biomass contains cellulose (38%–50%), hemicellulose (23%–32%), and lignin (15%–25%) [\[4\]](#).

### 1.22.2.2 Biofuel and Conversion Processes

Although biofuels are mainly considered as liquid fuels, such as bioethanol, biodiesel, and biomethanol, biogas and biopower are also biofuels. Bioethanol and biodiesel have by far the largest share of the global biofuels market. Total bioethanol from surplus corn in the United States and from sugarcane in Brazil reaches around 70% of the global bioethanol production capacity [\[6–8\]](#). The biofuel supply chain involves the growing/production of biomass, and then harvesting, collecting, storing, and transporting it to the biorefinery where it is converted to biofuel, bioproducts, heat, and power to be distributed to users. The unspecified term biomass usually contains 30% moisture, while the term dry biomass has 10% moisture. Food-based fuels are mainly bioethanol from corn, sugarcane, and biodiesel from plants, vegetable oils, and fats. The technology for these biofuels has reached a certain level of maturity and been accepted by society worldwide. However, the competition of biomass resources with food sources has created a discussion toward technoeconomic analysis and sustainability assessment of such biofuels.

Any type of biomass feedstock can be converted to biofuels by chemical, thermochemical, biochemical, and hydrothermal processes. Bioethanol, for example, can be produced either from sugarcane or corn as well as lignocellulosic biomass using

**Table 1** Comparison of various types of biomass

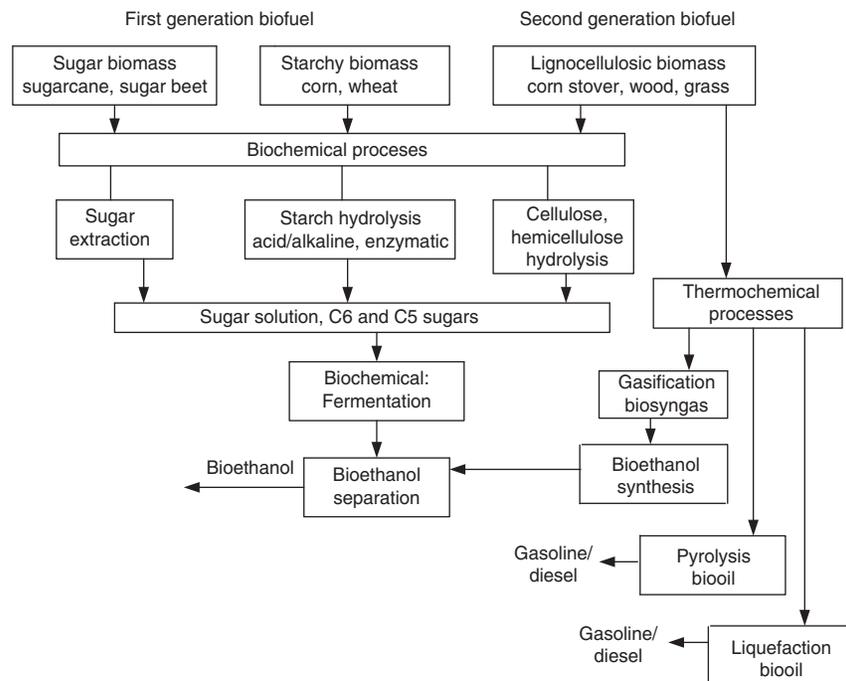
Generation	Type	Source	Examples
First	Food crops	Starch crops	Corn, wheat
		Sugar crops	Sugarcane, sugar beet, sweet sorghum
Second	Lignocellulosic crops	Feed	Grass
		Woody	Short-rotation crops, willow poplar
		Herbaceous	<i>Miscanthus</i> , switchgrass
Third	Aquatic	Microalgae	<i>Chlamydomonas reinhardtii</i> , chlorella, spirulina
		Macroalgae	Seaweed
		Water plants	Salt marshes, sea grass
Wastes	Natural	Agricultural	Animal manure, crop residues
		Forest	Logging residues, tree wastes
	Human-made	Municipal	Solid waste, sewage sludge, waste oil
		Industrial	Pulp and paper industry, sludge

**Table 2** Proximate and ultimate analyses of the second generation of biomass and wastes in wt% and dry base

Biomass type	Fixed C	Volatiles	Ash	C	H	O	N	S	HHV <sup>a</sup> , MJ kg <sup>-1</sup>
Redwood	16.10	83.50	0.40	53.50	5.90	40.30	0.10	0.00	21.03
Wheat straw	19.80	71.30	8.90	43.20	5.00	39.40	0.61	0.11	17.51
Corn stover	19.25	75.17	5.58	43.65	5.56	43.31	0.61	0.01	17.65
Bagasse	14.95	73.78	11.27	44.80	5.35	39.55	0.38	0.01	17.33
Sawdust	14.33	76.53	0.25	40.00	5.98	44.75	0.01	0.01	19.95
Manure and sludge			38.8	29.9	4.3	22.40	2.90	0.62	13.1
Municipal waste			27.1	40.4	4.9	25.30	0.91	0.35	16.5

<sup>a</sup>HHV: Higher heating values.

Source: Reproduced from Demirel Y. Energy: production, conversion, storage, conservation, and coupling. 2nd ed., London: Springer; 2016; Gaur S, Reed T, Teed TB. Thermal data for natural and synthetic fuels. New York, NY: CRC Press; 1998; Ptasincki KJ. Efficiency of biomass energy: an exergy approach to biofuels, power, and biorefineries. New York, NY: Wiley; 2016.



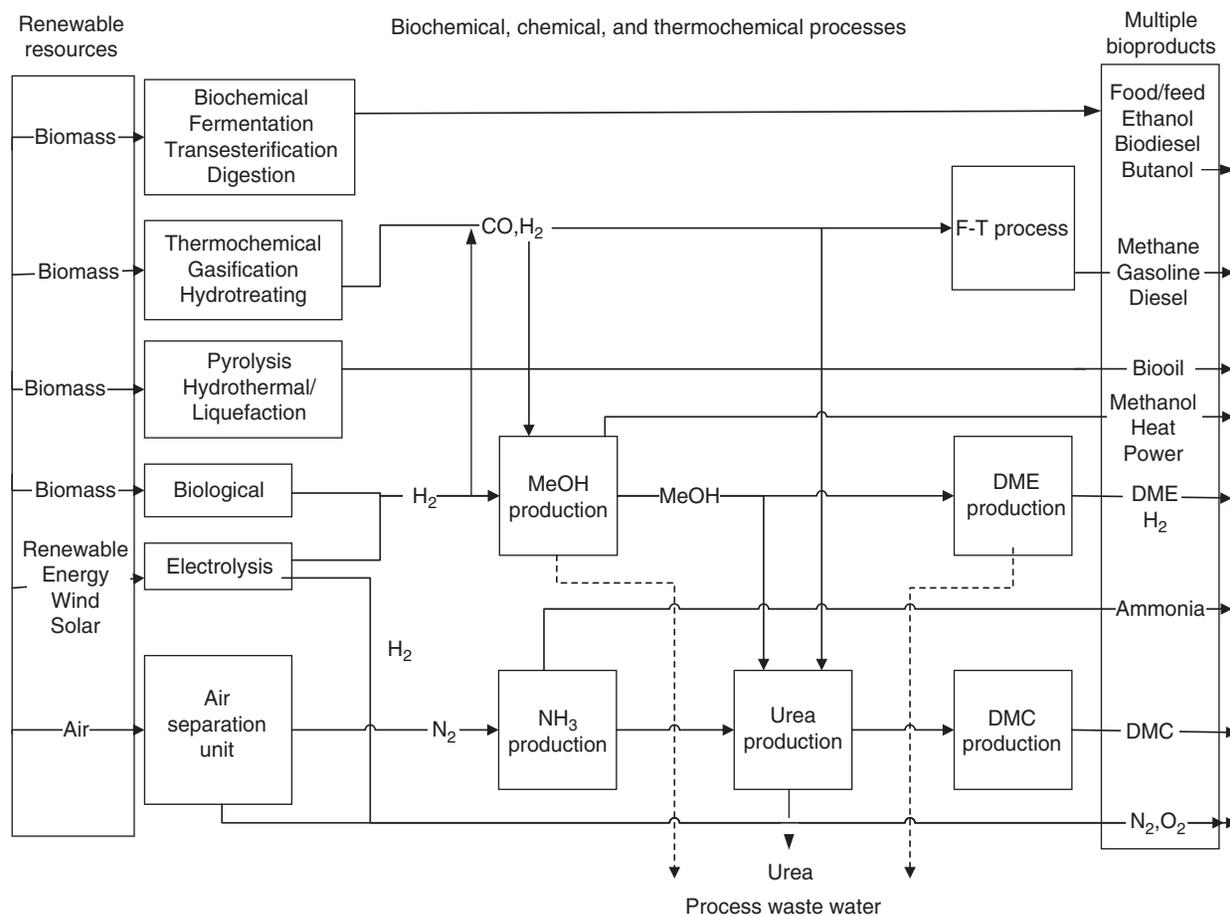
**Fig. 1** Biochemical and thermochemical routes for the first and second generation of biofuels.

biochemical and thermochemical conversion processes. The biochemical process of fermentation converts the first generation biomass of corn, sugarcane, and wheat to bioethanol, while biochemical and thermochemical processes convert the lignocellulosic biomass to bioethanol and other fuels and chemicals. Conversion of lignocellulosic feedstock requires first the complex process of conversion of hemicellulose and cellulose into fermentable sugars and consequently to bioethanol. The cost of the conversion processes of biomass increases in this direction: triglycerides → starch → lignocellulosic, while the cost of biomass increases in this order: lignocellulosic → starch → triglycerides. **Fig. 1** shows some of the basic steps of the conversion processes used in biofuel production.

### 1.22.3 Biorefinery Systems

Biomass can be converted to several renewable carbon compounds such as food/feed, chemicals beside biofuels, heat, and power in a biorefinery concept [9] similar to a currently existing petroleum refinery illustrated in **Fig. 2**. Since the biomass comes from diverse environments and requires various conversion processes, biorefinery is beneficial in converting various biomass feedstocks into various valuable products in a sustainable manner with positive impacts on economic activity, environment, and society [8]. There are two main operations in a biorefinery: first is the preparation of biomass by separating it into its constituent chemicals such as carbohydrates, triglycerides, protein, and lignin; and secondly converting them into various commodity and specialty products, power, and heat. Conversion processes are biochemical, chemical, thermochemical, and hydrothermal. Biochemical processes mainly refer to fermentation, anaerobic and aerobic digestion using microorganisms. Chemical processes mainly refer to transesterification of lipids, and F-T synthesis of biosyngas (mainly CO and H<sub>2</sub>) into biofuels [10]. Thermochemical processes refer to gasification, pyrolysis, and reforming, while hydrothermal processes use hot water and catalyst to liquefy various biomass feedstocks to biooil, which requires refining to biofuels. Use of existing petroleum refining and distribution with the biomass-based biooil, plant oil, lignin, biomass waste, and glycerol may be possible for the establishment of biorefinery to deliver jet fuel, diesel, gasoline, olefins, light gas, and liquid petroleum gas (LPG) [11]. The three possible options are [12,13]:

1. Fluid catalytic cracking involves the cracking of alkanes, alkenes, naphthene, and alkyl aromatics to a lighter product, followed by hydrogenation and coking reactions using solid catalyst such as Y-zeolites as binder, and alumina or silica-alumina. An effective H/C ratio of  $H/C = (H - 2O - 3N - 2S)/C$ , where H, C, O, S, and N are the moles of hydrogen, carbon, oxygen, sulfur, and nitrogen, respectively, is suggested for the biomass-derived oxygenates using catalytic cracking. H/C ratio is generally low in biomass feedstocks (<0.12).
2. Hydrotreating requires H<sub>2</sub> and can convert biomass-based biooil into more stable fuel with more energy density that is ready to blend with petroleum fuels. Hydrotreating adds hydrogen while removing sulfur, and oxygen (hydrodeoxygenation) using cobalt and nickel-based catalysts.
3. Use of biomass-derived syngas or H<sub>2</sub> by gasification/reforming to produce H<sub>2</sub>-rich syngas or pure H<sub>2</sub> required in fluid catalytic cracking and hydrotreating.



**Fig. 2** Block flow diagram of a biorefinery system for biofuel/bioproduct production from biomass feedstock and renewable resources. CO, carbon monoxide; DMC, dimethyl carbonate; DME, dimethyl ether; F-T, Fischer-Tropsch; MeOH, methanol; NH<sub>3</sub>, ammonia. Reproduced from Kumar A, Nouredini H, Demirel Y, Jones DD, Hanna MA. Simulation of corn stover and distillers grains gasification with Aspen Plus. *Transaction of American Society of Agricultural and Biological Engineers (ASABE)* 2009;52:1989–95; Cherubini F. The biorefinery concept: using biomass instead of oil for producing energy and chemicals. *Energy Convers Manag* 2010;51:1412–21; Phillips S, Aden A, Jechura J, Dayton D, Eggeman T. Thermochemical ethanol via indirect gasification and mixed alcohol synthesis of lignocellulosic biomass. Technical report NREL/TP-510-41168; 2007; Manganaro J, Chen B, Adeosun J, *et al.*, Conversion of residual biomass into liquid transportation fuel: an energy analysis. *Energy Fuels* 2011;25:2711–20.

The first step to use the cheap and abundant lignocellulosic biomass in a biorefinery is to convert it into alcohols by biochemical or thermochemical processes, biooil by fast pyrolysis or liquefaction. These oils have comparable properties to conventional fuel oil (see [Table 3](#)). With a renewable and affordable H<sub>2</sub> supply, hydrotreating can convert biooils into diesel and gasoline-type fuels using F-T synthesis. Gasification and upgrading of syngas into liquid “drop-in” fuels are possible at the pilot scale using various biomass feedstocks [14–16]. Catalysts for F-T synthesis are well developed yet sensitive to impurities. As [Fig. 2](#) shows, thermochemical conversion processes are not as feedstock-specific as biochemical conversion, allowing for a wide range of biomass feedstocks to be converted to various biofuels. This provides opportunities for refineries to be built in any location where adequate biomass can be produced to maintain their operations. Methanol (MeOH)-derived fuels include MeOH to gasoline technology, dimethyl ether (DME), dimethyl carbonate (DMC), and other products.

Central or distributed biorefineries are considered for using crop residues as biomass feedstock. One particular model considers locally pyrolyzing the biomass into biooil, char, and noncondensable gases, and transporting the biooil to a remote central biorefinery to convert into liquid transportation fuels with around 90% energy efficiency [17].

$$\left( \text{Energy efficiency of biomass to biofuel conversion} \right) = \frac{\left\{ \left( \frac{\text{LHV of biofuel produced per 1 kg of biomass}}{\text{of biomass}} \right) - \left( \frac{\text{External energy used in 1 kg biomass to biofuel conversion}}{\text{to biofuel conversion}} \right) \right\}}{\left( \frac{\text{LHV of the 1 kg biomass used in the conversion}}{\text{used in the conversion}} \right)} \quad (1)$$

**Table 3** Comparison of various properties of biomass-based biooils and petroleum-based fuel oil

Property	Biooil by pyrolysis	Biooil by liquefaction	Heavy petroleum fuel oil
Ultimate analysis			
C	54–58	73	85
H	5.5–7.0	8	11
O	35–40	16	1
N	0–0.2		0.3
Ash	0–0.2		0.1
Moisture, wt%	15–30	5	0.1
Specific gravity	1.2	1.1	0.94
Higher heating value (HHV), MJ kg <sup>-1</sup>	16–19	34	40
Viscosity, cP	0.2–1		1

Source: Reproduced from Czernik S, Bridgewater AV. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* 2004;18:590–8; Elliot DC, Schiefelbein GF. Liquid hydrocarbon fuels from biomass. *Am Chem Soc Div Fuel Chem* 1989;34:1160–6.

### 1.22.4 Conversion Processes

Biomass is an advantageous feedstock as it contains carbon, oxygen, and hydrogen in a variety of compounds, such as carbohydrate, lipids, and protein. On the other hand, high moisture content and low energy density create problems in biomass transportation and processing. Size reduction of cutting, crushing, and shearing using grinders, shredders, and clippers helps transport biomass in a cost-effective manner. In general, biomass feedstock preparation involves size reduction, densification, drying, and torrefaction. During torrefaction, biomass is heated at 200–300°C under an inert atmosphere to remove moisture and CO<sub>2</sub> resulting mass loss of about 30% and energy loss of around 10%. Reduced oxygen content improves gasification of biomass [18].

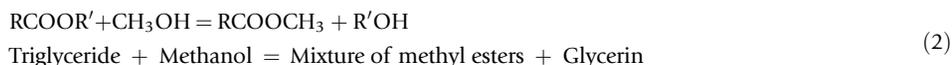
#### 1.22.4.1 Biochemical Processes

Various enzymes and microorganisms break down and convert organic compounds within biomass feedstocks into alcohols, biogas, biofuel, food/feed, and other chemicals. The chemical reactions in biochemical processes occur at lower temperatures as well as at lower conversion rates compared with the reactions in chemical and thermochemical conversion processes. As a result, biochemical processes are nonpolluting natural processes requiring low energy and few other chemicals. However, suitable process control systems are required to maximize the required product and reduce the side reactions. There are two biochemical processes operated at industrial scales: (1) fermentation of sugars in biomass crops to alcohols, primarily to bioethanol, and (2) anaerobic digestion of biomass and its wastes to methane known as biogas and residue that can be used as fertilizer. Both bacterial (*Escherichia coli*) (prokaryotic) and eukaryotic (yeast) cells are actively used in batch, fed-batch, or continuous fermentation. Beside these mainline processes, there are dark-fermentation, photofermentation, and others under development to produce H<sub>2</sub>, value-added chemicals, and dietary products from various biomass feedstocks [19]. Microbial electrolysis cell is also another process investigated for productions of H<sub>2</sub>, materials, and electricity [20].

The large-scale biochemical processes are used to produce bioethanol from mainly sugar crops, starch crops, and lignocellulosic feedstock by anaerobic fermentation using yeast. Another large-scale biochemical process is anaerobic digestion of wet biomass feedstock (< 15% solid), such as animal manure, agricultural residue, and sewage sludge from municipal waste water treatment to produce methane-rich biogas using bacteria (methanogenic), archaea, and fungi at 37–55°C. Biogas has a lower heating value (LHV) of 20–25 MJ Nm<sup>-3</sup> and can be used for heating, steam, and consequently electricity production. It can also be used as renewable natural gas after desulfurization and methane enrichment [21].

#### 1.22.4.2 Chemical Processes

The most-used direct chemical process in biofuel production is the transesterification of triglycerides of fatty acids into biodiesel (fatty acid methyl ester) using mainly MeOH or ethanol and a catalyst (mainly acids and alkali-NaOH) [22] and producing glycerin as a byproduct. The general transesterification reaction using MeOH is represented by



Triglycerides are esters of glycerol and are present in oilseed crops, such as soybean, rapeseed, and sunflower, as well as in animal fat. During the transesterification, methyl or ethyl esters of fatty acids are produced and used as biodiesel in compression-ignition engines. Waste cooking oil contains free fatty acid and is esterified with alkali (KOH) or acid first before being converted to biodiesel by transesterification [23].

Hemicellulose and cellulose within the lignocellulosic biomass contain a complex polymer of sugars that are known as polysaccharides (see Fig. 1). Hydrolysis of hemicellulose (C5 pentose units) and cellulose (C6 glucose units) using dilute inorganic acid into simple sugars is the second important chemical process for converting lignocellulosic biomass feedstock into bioethanol. As seen in Fig. 2, other commodity and specialty chemicals can also be produced by several processes in a biorefinery system, such as MeOH and DME.

F-T synthesis is another well-known indirect chemical process for producing biofuel from biosyngas, containing mainly CO and H<sub>2</sub> and produced from gasification of a biomass. A representative F-T reaction is



In the production of diesel fuel “*n*” can be in the range of 12–25; therefore, a H<sub>2</sub> to CO molar ratio of close to 2 is required. An iron-based catalyst and an operating temperature of 350°C will produce mostly gasoline, while a cobalt base and an operating temperature of 200°C will produce mostly diesel fuel. The crude biooil produced in the F-T synthesis is distilled to naphtha, distillate, and wax, which are processed through a series of refining and reforming steps with hydrotreatment and catalytic processes to produce gasoline and diesel at the required configurations [10,17].

#### 1.22.4.3 Thermochemical Processes

Thermochemical conversion processes of combustion, gasification, and pyrolysis take place at high temperatures (450–1200°C) and are very common for converting the second generation biomass feedstock and wastes into useful fuels and chemicals. In the indirect biomass gasification, heat for the gasification comes from an external source, while a part of the biomass is combusted in the direct gasification. A biomass, represented by C<sub>*n*</sub>H<sub>2*m*</sub>, is oxidized to CO<sub>2</sub> and water and releases heat of combustion, which can be used to produce steam and electricity in a Rankine cycle.



In a conventional gasification process, biomass (or other carbon-containing feedstock) reacts with limited oxygen (or air), CO<sub>2</sub>, and steam at high temperatures (750–1100°C) to produce synthesis (biosyngas) containing mainly H<sub>2</sub> and CO as well as CO<sub>2</sub>, methane, and others in small amounts [11]. The following reaction represents the steam gasification (reforming):



For dry basis, H<sub>2</sub> and CO contents of biosyngas are around 32 vol% and 29 vol%, respectively. After removing impurities (including nitrogen, methane, carbon dioxide) and enriching to the desired ratio of H<sub>2</sub> to CO, biosyngas can then be chemically converted into MeOH, ethanol, and other liquid fuels using F-T synthesis. The water-gas shift reaction can increase the hydrogen content from 6% to 6.5% in the initial biosynthesis gas to 30–50 vol% [24].



Overall yield and energy efficiency are 23%–41% and 32%–51%, respectively, for biomass-based hydrocarbon productions [25]. Purification of the syngas accounts for 60%–70% of the total capital cost.

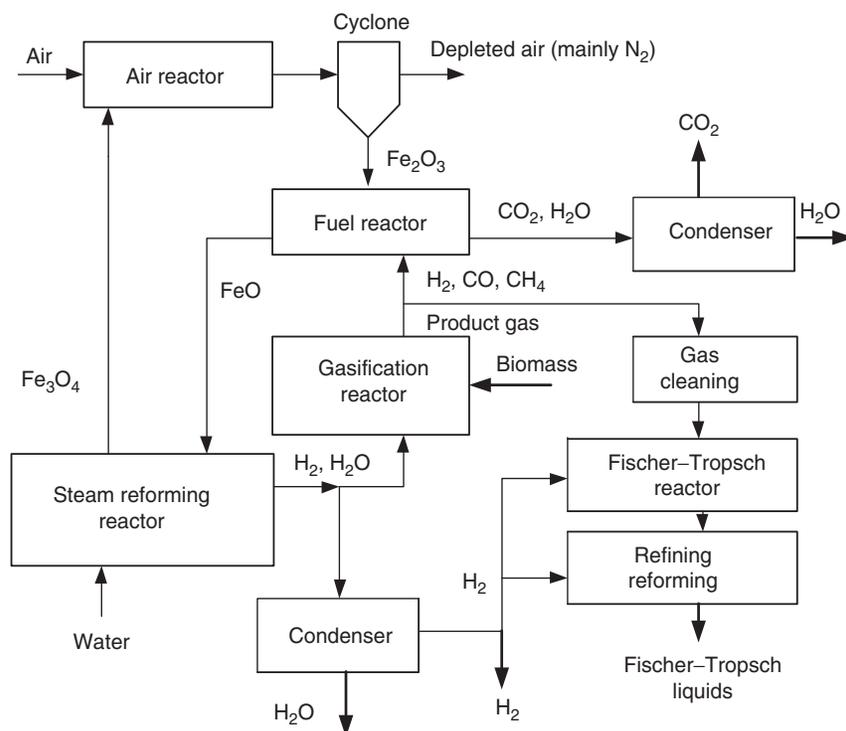
In chemical looping steam gasification (CLSG), an oxygen carrier, mainly a metal oxide, transfers oxygen to a biomass, preventing direct contact between the biomass and air [26,27]. An oxygen carrier such as Fe<sub>2</sub>O<sub>3</sub> binds oxygen in the air reactor and then provides O<sub>2</sub> in the fuel reactor to produce the product gas containing mainly CO and H<sub>2</sub>, as seen in Fig. 3. Thus, the oxygen carrier circulates between the fuel reactor and the air reactor. In CLSG, nitrogen is not allowed to come into contact with the biomass; thus, CO<sub>2</sub> does not become diluted by nitrogen, which is a major issue in restricting CO<sub>2</sub> capture from diluted CO<sub>2</sub> streams by solvents [28,29].

Pyrolysis uses fast heating to high temperatures under anaerobic conditions to break down biomass into a volatile mixture of hydrocarbons. This mixture of hot gases is condensed into a biooil with a rich mixture of hydrocarbons, some of which can be converted into biofuels. The raw biooil is an emulsion, rendering it incompatible with conventional petroleum oils and requiring additional upgrading. Table 3 shows the properties of biooil, which vary based on the conversion process. The most frequently proposed upgrading technology is hydrotreating.

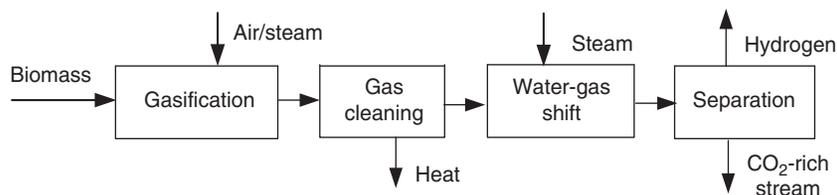
#### 1.22.4.4 Hydrothermal Liquefaction

Hydrothermal liquefaction of biomass also produces biooil through controlled reaction rates and reaction mechanisms using pressure and catalysts [30]. Catalysts used for upgrading liquefaction products include alkali, metals, and nickel and ruthenium heterogeneous catalysts. Hydrothermal liquefaction uses subcritical or supercritical water to liquefy biomass into a biooil (see Table 3). Elevated temperatures (200–400°C) are used in a pressurized vessel containing biomass (5–40 MPa), depolymerizing and converting cellulose, lignin, and hemicellulose into a soluble mixture that can be upgraded and processed in similar fashion as pyrolytic-based biooil [24]. The primary advantage of these liquefaction systems is that they do not require pretreatment and can work with high-moisture biomass feedstocks and municipal waste streams such as sewage sludge and wet algae at much lower temperatures compared with the gasification and pyrolysis processes.

Biooil has to be upgraded to fuels in the gasoline and diesel range by hydrodeoxygenation if it were to be used as transport fuel because of poor volatility, high viscosity, coking, corrosiveness, and poor cold-flow properties [11]. Catalytic upgrading



**Fig. 3** Biomass steam gasification with chemical looping for liquid transportation fuels by Fischer–Tropsch (F–T) synthesis. Reproduced from Demirel Y, Matzen M, Winters C, Gao X. Capturing and using CO<sub>2</sub> as feedstock with chemical-looping and hydrothermal technologies and sustainability metrics. *Int J Energy Res* 2015;39:1011–47.



**Fig. 4** Block flow diagram of biohydrogen production by gasification of biomass feedstock.

reduces the oxygen level of the biooil and increases the H<sub>2</sub> proportion, leading to the production of saturated C–C bonds that are fully compatible with petroleum infrastructure and use.

## 1.22.5 Biofuels

Biofuels are biomass feedstock-based fuels and include biohydrogen, bioethanol, biobutanol, biomethanol, biooil, biogas, and biodiesel. These biofuels are produced mainly by chemical, biochemical, thermochemical, and hydrothermal processes and are reviewed briefly in the following sections.

### 1.22.5.1 Biohydrogen

Hydrogen is a zero-emission fuel with combustion products of water and trace amount of NO<sub>x</sub>. Hydrogen can be produced mainly from the second generation of biomass feedstock by using thermochemical processes of gasification (steam reforming) and fast pyrolysis. **Fig. 4** shows a schematic of biohydrogen production by gasification of a biomass feedstock. Energy efficiency for biomass gasification for H<sub>2</sub> production is around 55%–65%.

Hydrogen can also be produced by microorganisms in biological processes [31] as well as electrolysis of water by using a renewable power source of wind, solar, or hydro [32]. Among them, thermochemical processes are more mature and suitable for large-scale productions, while biological processes are in the developing stages.

Steam methane reforming is a current and economical process to produce hydrogen in large scale with around 86% energy efficiency. Steam reforming can also be used with biomass feedstock including municipal organic waste, sewage sludge, and

agricultural waste. Supercritical water gasification (at 220–400 bar and 500–700°C) can use wet biomass with high gasification efficiency but at higher cost. The pressure swing adsorption process is widely used for hydrogen separation in the syngas with around 85% separation efficiency [33].

### 1.22.5.2 Bioethanol

Bioethanol can be produced using the first and second generation biomass feedstock as well as some other feedstock such as algae. The following sections briefly explain the various forms of bioethanol production.

#### 1.22.5.2.1 First generation bioethanol

First generation bioethanol uses feedstock containing sugar (sugarcane, sugar beet, sweet sorghum) and containing starch (corn, wheat, cassava). Wet and dry milling routes are used to produce bioethanol from corn. Dry milling requires less investment and produces dried distiller's grain with solubles (DDGS) beside bioethanol, while the wet milling produces oil and animal feed beside the bioethanol. Corn-grain is used to coproduce bioethanol and wet or DDGS as animal feed. Fig. 5 shows the basic steps of converting starch into bioethanol by biochemical process using 6-carbon sugar sources. Most corn is ground to a meal, and then the starch from the grain is hydrolyzed by enzymes to glucose (dry mill). The 6-carbon sugars are then fermented to ethanol by natural yeast and bacteria. The fermented mash is separated into ethanol and residue by distillation. Hydrated ethanol forms an azeotropic mixture; fuel grade ethanol (0.4 vol% water) can be achieved by azeotropic distillation, by means of molecular sieves, or by extractive distillation [34].

The average yield of converting corn starch to ethanol is around 100 gallons bioethanol per dry ton corn [35]. About one-third of every kilogram of corn grain is converted to ethanol, one-third to DDGS, and one-third to CO<sub>2</sub>. Ethanol is produced at ASTM D4806 standards and shipped to the refiner or distributor for blending with conventional fossil gasoline into finished gasoline.

Surplus corn in the United States and sugarcane in Brazil are used to produce bioethanol. Fermentation of a bushel of corn (approximately 25.4 kg) using the dry-mill process yields about 10.2 l of ethanol and approximately 7.9 kg of DDGS that contains 10% moisture. This coproduct is richer in protein, fat, minerals, and fiber relative to corn and hence is a valuable feed [14]. Bioethanol producers have adopted various technologies such as high-tolerance yeasts, continuous ethanol fermentation, cogeneration of steam and electricity, and molecular sieve driers to reduce ethanol production costs [35,36].

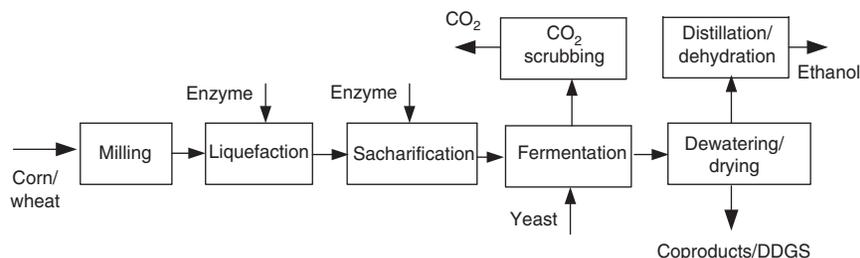
#### 1.22.5.2.2 Second generation bioethanol

Second generation bioethanol is produced from lignocellulosic biomass and other nonfood biomass resources. There are mainly two types of technology that are used to convert lignocellulosic biomass to fuels to meet the Renewable Fuel Standard (RFS) [36]: (1) biochemical and (2) thermochemical conversions [37]. Biochemical pathways for converting cellulosic biomass into fuels follow the process of pretreatment to release carbohydrates from the lignin shield, breaking down cellulose and hemicellulose to release sugars, fermentation of sugar to ethanol, distillation to separate the ethanol from the dilute aqueous solution, and conversion of the residue to electricity. In the thermochemical processes, the biomass is gasified or liquefied (pyrolysis) to produce biosyngas and biooil, respectively [27].

##### 1.22.5.2.2.1 Second generation bioethanol by biochemical processes

Cellulose, hemicellulose, and lignin are the structural components of lignocellulosic biomass to produce bioethanol. Lignocellulosic biomass includes corn stover, corn cobs, sorghum stalks, wheat straw, cotton residue, alfalfa stems, wood, fast-growing plants such as grass, and bagasse, which is the fiber residue left after sugarcane and sorghum stalks are crushed to extract their juice. Dedicated bioenergy crops refer to nonfood perennial crops that are grown primarily for use as bioenergy feedstocks, and include switchgrass (*Panicum virgatum* L.), *Miscanthus*, mixtures of native grasses, and short-rotation woody crops such as hybrid poplar and willow. Crop residues also help maintain soil quality (including fertility, structure, physical, chemical, and biochemical qualities) and reduce or mitigate soil erosion [38].

The three main steps of converting lignocellulosic feedstock to bioethanol are (1) hydrolysis of lignocellulosic polysaccharides into fermentable sugars (C6 and C5), (2) fermentation of these sugars into bioethanol, and (3) dehydration of ethanol to fuel



**Fig. 5** Main steps for the first generation biofuel production process producing bioethanol, dried distiller's grain with solubles (DDGS), and CO<sub>2</sub>.

grade to be blended with conventional gasoline. As the cellulose is protected by lignin and hemicellulose, pretreatment is required to hydrolyze hemicellulosic sugars and open up the structure of biomass. Solvent-based pretreatment technology can produce chemical-grade cellulose, hemicellulose sugars, and lignin. In comparison to the dilute-acid pretreatment method, most of the advanced pretreatment methods involve the use of enzymes in several stages of the pretreatment process. After pretreatment, cellulolytic enzymes are used to hydrolyze the cellulose polymers to C5 and C6 sugars (xylose and glucose). Unlike glucose, xylose is not readily fermented to ethanol. Genetically modified or metabolically engineered yeasts or bacteria are used to ferment both glucose and xylose to enhance yield of ethanol from lignocellulose [39]. One of the challenges is to develop glucose- and xylose-fermenting microorganisms genetically modified or metabolically engineered to withstand antimicrobial agents released during the pretreatment and hydrolysis steps and that are not inhibited by high alcohol concentrations.

Some other biomass feedstocks for bioethanol production can be macroalgae and sugarcane bagasse. Macroalgae do not need arable land, water, and expensive nutrients and can be used as a source for renewable sugars to produce bioethanol and biogas besides other fermentation-based chemicals. Brown macroalgae (*Saccharina latissimi*) in particular contain carbohydrates (>50%) without lignin and are suitable for fermentation after an enzymatic hydrolysis step [40].

#### 1.22.5.2.2.2 Second generation bioethanol by thermochemical processes

Fig. 6 shows the basic steps of the gasification process in which biomass (or other carbon-containing feedstock) is used to produce bioethanol. The general process areas include feed preparation, gasification, gas cleanup and conditioning, and alcohol synthesis and purification [11]. The biomass feedstock is dried to that required for proper feeding into the gasifier. Injected steam into the gasifier stabilizes the entrained flow of biomass and particles through the gasifier. The biomass chemically converts to a mixture of biosyngas components ( $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , etc.), tars, and a solid char, which are reformed to  $\text{CO}$  and  $\text{H}_2$ . For dry basis,  $\text{CO}$  and  $\text{H}_2$  contents of syngas are around 29 vol% and 32 vol%, respectively. The hot biosyngas is cooled and sent to an amine unit to remove the  $\text{CO}_2$  and  $\text{H}_2\text{S}$ . The biosyngas can then be chemically converted into  $\text{MeOH}$ , ethanol, and other liquid fuels using the F-T synthesis with suitable catalyst, mainly  $\text{Fe}$  or  $\text{Co}$ , at high temperature (200–350°C) and pressure (25–40 bar). Overall yield and energy efficiency are 23%–41% and 32%–51%, respectively, for biomass-based hydrocarbon production [25]. Purification of the syngas accounts for 60% to 70% of the total capital cost. Alcohols are fed to a flash separator and unused biosyngas is recycled to gas cleanup section. A distillation column separates the dehydrated alcohol feed into the mixture of  $\text{MeOH}$  and ethanol and the higher molecular weight alcohols of butanol and alcohols.

An important design parameter for thermochemical conversion of biomass to biofuel is the  $\text{H}_2/\text{CO}$  ratio. This ratio for the F-T process is around 2, while biomass gasification produces a raw biosyngas with ratios typically between 0.8 and 1.6. Hydrogen in the raw biosyngas is usually increased by using water-gas shift reaction:  $\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$   $\Delta H_{298\text{K}} = -41 \text{ kJ mole}^{-1}$ . The gasification process requires proper utilization of heat integration (using, e.g., a pinch analysis), which provides a systematic approach to optimize the energy integration [15].

Municipal solid wastes (MSWs) may contain paper, paperboard, textiles, wood, yard trimmings, and food scraps, which are biological materials that could be used to generate biofuels. Large cities with large volumes of MSW have installed trash incinerators to recover the energy. Any new biofuel facility using MSW should compete economically with the existing incineration facilities. MSW is a mixed stream that is highly heterogeneous and also contains microorganisms and some level of toxic substances (such as mercury in batteries, pesticide residues, and paints) that could contaminate a biochemical conversion process. MSW might be better suited for a thermochemical conversion process; however, once the technology matures, MSW would become an attractive feedstock. Various simulation and modeling studies of biomass (corn stover and distiller grain) gasifier can predict the flowrate and composition of product from given biomass composition and gasifier operating conditions. Mass balance, energy balance, and minimization of Gibbs free energy during the gasification can be applied to determine the product gas composition. Sensitivity analyses can be performed to investigate impact of steam-to-biomass ratio, equivalence ratio, and furnace temperature of the gasification [14–16].

#### 1.22.5.3 Fischer-Tropsch Diesel

Also known as a gas-to-liquid fuel, F-T diesel is produced when a gaseous fuel is converted to a liquid and refined to make diesel. Biomass feedstocks for F-T biofuels are wood, forest wastes, grass, agricultural wastes, manure and sludge, and MSW. Around 1 t of biomass with 30% moisture will produce 159 L of biodiesel fuel. Optimum size of a biomass-to-FT-liquid fuel plant is around 5–8 million tons year<sup>-1</sup> [37,41]. F-T diesel offers reduced emissions and is compatible with advanced emission-control devices. In

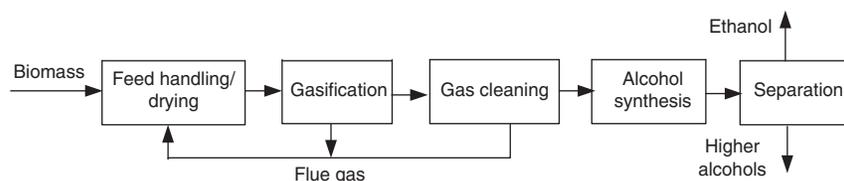


Fig. 6 Biomass gasification for alcohol production.

green diesel production, fats, algal oils, waste oils, or virgin oils are converted to low-sulfur diesel by hydrogenation and hydrodeoxygenation.

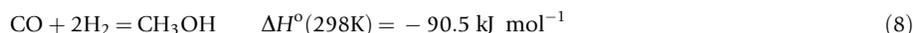
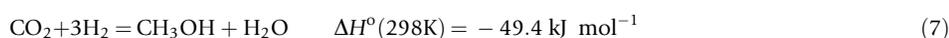
#### 1.22.5.4 Biobutanol

By the fermentation process, sugars can be converted into butyric, lactic, and acetic acids. Butyric acid is converted by fermentation into biobutanol. The electrodeionization process makes the entire fuel conversion process faster and less costly. Corn starch also can be converted to biobutanol via the acetone–butanol–ethanol fermentation pathway [42]. Coproducts include alcohols with lower molecular weight than butanol and acetone. Butanol's toxicity to the microorganisms that ferment sugar creates obstacles. If corn grain is the source of the sugars for fermentation, a residue similar to dried distillers' grain is produced. This might require additional processing to remove any toxic biobutanol and acetone residue before it could be used as an animal feed. Gas stripping can be used to extract the biobutanol. First, the wheat straw is pretreated with dilute sulfuric acid or other chemicals. Next, the material is fermented in a bioreactor containing three different types of commercial enzymes and a culture of *Clostridium beijerinckii* P260. The bacteria and enzymes function simultaneously; first, the enzymes hydrolyze the straw and release simple sugars, then the bacteria start fermenting those sugars into acetone, butanol, and ethanol. Butanol is produced in greatest quantity but the other two are also valuable components.

Isobutanol can be produced by anaerobic process using *E. coli* strains and continuous vacuum stripping for butanol fermentation. This process is still in the developing stage. The sugar to isobutanol conversion yield is around 85%. As the yield increases, butanol purification improves considerably. Butanol costs, water usage, and direct CO<sub>2</sub> emissions are all higher than that of cellulosic bioethanol [43], while butanol is far superior to ethanol in energy efficiency.

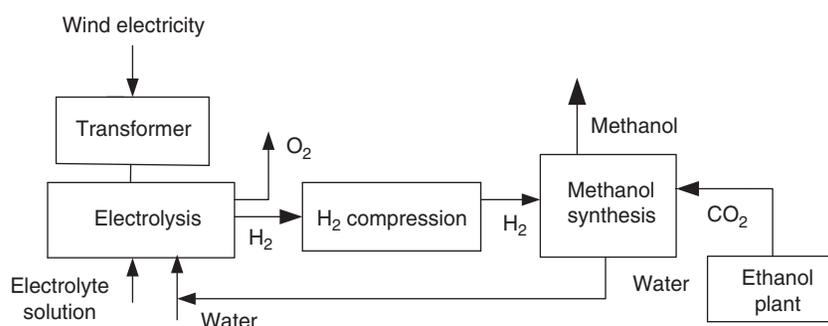
#### 1.22.5.5 Biomethanol

MeOH synthesis needs carbon-rich feedstock, H<sub>2</sub>, and a catalyst, mainly Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> and consists of three fundamental steps: (1) biomass reforming to produce biosyngas with an optimal ratio of [(H<sub>2</sub> – CO<sub>2</sub>)/(CO + CO<sub>2</sub>)] = 2, (2) conversion of biosyngas into crude MeOH, and (3) distillation of crude MeOH:



Selectivity for MeOH is high with a value of 99.7% at 5 MPa and 523K and with a H<sub>2</sub>/CO<sub>2</sub> ratio of 2.82. The energy efficiency for the concentrated CO<sub>2</sub> and H<sub>2</sub>-based MeOH is around 46% [44]. Some of the available sources for CO<sub>2</sub> are fermentation processes such as bioethanol production plants. Renewable H<sub>2</sub> comes from the electrolysis of water using hydropower, wind power, and solar photovoltaic power. Alkaline electrolysis technologies are the most mature commercial systems. For producing 1 kg H<sub>2</sub>, approximately 26.7 kg water is necessary. Fig. 7 shows a schematic of wind electricity-based hydrogenation of CO<sub>2</sub> to MeOH. Currently, the cost for hydrogen from electrolysis is roughly twice that from natural gas steam reforming; however, a significant GHG reduction (–1.07 kg CO<sub>2</sub> per kg MeOH) may be possible [45–47]. The electricity cost accounts for around 23%–65% of the MeOH production cost because of high stoichiometric hydrogen demand in the synthesis [48]. Biomass-based biomethanol and electricity production together may have a positive impact on the cost of the integrated process shown in Fig. 7.

The plant shown in Fig. 7 uses 18.6 metric ton (mt) H<sub>2</sub> day<sup>–1</sup> and 138.4 mt CO<sub>2</sub> day<sup>–1</sup>, and produces 97.0 mt MeOH day<sup>–1</sup> at 99.5 wt% together with 54.6 mt day<sup>–1</sup> of 99.5 wt% H<sub>2</sub>O wastewater. The reduction of GHG emission is around 1.07 kg CO<sub>2</sub>e kg<sup>–1</sup> MeOH as a feedstock. The hydrogen production cost is highly dependent on the electricity price, which may be around 75% of the final cost [45].



**Fig. 7** The integral methanol (MeOH) production facility based on the feedstock of renewable hydrogen and CO<sub>2</sub>. Reproduced from Matzen M, Alhajji M, Demirel Y. Technoeconomics and sustainability of renewable methanol and ammonia productions using wind power-based hydrogen. *Adv Chem Eng* 2015;5:128; Matzen M, Alhajji M, Demirel Y. Chemical storage of wind energy by renewable methanol production: feasibility analysis using a multi-criteria decision matrix. *Energy* 2015;93:343–53.

### 1.22.5.5.1 Biomethanol from sewage sludge

Sewage sludge is a residue of a municipal wastewater treatment plant. Mechanically dewatered sludge contains 12%–25% solid (LHV = 12.0 MJ kg<sup>-1</sup>) with an organic fraction of 56% of dry solids rich in carbon (50%), hydrogen (7%), and oxygen (31%) [44]. This may lead energy recovery by producing biofuels as well as bioproducts beside the incineration commonly used. One way for energy recovery is the gasification of the sludge and conversion of syngas produced into MeOH as well as other chemicals. In the low-pressure MeOH process catalytic synthesis takes place at 77 bar and 200°C using the cleaned syngas. This will help minimize waste as well as recover energy.

### 1.22.5.6 Biodimethyl Ether

DME is the simplest ether (CH<sub>3</sub>OCH<sub>3</sub>) and can be produced by catalytic biomethanol dehydration:



DME is a colorless, nontoxic, highly flammable gas at ambient conditions, but can be handled as a liquid under slight pressure (0.5 MPa). The properties of DME are similar to those of LPG with a LHV of 28.4 MJ kg<sup>-1</sup> and density of 0.67 kg L<sup>-1</sup>. It has the conventional diesel fuel equivalency of 0.59 as the LHV of diesel is 43.1 MJ kg<sup>-1</sup>. DME is not a GHG and can be used as a substitute for diesel fuel or domestic gas [44].

### 1.22.5.7 Biodiesel

Seed crops contain high levels of protein and oil with various numbers of carbon atoms and double bonds as shown in Table 4. Food and nonfood oils, animal fats, and waste cooking oil can be converted into biodiesel. The type of oil affects the quality of biodiesel, conversion process, and operating conditions. Soybean and palm oils are the two largest oilseed crops. High level of protein produces high economic value meal. On a dry-weight basis, soybean contains around 41% protein, 21% oil, and 29% carbohydrate, on average. Triacylglycerol (triglycerides: C<sub>55</sub>H<sub>98</sub>O<sub>6</sub>) (94%) are the primary component in the soybean oil, while phospholipid content is around 3.7%. Triacylglycerol contains three fatty acids attached to a glycerol molecule (C<sub>3</sub>H<sub>5</sub>O<sub>3</sub>). Typical soybean oil has the density (at 20°C) of 0.916 g mL<sup>-1</sup>, melting point of 0.6°C, and heat of combustion of 9.0 kcal g<sup>-1</sup> (38 kJ g<sup>-1</sup>) [49].

#### 1.22.5.7.1 Biodiesel from plant oils

Several countries produce biodiesel from rapeseed oil, palm oil, and soybean oil. In the United States, biodiesel is produced mostly from soybean oil. Other vegetable oils and animal fats such as canola, camelina, and jatropha constitute a small fraction of biodiesel feedstock. Soybean seeds yield about 18% oil and the remaining meal, which is the primary product of soybean and sold as a highly nutritious animal feedstuff. Because of the high yield of the meal, this coproduct may provide better monetary returns per ton of seed than the oil used in biofuel production.

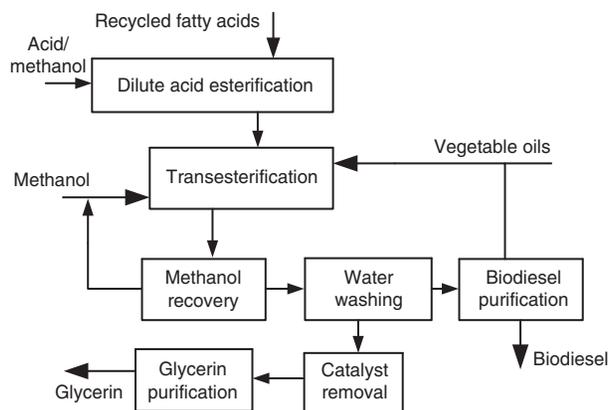
Chemical conversion technology is the transesterification of triglyceride with alcohol (usually MeOH and ethanol) to produce biodiesel and glycerin that can be used for pharmaceutical formulation, soap production, and other uses (see Fig. 8). It can be blended with conventional diesel (typically 20%) to reduce vehicle emissions. Soybean-based biodiesel mainly uses MeOH. Methyl esters from typical soybean oils are palmitate (10%), stearate (4%), oleate (23%), linoleate (55%), and linolenate (7%). Biodiesel produced from oilseeds, such as soybean or sunflower, leaves behind a protein-rich meal that is an excellent feedstuff for poultry, pigs, and dairy cattle [36]. It can also be used as a feedstock to produce hydrogen and other bioproducts such as glycerol carbonate, which may be economically viable with technical improvements [50,51].

Used frying or cooking oils (mainly olive oils and sunflower oils) contain a large amount of free fatty acids, so an esterification step is necessary before transesterification to produce biodiesel. This reaction is usually carried out in batch reactors at ambient pressure and 60°C where the esterification reaction acts as the limiting step of the production. Based on the experimental results, biodiesel from used frying oil does not fulfill all the specifications from the EN 14214 standard due to the presence of polar compounds with the chemical modifications in the oil during cooking [52].

**Table 4** Fatty acid composition (wt%) of various oils and fats

Oil or fat	Typical oil content %	Number of carbon atoms: number of double bonds						
		14:0	16:0	18:0	18:1	18:2	18:3	20:1
Rapeseed	39–43	–	4.3	1.3	59.9	21.1	13.2	
Soybean	16–18	–	6–10	2–5	20–30	50–60	5–11	
Sunflower	40–50	–	7.2	4.1	16.2	72.5	–	
Jatropha	28–38	–	11.3	17.0	12.8	47.3	–	1.8
Tallow	24–32	3–6	24–32	20–25	27–43	2–3	–	

Source: Reproduced from Van Gerpen J. Biodiesel from vegetable oils. In: Vertes aa, Qureshi N, Yukawa H, Blaschek HP, editors. Biomass to biofuels: strategies for global industries. Chichester: Wiley; 2010.



**Fig. 8** Biodiesel production from fatty acids and vegetable oils.

Solid catalysts are increasingly selected for the transesterification reaction of vegetable oils to produce biodiesel. Heterogeneous catalysts are environmentally benign, and can be used in continuous processes. Alkali earth metal oxides (magnesium oxide, calcium oxide, and strontium oxide) and transition metal oxides (zirconium oxide, titanium oxide, and zinc oxide) are studied for transesterification of oils. Alumina, silicate, zinc oxide, and zirconium oxide are used as catalyst supporting materials [53].

#### 1.22.5.7.2 Green diesel

Green diesel production requires large volumes of  $H_2$  and a catalyst to hydrogenate triglycerides into a high-cetane diesel fuel [54] by removing all of the oxygen from the triglyceride and saturating all of the olefinic bonds in the fatty acids. The primary products from this hydrogenation are water,  $CO_2$ , propane, and a mixture of normal paraffin. Green diesel is fully compatible with petroleum-based diesel. It can even be produced by coprocessing triglycerides along with other petroleum streams in conventional refinery diesel hydrotreaters.

#### 1.22.5.7.3 Biodiesel from algae

Oil-rich microalgae strains are capable of producing the feedstock for a number of transportation fuels, for example, biodiesel, green diesel, gasoline, and jet fuel, while mitigating the effects of  $CO_2$ . There are many different kinds of algae that grow in nearly any water resource in a variety of colors and forms, and can be found everywhere on Earth. Algae require water, sunlight, carbon, and nutrients like nitrogen and phosphorus to grow. One notable group is blue-green algae, which consists of prokaryotic cells (or bacteria) that use photosynthesis that draw  $CO_2$  from the atmosphere. Using them to create biofuel can significantly reduce GHG emissions from transportation fuels, power plants, and refineries. Blue-green algae, or cyanobacteria strains, have an extremely high photosynthetic rate and are ideal for producing triglycerides and biofuels. Cyanobacteria strains can also be engineered to produce photosynthesis-based biofuels [55]. Certain strains of algae could potentially produce up to 60 times more oil than plants like soybeans and offer the highest-yield feedstock for biodiesel [56].

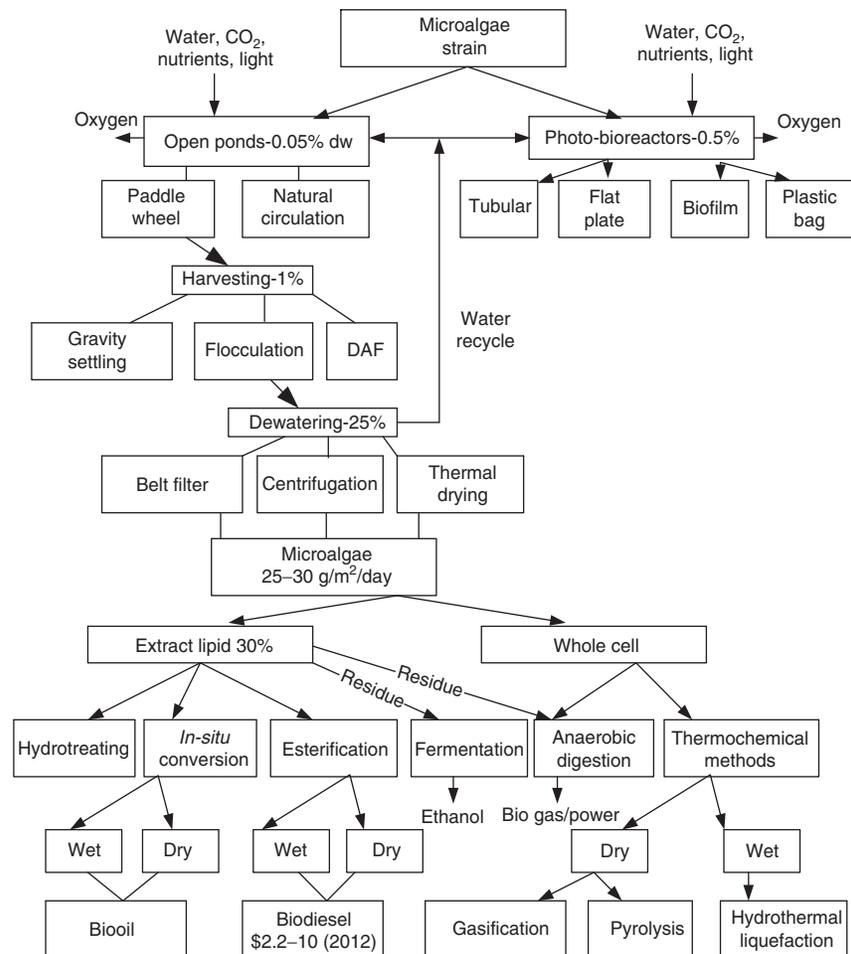
**Fig. 9** shows algae-based biofuel and bioproduct pathways with the following steps:

1. Algae growth in open ponds or in photobioreactors, which may be tubular, flat plate, plastic bag, or biofilm.
2. Algae harvesting can be achieved via dissolved air flotation, gravity settling, and flocculation.
3. Dewatering is possible with centrifugation, thermal drying, and belt filter.
4. Processing microalgae biomass by either lipid extraction or whole cell. The extracted lipid can be fed into hydrotreating for green biodiesel, in situ conversion to biooil, or transesterification process to produce biodiesel and glycerin. The residue after the lipid extraction can be
  - a. fed into anaerobic digestion to produce biogas and biopower.
  - b. used as a feedstock for fermentation to alcohols.
  - c. used as fertilizer. Whole cell can be used in anaerobic digestion as well as in thermochemical conversion (pyrolysis, hydrothermal liquefaction) processes.

As **Fig. 9** shows, a specific biofuel or biooil pathway can be selected and analyzed if it is feasible and sustainable since the processing cost is a great concern for biodiesel from algae [22].

Ultrasound-based methods of algae harvesting are currently under development, and other additional methods are currently being developed. Harvesting algae and extracting oil are costly. In addition, a large amount of water is needed for large-scale production, which involves pumping it out of the production system and back in again. The smallest practical size for an algal biodiesel plant is 1000 ha, which pumps about 1 million  $m^3$  of water a day. This is about twice the amount of fresh water used for agricultural irrigation [55–58].

Many commercial manufacturers of vegetable oil use mechanical pressing and chemical solvent (hexane, benzene, or ether) to extract the oil. Estimates of the cost to extract oil from microalgae vary, but are likely to be around three times that of palm oil.



**Fig. 9** Algae-based biofuel pathways, cultivation, harvesting, conversion. Residue of lipid extraction goes to fermentation as well as anaerobic digestion; whole cell: anaerobic digestion and thermochemical methods (gasification, pyrolysis, and hydrothermal liquefaction). DAF, dissolved air flotation.

Enzymatic extraction uses enzymes to degrade the cell walls and costs much more than solvent extraction. Enzymatic extraction can be supported by ultrasonication, which may cause faster extraction and higher oil yields. Fig. 10 shows the block flow diagram for algal biomass production using a photobioreactor and solvent extraction of lipid with solvent recovery [58].

Algae strains can be genetically engineered to produce desirable ingredients such as more lipids and polyunsaturated oil components known to promote and maintain health [59]. Recently, algae biomass created via photosynthetic microbial bio-production techniques has gained attention as a feedstock for biofuels [20]. Usually, algae with high oil contents grow relatively slowly; strains capable of producing large amounts of lipids tend to do so when they are starved of nutrients. Microbes can produce fats or materials that can be converted to biofuel by redirecting the protein utilization system. Mostly, the biofuel-producing algae have not made use of the protein like a carbon supply for biofuel but have used it for growth. Altered nitrogen metabolism may induce the biorefining process. The cells retain the nitrogen and take out just the ammonia. Once done with the biofuel production, the residue may be used as a fertilizer [60–62].

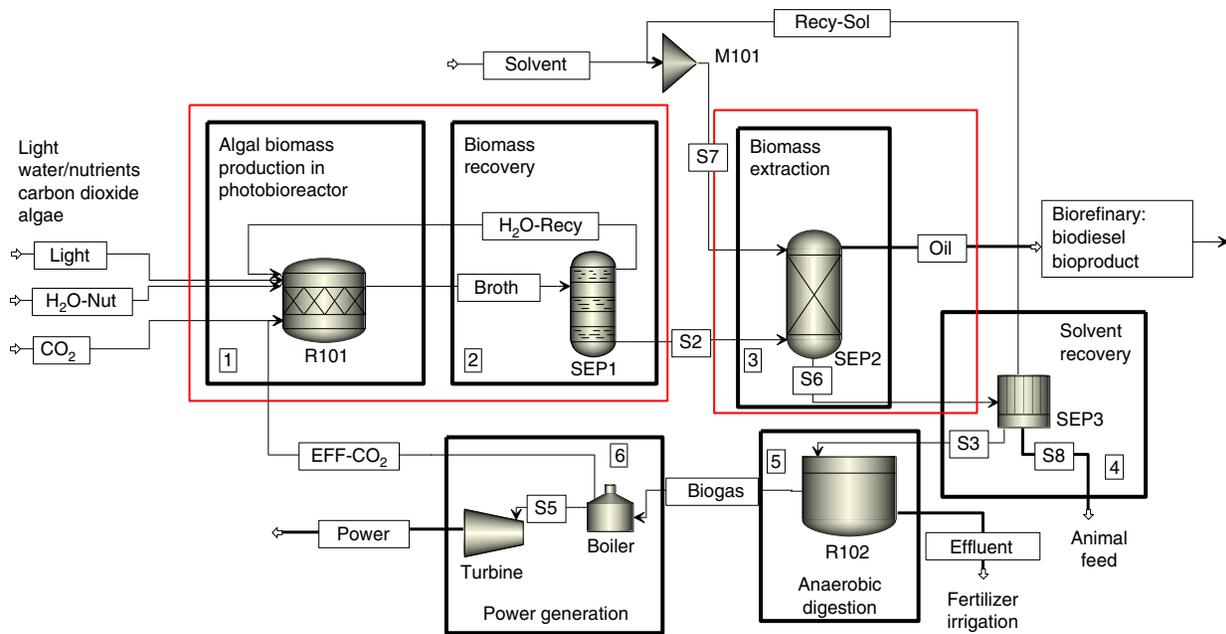
#### 1.22.5.7.4 Nutrient recovery from municipal wastewater for algae-based biofuel production

There are efforts toward recovering nutrients and water necessary for algae biomass growth from municipal wastewater treatment plants [63,64]. Fig. 11 shows the general block flow diagram for algal biodiesel and biopower productions using the recovered nutrients, mainly phosphorous and nitrogen, for algae biomass growth in a pond.

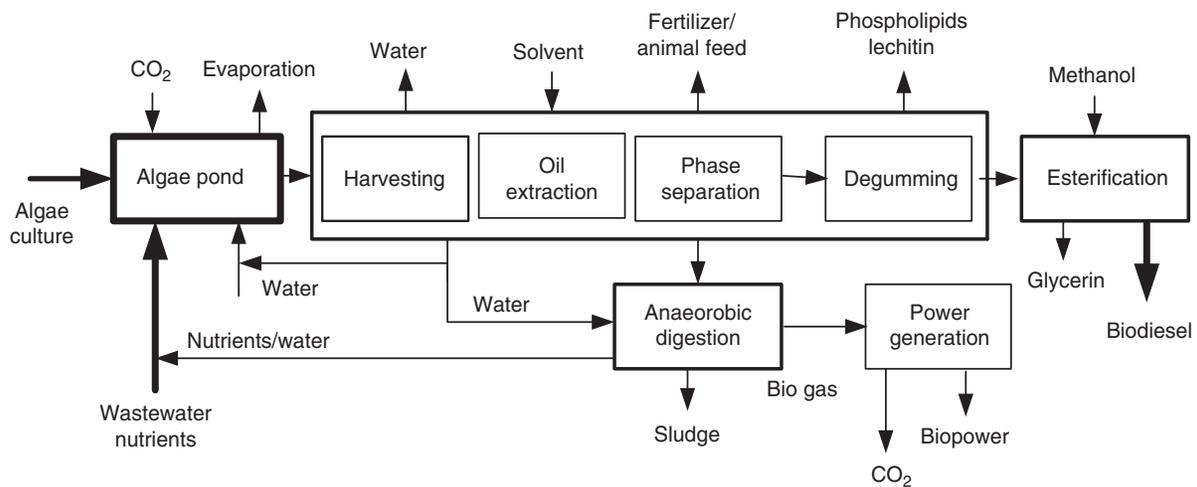
151.5 mt of algal biomass can produce 27 mt crude lipid for biodiesel production, 124.5 mt residue for fertilizer or animal feed by using around 758 m<sup>3</sup> solvent [55]. A common algae cultivation can be done side by side with wastewater treatment plants to recover nutrients. Thence the processes may be more efficient and less expensive. The algae can use the extra nitrogen and phosphorous in the existent water and make it safer for marine flora and fauna.

#### 1.22.5.7.5 Jet fuel from camelina

Camelina oil seems right for the conversion to a hydrocarbon green jet fuel. It meets or sometimes exceeds all petroleum jet fuel specifications. Camelina oil is compatible with existing fuel infrastructure. The life cycle analysis shows that camelina is one of the



**Fig. 10** Algae biomass feedstock preparation to produce triglyceride acids, bioproduct, and biopower. R101: Reactor; SEP1: Separator (centrifuge); SEP2: Extractor; SEP3: Distillation column; R102: Reactor.



**Fig. 11** A block flow diagram for nutrient recovery from municipal wastewater for algae biomass growth and biofuel and biopower production.

leading near-term options and is even better in terms of affordable price and availability of large-scale quantities of second generation feedstocks [65].

### 1.22.6 Further Discussions

#### 1.22.6.1 Comparison of Biomass Used for Bioethanol Production

A large area of farmland needs to be diverted for corn production for corn-based bioethanol. Lignocellulosic biomass minimizes the potential conflict between the land use for food and biofuel productions. Some benefits and problems of bioethanol are that (1) it can be added to gasoline up to 10% in existing cars; (2) new cars can run on a 20% mix of ethanol with gasoline; (3) only minor changes are necessary for new cars to run on any mix of ethanol and gasoline, such as 85% ethanol (E85); (4) bioethanol can provide nations with energy security and significantly reduce GHG emissions; (5) corn-bioethanol may not be sustainable as corn is subsidized, grown, and harvested using fossil fuels, synthetic fertilizers, pesticides, and considerable amount of water,

**Table 5** Comparison of ethanol plants using starch and lignocellulosic feedstock

<i>Corn starch</i>	<i>Corn stover</i>
Corn starch has alpha-linked glucose polymer easily broken down to glucose monomers and fermented to ethanol; conversion to ethanol takes around 2 days. Treatment is around 80–90°C	Cellulose has beta-linked glucose polymer difficult to break down to glucose monomers; the conversion is longer (3 days) and more energy intensive; pretreatment requires dilute acid to make the cellulose digestible by cellulose enzyme at 180–200°C
Fiber from corn yields distiller's dried grains with solubles (DDGS)	Have hemicellulose, which is a more complex polymer of several five-carbon sugars of xylose and arabinose, which can be fermented to ethanol with the use of proper microorganisms
Enzymes: alpha-amylase and gluco-amylase convert 100% of the starch to glucose	Maximum theoretical yield 91 gal t <sup>-1</sup> at 15% moisture, real yield is around 75 gal t <sup>-1</sup>
DDGS is high in protein and sold as animal feed	Lignin (14.7% of residue), currently is used as a fuel. Other organics (17.1% of residue)
The feedstock is the largest cost contributor	Requires more feed handling; to be delivered in bales that must be washed, shredded, and milled to a conveyable particle size
Corn, yeast, urea, and enzymes are purchased raw materials	Cellulosic feedstock to plant gate: \$30–\$53/t <sup>-1</sup> -dry. About 33% of the stover is available for collection.
Requires milling to a fine meal	Capital cost is around four times higher compared with the corn-ethanol plant

Source: Hahn-Hagerdal B, Galbe M, Gorwa-Grauslund MF, Liden G, Zacchi G. Bio-ethanol—the fuel of tomorrow from the residues today. *TRENDS in Biotechnol* 2006;24:549–56; Pimantel D, Patzek TW. Ethanol production using corn, switchgrass, and wood; biodiesel production using soybean and sunflower. *Nat Resour Res* 2005;14:65–76; Sandor D, Wallace R, Peterson S. Understanding the growth of the cellulosic ethanol industry. Technical report NREL/TP-150-42120;2008.

which may impact the environment adversely; and (6) 100% bioethanol cannot be transported through existing pipelines, because of its chemical properties. **Table 5** compares the bioethanol plants using the first and second generation biomass feedstocks [66].

### 1.22.6.2 Chemical and Fuel Properties of Biofuels

**Table 6** compares the properties of biofuels and gasoline. Carbon content of gasoline is much higher with no oxygen, while biofuels contain high levels of oxygen and less carbon. These properties result in considerably LHVs for biofuels, while lowering the ratio of stoichiometric air to fuel ratio. Bioethanol is blended with gasoline causing corrosion in fuel transporting pipes and some problems of ethanol transport. The Renewable Fuels Association is currently exploring whether a dedicated ethanol pipeline would provide the same transport security. The Association for oil pipelines is also conducting a study of whether gasoline blends, those with up to a 20% ethanol additive, could utilize existing oil pipelines. **Table 7** shows that the fuel properties of biodiesel from soybean oil and the conventional diesel are comparable.

### 1.22.6.3 Energy Efficiencies of Biofuels

Ptasinski [7] provides the energy and exergy analyses of biofuels. Energy efficiency for biomass to biofuel can be estimated by

$$\left( \text{Energy efficiency of biomass to biofuel conversion} \right) = \frac{\left\{ \left( \begin{array}{l} \text{LHV of biofuel} \\ \text{produced per 1 kg} \\ \text{of biomass} \end{array} \right) - \left( \begin{array}{l} \text{External energy} \\ \text{used in 1 kg biomass} \\ \text{to biofuel conversion} \end{array} \right) \right\}}{\left( \begin{array}{l} \text{LHV of the 1 kg biomass} \\ \text{used in the conversion} \end{array} \right)} \quad (10)$$

Energy balance studies reveal the ratio of the energy contained in the final bioethanol produced to total fossil energy used during the production. **Table 8** shows such ratios for bioethanol production from various feedstock. The table indicates that sugarcane and lignocellulosic feedstocks have the highest energy ratios, mainly because of the use of bagasse and lignin as energy source within the production stage. Energy return on investment (EROI) shows the ratio of energy of a fuel to the total energy invested to produce that fuel [67]. The values of EROI for biofuels are generally lower compared with those of conventional fossil fuels (see **Table 8**). At the societal level, declining EROI means that an increasing proportion of energy output and economic activity must be diverted to attaining the energy needed to run an economy, leaving fewer discretionary funds available for the nonessential purchases that often drive growth [67]. The cost ratio  $C_r$  shows the biofuel cost to fossil fuel cost used in the production process.

The emissions of GHGs from the transportation sector are around 25% of the global energy-related emissions. This is one of the main reasons to replace fossil fuels with biofuels. However, use of biofuels also causes GHG emissions occurring from different stages of the life cycles of biofuels, which include growing, cultivating biomass, and production of biofuels [68,69]. Combustion of biofuels recycles CO<sub>2</sub> captured during photosynthesis. In order to characterize the environmental impact of biofuels GHG emissions caused by biofuels with respect to fossil fuels can be compared. **Table 8** shows approximate avoided GHG emissions because of the biomass feedstock used in bioethanol production. There are some publications reporting an increase of GHG

**Table 6** Properties of bioethanol, biomethanol, biobutanol, bioisobutanol, and conventional gasoline

Properties	Methanol (MeOH)	Ethanol	Butanol	Isobutanol	Gasoline
Ultimate analysis, wt%					
C	37.5	52.1	64.8	64.8	85–88
H	12.6	13.1	13.5	13.5	12–15
O	49.9	34.7	21.6	21.6	–
Density (20°C), kg m <sup>-3</sup>	791	789	809	802	690–800
Normal boiling point, °C	65.0	78.5	117.7	107.9	27–225
Motor octane number	91	92	84	90	80–88
Higher heating value (HHV) (20°C), MJ kg <sup>-1</sup>	22.3	29.8	37.3	37.2	47.2
Stoichiometric air/fuel ratio kg kg <sup>-1</sup>	6.4	8.9	11.2	11.2	14.7
Flash point, °C	12	13	37	28	–43
Autoignition temperature, °C	470	363	340	415	250–300
Energy density, MJ L <sup>-1</sup>	16	21.4	26.9	26.6	30–33
CO <sub>2</sub> production, MJ kg <sup>-1</sup> fuel	15	13	15	15	14

Source: Reproduced from Klass DL. Biomass for renewable energy, fuel, and chemicals. San Diego: Academic Press;1998; Demirel Y. Energy: production, conversion, storage, conservation, and coupling. 2nd ed. London: Springer; 2016; Tao L, Tan ECD, McCormic R, *et al.*, Techno-economic analysis and life-cycle assessment of cellulosic isobutanol and comparison with cellulosic ethanol and n-butanol. Biofuels Bioprod Biorefining 2014;8:30–48.

**Table 7** Properties of biodiesel from soybean and conventional diesel

Properties	Biodiesel	Diesel (No. 2)
Density, kg m <sup>-3</sup>	886	849.5
Viscosity (40°C) mm <sup>2</sup> s <sup>-1</sup>	3.89	2.98
Flash point, °C	188	74
Cloud point, °C	3	–12
Pour point, °C	–3	–23
Sulfur content, wt%	0.012	0.036
Cetane number	55	49
Higher heating value (HHV), MJ kg <sup>-1</sup>	39.8	45.4
Stoichiometric air/fuel ratio, kg kg <sup>-1</sup>	12.5	14.5

Source: Reproduced from Klass DL. Biomass for renewable energy, fuel, and chemicals. San Diego: Academic Press; 1998.

**Table 8** Energy ratio and energy return on investment (EROI) for bioethanol production from various feedstocks

Feedstock	Energy ratio <sup>a</sup>	EROI	C <sub>r</sub> <sup>c</sup>	Greenhouse gas (GHG) emissions change <sup>b</sup> (%)
Sugarcane	≈ 8	0.8–10	≈ 0.5	–87 to –96
Sugar beets	≈ 2		≈ 1.2	–35 to –56
Sweet sorghum	≈ 1			
Corn	≈ 1.5	0.84–1.65	≈ 0.6	–21 to –38
Wheat	≈ 2			–19 to –47
Lignocellulosic	≈ 2–36	0.69–6.61	≈	–37 to –82
Gasoline	≈ 0.8			

<sup>a</sup>Energy from biofuel/fossil energy used in production of biofuel.

<sup>b</sup>Approximate avoided GHG emissions because of the biomass feedstock used in bioethanol production.

<sup>c</sup>C<sub>r</sub>: Cost ratio.

Source: Worldwatch Institute, Biofuels for transport: global potential and implications for sustainable energy and agriculture. Earthscan, London: BMELV; 2007; Basset N, Kermah M, Rinaldi D, Scudellaro F. The net energy of biofuels, EPROBIO IP; 2010.

emissions from biofuels [70]. As **Table 8** shows corn has the lowest energy ratio and reduction in GHG emissions because of the relatively large use of fossil fuel energy in the production of bioethanol.

Pure ethanol is completely miscible with conventional gasoline. The HHVs (at 20°C) for ethanol and gasoline are 29.8 MJ kg<sup>-1</sup> and 47.2 MJ kg<sup>-1</sup>, respectively [5]. This suggests that a blend of bioethanol and gasoline will have lower total energy in a vehicle. With 10 vol% ethanol the fuel consumption is around 3.3% higher compared with the pure gasoline [8]. Flex-fuel engines can utilize higher percentage (85 vol%) of ethanol. Since the ethanol is oxygenated fuel (oxygen: 35 wt%), its combustion is cleaner. Ethanol is also a fuel for the direct ethanol fuel cells.

**Table 9** Energy ratio for biodiesel production processes from various feedstocks and change in life cycle greenhouse gases (GHG) emissions per kilometer traveled by replacing diesel with 100% biodiesel fuel; the cost ratio (price of biodiesel/price of fossil fuel) for biodiesel is around 1.2

Feedstock	Energy ratio	Energy return on investment (EROI)	GHG emissions change (%)
Rapeseed	≈ 2.5	1.0–1.5	– 21 to – 51
Soybeans	≈ 3	0.7–2.0	– 63 to – 78
Sunflower	≈ 3	0.4–1.2	
Castor	≈ 2.5		
Palm oil	≈ 2.5–9		
Jatropha	≈ 1.4		
Waste vegetable oil	≈ 5–6		– 92
Diesel (crude oil)	0.8–0.9		

Source: Hall CAS, Lambert JG, Balogh SB. EROI of different fuels and the implications for society. *Energy Policy* 2014;64:141–52; Pradhan A, Shrestha DS, McAloon A, *et al.*, Energy life cycle assessment of soybean biodiesel revisited. *Trans ASABE* 2011;54:1031–9; Worldwatch Institute, Biofuels for transport: global potential and implications for sustainable energy and agriculture. Earthscan, London: BMELV; 2007; Basset N, Kermah M, Rinaldi D, Scudellaro F. The net energy of biofuels, EPROBIO IP; 2010; EPA, Available from: <https://www.epa.gov/renewable-fuel-standard-program>; 2016 [accessed: 07.12.16].

**Table 9** shows the energy ratio that is the biodiesel energy output to fossil energy inputs in the production process with different feedstock. This table indicates that the energy ratios for all the biodiesels from various feedstocks are higher than 1 suggesting that biodiesels are renewable energy with positive net energy outputs and reductions in GHG emissions.

#### 1.22.6.4 Renewable Fuel Standard

The US Congress created the RFS program in an effort to reduce GHG emissions and expand the nation's renewable fuels sector while reducing reliance on imported oil. The RFS program was authorized under the Energy Policy Act of 2005 and expanded under the Energy Independence and Security Act of 2007. This new RFS is known as RFS2. The Clean Air Act requires the EPA to set the RFS volume requirements annually; for example, cellulosic biofuel volumes for 2016 and 2017 are approximately 870 and 1180 million liters respectively [36,71].

##### 1.22.6.4.1 Categories of renewable fuel

A renewable fuel pathway includes three critical components: (1) feedstock (a biomass), (2) production process (a technology used to convert biomass into renewable fuel), and (3) fuel type. Renewable fuels include liquid and gaseous fuels, and electricity derived from renewable feedstock sources. To qualify for the RFS program, the fuel must be intended for use as transportation fuel, heating oil, or jet fuel. Qualifying fuel pathways are assigned one or more "D" codes representing the type of renewable identification number (RIN) they are eligible to generate. RINs are credits used for compliance, and are the "currency" of the RFS program; renewable fuel producers generate RINs, market participants trade RINs, and obligated parties obtain and then ultimately retire RINs for compliance. The RFS program includes four categories of renewable fuel, each with specific fuel pathway requirements and RIN D-codes [36,71]:

- Advanced biofuels (D5) are produced from any type of renewable biomass (sugarcane, biobutanol, bionaphtha) except corn starch ethanol. Required life cycle GHG emissions reduction is at least 50% compared to the petroleum baseline.
- Biomass-based diesel (D4) includes biodiesel and renewable diesel produced from biomass such as soybean oil, canola oil, waste oil, or animal fats. Required life cycle GHG emissions reduction is at least 50% compared to the diesel baseline.
- Cellulosic biofuel (D3 or D7) produced from cellulose or hemicellulose of corn stover, wood chips, *Miscanthus*, or biogas. To be eligible for D7 RINs the fuel must be cellulosic diesel. Required life cycle GHG emissions reduction is at least 60% compared to the petroleum baseline.
- Conventional renewable biofuel (D6) includes ethanol derived from corn starch, or any other qualifying renewable fuel. Required life cycle GHG emissions reduction is at least 20% compared to the average petroleum baseline.

#### 1.22.6.5 Biofuel Assessment Models

Some economic models are used to assess the effects of biofuel production. The four main economic models are the Food and Agricultural Policy Research Institute (FAPRI) model, the Forest and Agricultural Sector Optimization (FASOM) model, the Global Trade Analysis Project (GTAP) model, and the Policy Analysis System (POLYSYS) model. Three of the models, that is, FAPRI, FASOM, and POLYSYS, are partial equilibrium models as they focus on the agricultural sector and do not include all the sectors of the economy. GTAP is a general equilibrium model and covers all sectors of the economy and all regions of the world focusing on the trade dimensions [36]. All four models were developed before the implementation of RFS2, and have been modified in recent years to include varying degrees of biofuel coverage. The FAPRI and GTAP models include corn-grain ethanol,

sugarcane ethanol, and oilseed-based biodiesel, which are the first generation biofuels. These models plan to expand the database to include second generation biofuels. The FASOM and POLYSYS models include second generation biofuels from lignocellulosic feedstocks presently used. The FASOM is the only model of the four to include electricity generation from cellulosic feedstocks [36].

#### **1.22.6.5.1 Life cycle assessment**

Integrated system analyses, technoeconomic analyses, and life cycle assessments (LCAs) provide the total economic and environmental benefits and drawbacks of a biofuel process that can be quantified. LCA is an analytic method for identifying, evaluating, and minimizing the environmental impacts of emissions and resource depletion associated with a specific process [5]. Material and energy balances are used to quantify the emissions, resource depletion, and energy consumption of all processes involved, including raw material extraction, processing, final disposal of products and byproducts, and required in operating the process of interest. The results of this inventory are then used to evaluate the environmental impacts of the process so efforts can focus on mitigation. LCA studies have been conducted on the following systems: direct-fired biomass power plant using biomass residue, anaerobic digestion of animal waste, bioethanol from corn stover, comparison of biodiesel and petroleum diesel used in an urban bus. For these analyses, the software package used to track the material and energy balances in each system is Tools for Environmental Analysis and Management (TEAM) [72–74].

#### **1.22.6.5.2 Risk assessment for biofuels**

Risk analysis deals with several criteria, such as financial risk, environmental risk, technical risk, and social risk. For a standalone plant, such as heat production in a sawmill for drying wood, availability and failure risk will be of minor importance for realization. However, for emerging technologies, some risk of unexpected failure or production breakdown should be taken into consideration. If the bioenergy plant is integrated into an industrial production (e.g., energy supply of a pulp and paper mill) availability of the feedstock has to be extremely high (~99.5%) and the risk of unexpected failure extremely low. A failure of the bioenergy plant would induce a stop to the whole production. Most developers will carry out some form of risk assessment as part of their project activities. Technoeconomic assessment (TEA) can be used to help inform this risk assessment, and conversely, risk assessment can identify key areas that could be tested in a sensitivity analysis as part of the TEA. For a novel technology, it might be relevant to test the robustness of the TEA to availabilities. In a new market, it might make sense to test the impact of increases in feedstock cost or of having to switch to an alternative supplier [1,75].

#### **1.22.6.6 Right Way to Use Biofuels**

Caution should be exercised if biofuels are considered as alternative sources of energy. The diversion of land to corn production and a greater demand for corn from the biofuel industry helped increase the price of wheat, corn, soybean, and rice in the mid-2000s [74,75]. Dead zones have overload of nitrogen and phosphorus, which kill the aquatic flora and fauna, and marine life. To clean the dead zones, one needs to purify and oxygenate the existent waterways by removing the excess fertilizer run-off nitrogen and phosphorus. So we have to be aware of those alternative energy resources that may do more harm than good. We know that once destroyed we will never be able to restore the flora and fauna of the natural habitat.

Biomass is the organic matter that can come from sustainable sources, but could also come from natural forests and grasslands. The wrong sources of biofuel can destroy forests and they can become the breeding ground of cropland or sterile tree plantations at the cost of wildlife of the area. A new campaign has been started by the Natural Resources Defense Council to warn people to use discretion while using biofuels. The right kind of biofuels will deal with the unemployment problem and will lead us toward green jobs, a stronger economy, a safer economy, and ultimately toward greener pastures [36].

##### **1.22.6.6.1 Safety of biofuels**

Safety concerns include health and welfare of the animals consuming the coproducts and the safety of the foods that are derived from these animals because of the presence of antibiotic residues and mycotoxins in distillers' grains, which are used as animal feed. In corn-based ethanol production, bacterial contamination during the fermentation [76] competes with the yeast activity for sugars and micronutrients, and they produce organic acids, which may inhibit yeast and reduce ethanol yield. To prevent this, antibiotics, including virginiamycin, erythromycin, and tylosin, are sometimes added into the feed, which is regulated by the US Food and Drug Administration (FDA), the Department of Agriculture (USDA), and related organizations worldwide. When byproducts containing antibiotics are inadvertently fed to livestock, residues in meat, milk, or eggs could result in unacceptably high levels of the antibiotics in human foods [36].

##### **1.22.6.6.2 Economic assessment of biofuels**

Biomass feedstocks can be used to produce food/feed, fuel, fiber, fertilizers, polymers, chemical feedstock, pharmaceuticals, heat, and electricity. Second generation biomass resources are geographically more evenly distributed than fossil fuel resources, which may lead to energy security. Biofuels from lignocellulose generate low net GHG emissions and reduce the adverse effects of climate change. Biofuels might create local economic activity and employment. Most agricultural biomass production, except of forest products, is seasonal and results in a large volume of feedstock material that needs to be stored with little or no loss of dry matter for year-round supply to a biorefinery. To avoid transporting bulky biomass with low energy content, regional preprocessing infrastructure can be set up to clean, sort, chop or grind, control moisture, densify, and package the feedstocks before

transporting them to biorefineries. In contrast, forest products are available year-round so that long-term storage might not be necessary [77].

Biofuels are currently not cost-efficient compared with the fossil fuels. However, biofuels are promoted worldwide by tax credits and subsidies in order to reduce petroleum imports and GHG emissions from vehicles, and encourage local economies. There is a strong indication that as the biofuel technology becomes more energy efficient and more advanced with technological improvements, the production cost will be reduced by around 50% by 2030. Bioethanol production from sugarcane bagasse using liquefaction with simultaneous saccharification and cofermentation process shows that the overall bioethanol yield affects the minimum selling price, which is varied between  $\$0.50 \text{ l}^{-1}$  and  $\$0.63 \text{ l}^{-1}$  2016 US\$ [78]. Lignocellulosic biofuel production does not result in an appreciable amount of coproducts. Investment costs of lignocellulosic biorefinery have been estimated to be four to five times higher than a starch-based bioethanol production of similar size [79]. Efficient and affordable depolymerization of cellulose and hemicellulose to soluble sugars and fermentation of them with free inhibitory compounds may advance process integration steps, freshwater usage, and energy costs, which are key to this type of process [3]. Assessment of three decades of a sugarcane bioethanol program since 1975 in Brazil shows that bioethanol can provide improvements in energy security, foreign exchange savings, employment, and reduction in GHG emissions with the right policies on biomass supply chain [78,80,81].

**Table 10** shows the large amounts of water requirements of bioethanol and biodiesel productions from various biomass feedstocks. The effects of biofuel production on the worldwide trade of grains, livestock, biomass, and crude oil are a part of economic assessment. The biofuel industry also has some economic effects related to national budget spending such as tax credits, subsidies, incentives, and other policy matters. The diversion of land to corn production and a greater demand for corn from the biofuel industry coincided with an increase in the price of the staple commodities (wheat, corn, soybean, and rice) at an average of 102% in the mid-2000s [75]. The rapid nature of the increase was disruptive to food processors and to households.

Technoeconomic analysis of MeOH production from biomass-based syngas shows that overall energy efficiency is around 55% based on HHV. The level of emission is around  $0.2 \text{ kg CO}_2$  per kg MeOH, which is mainly from biomass growing, harvesting, and transportation. MeOH from biomass is at least 2–3 times more expensive than that of the fossil fuel-based MeOH [82]. MeOH synthesis from water, renewable electricity, and carbon may lead to chemical storage of renewable energy, carbon recycle, and fixation of carbon in chemical feedstock [45,82]. Renewable hydrogen-based MeOH would recycle carbon dioxide as a possible alternative fuel to diminishing oil and gas resources [45]. There are already vehicles that can run with M85, a fuel mixture of 85% MeOH and 15% gasoline [5]. MeOH can be used with the existing distribution infrastructure of conventional liquid transportation fuels. In addition, fuel cell-powered vehicles are also at a fast developing stage, although they are not yet available commercially. Technological advances such as these would lead to a MeOH economy [83].

### 1.22.6.6.3 BioBreak model for second generation biomass feedstock

For an existing lignocellulosic biomass market, the purchase price for feedstocks should be obtained by surveying biorefineries, and the marginal costs of producing and delivering biomass feedstocks to a biorefinery should be calculated based on observed production practices. Often, models such as the biofuel breakeven (BioBreak) model can be used to evaluate the cost and feasibility of a regional market for a biomass feedstock and biofuel refining process. BioBreak is a flexible breakeven model that represents the regional feedstock supply system and biofuel biorefinery. BioBreak estimates the two costs [36]:

1. Willingness-to-pay (WTP) is the maximum price that a biorefinery will pay for a dry ton of biomass delivered at the gate. WTP is a function of the price of bioethanol, the conversion yield in gallons per dry ton of, and the cost of processing biomass.

**Table 10** Comparison of water requirements for ethanol and biodiesel productions

<i>Biofuel crop</i>	<i>Water use</i>	<i>Biofuel conversion</i>	<i>Crop water use</i>	<i>Crop water use per unit energy</i>
	$\text{m}^3 \text{ water kg}^{-1} \text{ crop}$	$\text{liter fuel kg}^{-1} \text{ crop}$	$\text{m}^3 \text{ water kg}^{-1} \text{ fuel}$	$\text{m}^3 \text{ water GJ}^{-1}$
Ethanol				
Corn (grain)	833	409	2580	97
Sugarcane	154	334	580	22
Corn stover	634	326	2465	92
Switchgrass	525	336	1980	74
Grainsorghum	2672	358	9460	354
Sweetsorghum	175	238	931	35
Biodiesel				
Soybean	1818	211	9791	259
Canola	1798	415	4923	130

Source: Reproduced from Stone KC, Hunt PG, Cantrell KB, Ro KS. The potential impacts of biomass feedstock production on water resource availability. *Bioresour Technol* 2010;101:2014–25.

2. Willingness-to-accept (WTA) is the minimum price that a biomass producer would accept for a dry ton biomass delivered at the gate of a biorefinery. WTA depends on the biomass opportunity cost, as well as production and delivery costs of biomass in a long time range.

Assumptions used in the BioBreak model are:

- Producer minimizes costs on the long-run average cost curve.
- Yield distribution for biomass crops is based on the expected mean yield.
- Transportation cost is based on the average hauling distance for a circular capture region.
- Biorefinery has a 189-million-liter annual capacity to be competitive in the market.
- Each biorefinery uses a single feedstock with no market disruptions.
- Impact of energy price uncertainty on biofuel investment is not considered.

#### 1.22.6.6.3.1 Willingness-to-pay for lignocellulosic bioethanol production

Eq. (9) shows the processor's WTP for 1 dry ton of cellulosic material delivered to a biorefinery:

$$\text{WTP} = (P_{\text{gas}}E_V + T + V_{\text{CP}} + V_{\text{O}} - C_I - C_{\text{O}})Y_E \quad (9)$$

The market price of bioethanol is estimated as the energy equivalent price of gasoline, where  $P_{\text{gas}}$  denotes per-gallon price of gasoline and  $E_V$  denotes the energy equivalent factor of gasoline to ethanol. Based on historical data for conventional gasoline and crude oil, the following relationship between the price of gasoline and oil is assumed:  $P_{\text{gas}} = 0.13087 + 0.023917P_{\text{oil}}$ . Beyond direct ethanol sales, the ethanol processor also receives revenues from tax credits  $T$ , coproduct production  $V_{\text{CP}}$ , and octane benefits  $V_{\text{O}}$  per gallon of processed bioethanol. Biorefinery costs are separated into two components: investment costs  $C_I$  and operating  $C_{\text{O}}$  costs per gallon. To determine the processor's maximum WTP per dry ton of feedstock, a conversion ratio is used for gallons of ethanol produced per dry ton of biomass  $Y_E$ . Therefore, Eq. (9) provides the maximum amount the processor can pay per dry ton of biomass delivered to the biorefinery and still break even [36]. The values of the variables in Eq. (9) are based on the following assumptions and listed in Table 11:

- Price of oil ( $P_{\text{oil}}$ ). The three oil price levels: \$52, \$111, and \$191 per barrel, which are the low, reference, and high price projections for 2022 [85] in 2008 US\$.
- Energy equivalent factor ( $E_V$ ) and octane benefits ( $V_{\text{O}}$ ). The energy equivalent ratio ( $E_V$ ) for ethanol to gasoline is fixed at 0.667. Blending gasoline with ethanol increases the fuel's octane value. For simplicity, the value of  $V_{\text{O}}$  was fixed at \$0.10 per gallon.
- Coproduct value ( $V_{\text{CP}}$ ). Excess energy is the only coproduct, and Aden *et al.* [81] estimated that cellulosic ethanol production yields excess energy valued at approximately \$0.14–0.21 per gallon of ethanol, after updating to 2007 energy costs [86].
- Conversion ratio ( $Y_E$ ) is assumed to be a conversion ratio with a mean value of 70 gallons per dry ton feedstock as representative of current and near-future technology (baseline scenario) (and a mean of 80 gallons of the long-run conversion ratio) in the sensitivity analysis.
- Investment costs ( $C_I$ ) are based on laboratory- or pilot-scale operations and estimated cost data for an optimized  $n$ th biorefinery for biochemical conversion of corn stover to ethanol. Aden *et al.* [80] updated to 2007 capital cost and feedstock cost. The model assumes a mean (likeliest) value of \$0.94 (\$0.85) per gallon for baseline biorefinery capital investment cost.
- Operating costs ( $C_{\text{O}}$ ) are separated into two components: enzyme costs and nonenzyme operating costs. Nonenzyme operating costs, including salaries, maintenance, overhead, insurance, taxes, and other conversion costs, were fixed at \$0.36 per gallon. Aden *et al.* [81] assumed set enzyme costs at \$0.10 per gallon, which may vary between \$0.40 and \$1.00 per gallon at current yields and technology.
- Biofuel production incentives and tax credits ( $T$ ) for cellulosic ethanol producers designated by the Food, Conservation, and Energy Act of 2008 of \$1.01 per gallon was considered in the sensitivity analysis and was denoted as the "producer's tax credit."

#### 1.22.6.6.3.2 Willingness-to-accept for lignocellulosic bioethanol production

Eq. (10) shows the biomass supplier's WTA for 1 dry ton of cellulosic material delivered to the biorefinery [36]

$$\text{WTA} = \{(C_{\text{ES}} + C_{\text{Opp}})/Y_{\text{B}} + C_{\text{HM}} + \text{SF} + C_{\text{NR}} + C_{\text{S}} + \text{DFC} + \text{DVC} * D\} - G \quad (10)$$

The value of WTA is equal to the total production costs less the government incentives  $G$  (e.g., tax credits and production subsidies) for one dry ton of feedstock. Depending on the type of biomass feedstock, costs include establishment and seeding  $C_{\text{ES}}$  per acre, land and biomass opportunity costs  $C_{\text{Opp}}$  per acre, harvest and maintenance  $C_{\text{HM}}$ , stumpage fees  $\text{SF}$ , nutrient replacement  $C_{\text{NR}}$ , biomass storage  $C_{\text{S}}$ , transportation fixed costs  $\text{DFC}$ , and variable transportation costs calculated as the variable cost per mile  $\text{DVC}$  multiplied by the average hauling distance to the biorefinery  $D$ . Therefore, the biomass yield per acre  $Y_{\text{B}}$  is used to convert the per acre costs into per dry ton costs. Eq. (10) provides the minimum price the supplier can accept for one dry ton of biomass delivered to the biorefinery and still break even [36]. The values of the variables in Eq. (10) are based on the following assumptions and listed in Table 12:

- Nutrient replacement costs ( $C_{\text{NR}}$ ) range from \$5 to \$21 per dry ton after adjusting for 2007 costs and represent the added value by the uncollected cellulosic material to the soil through enrichment and protection against rain, wind, and radiation, thereby limiting the loss of vital soil nutrients such as nitrogen, phosphorus, and potassium.

**Table 11** BioBreak model assumptions to estimate willing to pay WTP cost by processor

Parameter	Feedstock	Mean value
Oil price ( $P_{Oil}$ )	All	\$52 brl <sup>-1</sup> ; \$111 brl <sup>-1</sup> ; \$191 brl <sup>-1</sup>
Energy equivalent factor ( $E_i$ )	All	0.68
Tax ( $T$ )	All	\$1.01 gal <sup>-1</sup>
Byproduct value ( $V_{BP}$ )	Stover	\$0.16 gal <sup>-1</sup>
	Switchgrass (all)	\$0.18 gal <sup>-1</sup>
	<i>Miscanthus</i> (all)	\$0.18 gal <sup>-1</sup>
	Wheat straw	\$0.18 gal <sup>-1</sup>
	Short rotation woody crops (SRWC)	\$0.14 gal <sup>-1</sup>
	Forest residue	\$0.14 gal <sup>-1</sup>
	Alfalfa	\$0.18 gal <sup>-1</sup>
Octane ( $V_o$ )	All	\$0.10 gal <sup>-1</sup>
Capital cost ( $C_i$ )	All	\$0.91 gal <sup>-1</sup>
Nonenzyme operating cost	All	\$0.36 gal <sup>-1</sup>
Enzyme cost	All	\$0.50 gal <sup>-1</sup>
Yield ( $Y_E$ )	All – current	70 gal t <sup>-1</sup>
	All – future	80 gal t <sup>-1</sup>

SRWC: short-rotation woody crops; brl: barrel.

Source: Reproduced from National Research Council, Renewable fuel standard: potential economic and environmental effects of U.S. biofuel policy, The National Academic Press. Available from: <http://nap.edu/13105>; 2011 [accessed 12.07.16].

- Harvest and maintenance costs ( $C_{HM}$ ) and stumpage fees (SF) are assumed a mean value of \$27–\$46 per dry ton for harvest and maintenance with an additional stumpage fee with a mean value of \$20 per dry ton for short-rotation woody crops.
- Transportation costs (DVC, DFC, and  $D$ ). The BioBreak model uses breakdown of variable and fixed transportation costs. One-way transportation distance  $D$  has been evaluated up to around 140 miles for woody biomass and between 5 and 75 miles for all other feedstocks. BioBreak calculates the average hauling distance  $D$  as a function of annual biorefinery biomass demand, annual biomass yield, and biomass density using the formulation by French [84] for a circular area with a square road grid. The average hauling distance is between 13 and 53 miles.
- Biomass storage costs ( $C_S$ ) depends on the feedstock, harvest technique, and storage area. Adjusted for 2007 costs, storage cost estimates range between \$2 and \$23 dryton<sup>-1</sup>. The mean (likeliest) cost for woody biomass storage is \$11.50 (\$12) dryton<sup>-1</sup>, while corn stover, switchgrass, *Miscanthus*, wheat straw, and alfalfa have a mean value of \$11 dryton<sup>-1</sup>.
- Establishment and seeding costs ( $C_{ES}$ ) are assumed to not incur for corn stover, wheat straw, and forest residue suppliers, whereas all other feedstock suppliers would have to be compensated for their establishment and seeding costs. The model assumes a mean cost per acre per year of \$40 for switchgrass, \$150 for *Miscanthus*, \$52 for short rotation woody crops (SRWC), and \$165 for alfalfa.
- Opportunity costs ( $C_{Opp}$ ) of using biomass for ethanol production are assumed a mean opportunity cost per acre of \$50–150 for switchgrass and \$75–150 for *Miscanthus*.
- Biomass yield ( $Y_B$ ) is variable; the mean yield of various feedstock is between 1 and 8.5 t.
- Biomass supplier government incentives ( $G$ ) are the dollar/dollar matching payments provided in the Food, Conservation, and Energy Act of 2008 up to \$45 per dry ton of feedstock for collecting, harvesting, storing, and transporting (CHST), which is a temporary (2-year) payment.

For the economic analysis, the BioBreak model estimates the price gap (PG):  $PG = WTA - WTP$ ; if the PG is negative or zero, a biomass market is economically feasible, otherwise the biomass market is not sustainable under the assumed biomass production and conversion technology [1]. Table 13 presents the mean values of WTP, WTA estimated by the BioBreak model, and price gap per dry ton without policy incentives in 2007 US\$. The value of PG decreases with higher oil prices and vice versa. The value of PG increases to between \$110 and \$168 per dry ton of biomass with an oil price of \$52 per barrel. The breakeven price is also sensitive to the conversion rate of biomass to ethanol. The baseline results assume a conversion rate of 70 gallons per dry ton biomass. Table 13 shows the price gap values with policy incentives. Any policy incentives for either the processor or supplier will decrease the price gap needed for market viability. The 2008 farm bill provides a \$1.01 per gallon tax credit to lignocellulosic biofuel blenders. Policy incentives for carbon emissions could also affect the PG for a possible interaction of biofuel policy with possible carbon policies [36].

A possible government intervention to encourage biomass production is to eliminate the price gap between the processor's WTP and the supplier's WTA by placing a price on carbon such as a carbon tax or carbon credit. Such a credit should be at a level in order to establish a viable biomass fuel market. The implicit price can be viewed as attributable to energy security and rural development benefits in addition to GHG reduction benefits. BioBreak extends the breakeven analysis by using the GREET model and GHG emissions savings from cellulosic ethanol relative to conventional gasoline. Maintaining a low price gap plays an important role in sustaining a lignocellulosic ethanol market [36].

**Table 12** BioBreak model assumptions to estimate willing to accept (WTA) price by producer for feedstock. The values with the highest probability density are within the parentheses.

Supplier breakeven (WTA) – Parameter assumptions			
Parameter	Feedstock	Mean value	
Nutrient replacement ( $C_{NR}$ )	Stover	\$13.6 t <sup>-1</sup> (\$14.6)	
	Switchgrass	\$15.6 t <sup>-1</sup> (\$16.6)	
	<i>Miscanthus</i>	\$8.35 t <sup>-1</sup>	
	Wheat straw	\$5.6 t <sup>-1</sup>	
	Forest residue	\$15.6 t <sup>-1</sup>	
Harvest and maintenance ( $C_{HM}$ )	Stover	\$43 t <sup>-1</sup> (\$46)	
	Switchgrass	\$36 t <sup>-1</sup> (\$38)	
	<i>Miscanthus</i>	\$45 t <sup>-1</sup> (\$48)	
	Wheat straw	\$32 t <sup>-1</sup> (\$33)	
	Short rotation woody crops (SRWC)	\$26 t <sup>-1</sup>	
	Forest residue	\$26 t <sup>-1</sup>	
Stumpage fee (SF)	Alfalfa	\$57 per acre	
Distance fixed cost (DFC) (distance variable cost (DVC))	SRWC	\$20 t <sup>-1</sup>	
	Stover	\$8.50 t <sup>-1</sup> [\$0.35 t <sup>-1</sup> mile <sup>-1</sup> ]: 36 miles	
	Switchgrass	\$8.50 t <sup>-1</sup> [\$0.35 t <sup>-1</sup> mile <sup>-1</sup> ]: 16–21 miles	
	<i>Miscanthus</i>	\$8.50 t <sup>-1</sup> [\$0.35 t <sup>-1</sup> mile <sup>-1</sup> ]: 14 miles	
	Wheat straw	\$8.50 t <sup>-1</sup> [\$0.35 t <sup>-1</sup> mile <sup>-1</sup> ]: 37 miles	
	SRWC	\$10 t <sup>-1</sup> [\$0.5 t <sup>-1</sup> mile <sup>-1</sup> ]: 17 miles	
	Forest residue	\$10 t <sup>-1</sup> [\$0.5 t <sup>-1</sup> mile <sup>-1</sup> ]: 53 miles	
	Alfalfa	\$8.50 t <sup>-1</sup> [\$0.35 t <sup>-1</sup> mile <sup>-1</sup> ]: 43 miles	
	Distance: 13–53 miles		
	Annual biomass demand (BD)	All	772,000 t <sup>3</sup>
Yield ( $Y_B$ )	Stover (CS)	2.1 t	
	Alfalfa (1st year)	1.25 t	
	Alfalfa (2nd year)	4 t	
	Switchgrass	3–6 t	
	<i>Miscanthus</i>	7–9 t	
	Wheat straw	1 t	
	SRWC	5 t	
	Forest residue	0.5 t	
	Biomass density (B)	Alfalfa	0.15 t m <sup>-3</sup>
		Others	0.20 t m <sup>-3</sup>
Storage ( $C_S$ )	All	\$10–11 t <sup>-1</sup>	
Establishment and seeding ( $C_{ES}$ )	Switchgrass	\$40 acre <sup>-1</sup>	
	<i>Miscanthus</i>	\$150 acre <sup>-1</sup>	
	SRWC	\$52 acre <sup>-1</sup>	
	Alfalfa (1st year)	\$165 acre <sup>-1</sup>	
	Opportunity cost ( $C_{Opp}$ )	Switchgrass	\$50–150 acre <sup>-1</sup>
	<i>Miscanthus</i>	\$75–150 acre <sup>-1</sup>	
	Wheat straw	\$1.80 acre <sup>-1</sup>	
	Alfalfa (1st year)	\$175 acre <sup>-1</sup>	

Average hauling distance is calculated using the formulation by French [84]. Equivalent to 2.205 t per day delivered to a biorefinery operating 350 days per year. Switchgrass establishment seeding cost is amortized over 10 years at 10%, *Miscanthus* over 20 years at 10%, and woody biomass over 15 years at 10%. The values are annual payments per acre. All per-acre costs are converted to per-ton costs using the yield assumptions provided in the table. Midwest opportunity cost is assumed to be positively correlated with corn yield through stover yield with a correlation of 0.75.

Source: Reproduced from National Research Council, Renewable fuel standard: potential economic and environmental effects of U.S. biofuel policy, The National Academic Press. Available from: <http://nap.edu/13105>; 2011 [accessed 12.07.16].

Anex *et al.* [79] compared the cost of producing bioethanol by fermentation, gasoline or diesel by gasification and F-T process, and gasoline or biodiesel by fast pyrolysis (see Table 14) for a required selling price for the liquid fuel to give a 10% discounted cash flow rate of return on a project with a 20-year life. All capital and operating costs are referenced to 2007 US\$. Corn stover is priced at \$75 per dry ton. Because the three technologies produce fuels with different energy contents, the results are presented in terms of gallons of gasoline equivalent (GGE). The study was based on a consistent biorefinery size of 2205 dry tons per day of corn stover. The only byproducts from the biorefinery are the fuel generated from the unconverted biomass and electricity.

A report on sustainable development of algal biofuels in the United States [87,88] identified EROI, GHG emissions, water use, supply of nitrogen, phosphorus, CO<sub>2</sub>, and appropriate land resources as potential sustainability concerns of high importance. The committee did not consider any one of these sustainability concerns a definitive barrier to sustainable development of algal biofuels because mitigation strategies for each of those concerns have been proposed and are being developed. However, all of the

**Table 13** BioBreak simulated mean willingness-to-pay (WTP), willingness-to-accept (WTA), and price gap (PG=WTA–WTP) per dry ton without policy incentives in 2007 US\$; the values of WTA are estimated for each feedstock at select percentiles over the 10,000 Monte Carlo simulations at an oil price of \$111 per barrel. Conversion efficiency of biomass to fuel is assumed to be 70 gallons per dry ton biomass

	WTA, US\$	WTP, US\$	PG, US\$	PG per GGE <sup>a</sup>
Stover	92	25	67	1.43
Stover – alfalfa	92	26	66	1.42
Alfalfa	118	26	92	1.97
Switchgrass	133	26	106	2.28
<i>Miscanthus</i>	115	26	89	1.90
Wheat straw	75	27	49	1.04
SRWC	89	24	65	1.39
Forest residues	78	24	54	1.16

<sup>a</sup>GGE: gallon of gasoline equivalent.

Source: Reproduced from National Research Council, Renewable fuel standard: potential economic and environmental effects of U.S. biofuel policy, The National Academic Press. Available from: <http://nap.edu/13105>; 2011 [accessed 12.07.16].

**Table 14** Summary of economics of biofuel conversion per dry ton of feedstock

	Ethanol by fermentation		Gasoline or diesel by gasification and F–T		Gasoline or diesel by pyrolysis with purchased H <sub>2</sub>
	90 gal t <sup>-1</sup>	70 gal t <sup>-1</sup>	High temp.	Low temp.	High yield
Single plant capital, million US\$	380	380	606	498	200
Million gallons of fuel per year	69.5	52.4	41.7	32.3	58.2
Million gallons of gasoline equivalent per year	46.3	34.9	41.7	32.3	58.2
Cost to produce					
<i>n</i> th plant million US\$	375	500	430	480	210
Pioneer plant, million US\$	650	850	800	750	350
Number of plants to meet 16 billion gallons of ethanol equivalent biofuels in 2022	230	305	256	331	183
Capital costs for RPS2, billion US\$	88	116	155	165	37
Price gap, billion US\$ per year					
At US\$52 per barrel	25	39	31	37	8
At US\$111 per barrel	10	24	16	21	–7
At US\$191 per barrel	–10	3	–4	1	–28
Biomass feed requirements					
Million dry tons per year	178	236	175	226	133
Million acres at 5 t per acre	36	47	35	45	27

Source: Reproduced from Anex RP, Aden A, Kazi FK, *et al.*, Techno-economic comparison of biomass-to transportation fuels via pyrolysis, gasification, and biochemical pathways. Fuel 2010;89:S29–35; Aden A, Ruth M, Ibsen K, *et al.*, Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover. Golden, CO: National Renewable Energy Laboratory (NREL); 2002; Swanson RM, Satrio JA, Brown RC, Hsu DD. Techno-economic analysis of biofuels production based on gasification. Golden, CO: NREL; 2010; Wright MM, Satrio JA, Brown RC, Saugaard DE, Hsu DD. Techno-economic analysis of biomass fast pyrolysis to transportation fuels. Golden, CO: National Renewable Energy Laboratory; 2010.

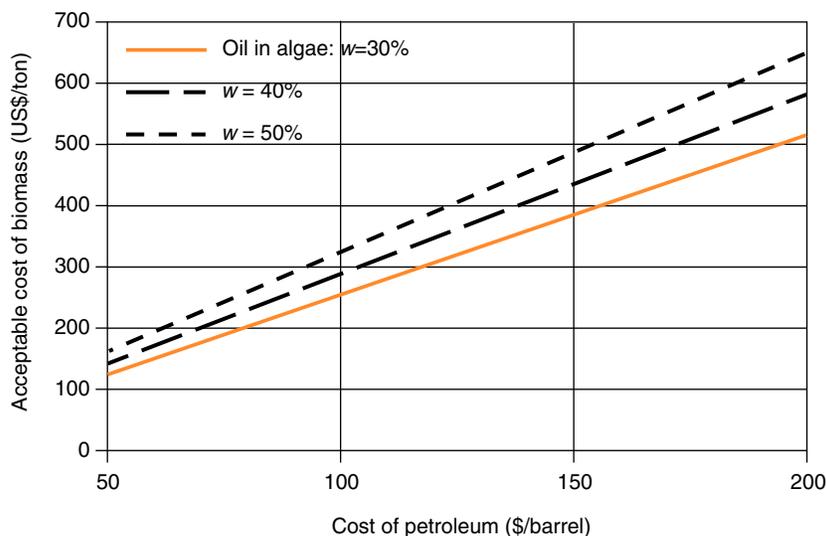
key sustainability concerns have to be addressed to some extent and in an integrative manner. Therefore, research, development, and demonstration are needed to test and refine the production systems and the mitigation strategies and to evaluate the systems and strategies if the sustainable development of algal biofuels has any chance of being realized.

#### 1.22.6.6.4 Optimum cost of algae biomass

The quantity of algal biomass ( $M_{AB}$ , tons) representing the energy equivalent of a barrel of crude petroleum is [89]

$$M_{AB} = \frac{E_{\text{petroleum}}}{Q(1-w)E_{\text{biogas}} + YwE_{\text{biodiesel}}} \quad (11)$$

where  $E_{\text{petroleum}}$  ( $\sim 6100 \text{ MJ brl}^{-1}$ ) is the energy contained in a barrel of petroleum,  $Q$  ( $\text{m}^3 \text{ t}^{-1}$ ) is the biogas volume produced by anaerobic digestion ( $400 \text{ m}^3 \text{ t}^{-1}$ ),  $E_{\text{biogas}}$  ( $\text{MJ m}^{-3}$ ) is the energy content of biogas ( $\sim 2.4 \text{ MJ m}^{-3}$ ),  $Y$  is the yield of biodiesel from



**Fig. 12** Acceptable cost of biomass with oil percentages of  $w=30%$ ,  $w=40%$ , and  $w=50%$  at a cost of petroleum estimated from Eq. (12). Reproduced from Chisti Y. Biodiesel from microalgae beats bioethanol. Trends in Biotechnol 2007;26:126–31.

**Table 15** Possible bioproducts from microalgae

Chemicals	Usage	Approx. value, \$ kg <sup>-1</sup>
Phycobiliproteins	Medical diagnostics	> 10,000
Astaxanthin	Food supplement: human, animal, aquaculture	> 2500
Xanthophyll	Fish feeds	~ 1000
Beta-carotene	Food supplement	> 500
Health supplements	Dietary supplements	~ 10
Biofuels	Energy	< 1.0

Source: Reproduced from Zemke P, Wood B, Dye D. Technoeconomic analysis of algal photobioreactors for oil production. Utah State University. Available from: <http://www.nrel.gov/biomass/pdfs/zemke.pdf>; 2008 [accessed 20.07.16].

algal oil (80% by weight),  $E_{\text{biodiesel}}$  is the average energy content of biodiesel (37,800 MJ t<sup>-1</sup>), and  $w$  is the oil content of algae biomass. Assuming that a barrel of crude oil has the same energy of  $M$  tons of algae, the maximum acceptable cost of algae  $C_{\text{Algae}}$  becomes

$$C_{\text{Algae}} = \frac{C_{\text{petroleum}}}{M_{\text{AB}}} = \frac{C_{\text{petroleum}}}{E_{\text{petroleum}}} (Q(1 - w)E_{\text{biogas}} + YwE_{\text{biodiesel}}) \quad (12)$$

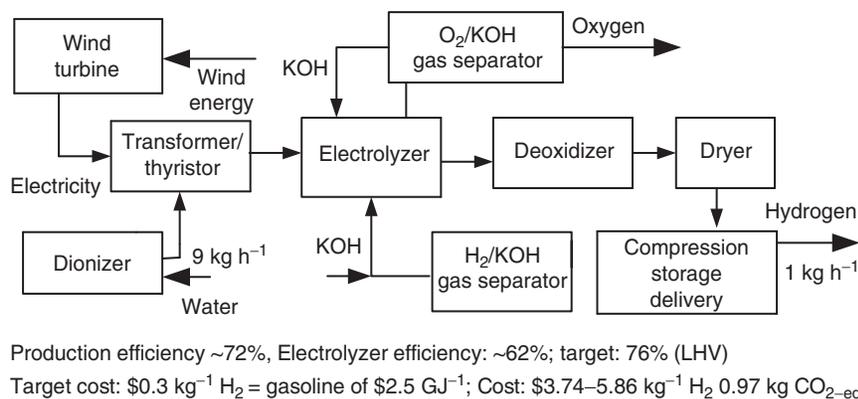
Fig. 12 shows the acceptable cost of algae biomass with respect to crude oil prices. When the cost of petroleum is \$100 brl<sup>-1</sup>, biodiesel produced from algae oil costing \$2.61 gal<sup>-1</sup> is likely to be competitive with petroleum diesel.

Table 15 shows some possible bioproducts from algae biomass with their selling prices. The table indicates that such bio-product production from algae, besides the biofuels, may have positive impact on the overall economic feasibility of algae-based biofuels and technology.

## 1.22.7 Case Studies

### 1.22.7.1 Biohydrogen Production

Fig. 13 shows the schematic of wind energy-based renewable hydrogen production. The system includes the transformer, thyristor, electrolyzer unit, feed water demineralizer, hydrogen scrubber, gas holder, two compressor units, deoxidizer, and twin tower dryer. For producing 1 kg H<sub>2</sub>, approximately 26.7 kg water is necessary. The total GHG emission is around 0.97 kg CO<sub>2</sub>e kg<sup>-1</sup> H<sub>2</sub> [90,91]. The hydrogen production cost is highly dependent on the electricity price, which may be around 75% of the final cost. Therefore electrolysis plants take advantage of low electricity prices at off-peak hours. These electrolyzers have energy efficiencies of 57%–75%. The typical current density is 100–300 mA cm<sup>-2</sup> [90,91]. Table 16 shows the typical energy consumption in a Norsk Hydro bipolar alkaline electrolyzer.



**Fig. 13** Schematic for alkaline electrolysis of water for hydrogen production with compression, storage, and delivery Reproduced from Matzen M, Alhajji M, Demirel, Y. Chemical storage of wind energy by renewable methanol production: Feasibility analysis using a multi-criteria decision matrix. Energy 2015;93:343–53.

**Table 16** Energy usage for the Norsk Hydro bipolar alkaline electrolyzer

	System energy required kWh kg <sup>-1</sup> H <sub>2</sub>	Hydrogen production at highest rate kg h <sup>-1</sup> (kg year <sup>-1</sup> )	Electrolyzer energy required at maximum rate, kW
High pressure (~16 bar)	53.4	5.4 (47,000)	290
Atmospheric	53.4	43.4 (380,000)	2300

Source: Reproduced from Norsk, Electrolyzer. (n.d.). Available from: [http://large.stanford.edu/courses/2010/ph240/pushkarev2/docs/norsk\\_electrolysers.pdf](http://large.stanford.edu/courses/2010/ph240/pushkarev2/docs/norsk_electrolysers.pdf); 2014 [accessed 10.02.16].

The H<sub>2</sub> production cost is around \$65 GJ<sup>-1</sup> using wind electricity, \$30 GJ<sup>-1</sup> using nuclear power, and \$600 GJ<sup>-1</sup> using photovoltaic electricity based on 2007 US\$ [92]. The cost of electrolytic hydrogen depends on the cost of electricity as well as the capital cost of the electrolyzer systems and their operating efficiency [93]. Capital cost of electrolyzer increases considerably as the wind farm availability and electrolyzer capacity decrease [92]. The unit cost estimates of wind power-based electrolytic H<sub>2</sub> are also limited geographically and range from \$3.74 kg<sup>-1</sup> H<sub>2</sub> to \$5.86 kg<sup>-1</sup> H<sub>2</sub> [10]. Typical output concentrations are 99.9% to 99.9998% for H<sub>2</sub> and 99.2% to 99.9993% for O<sub>2</sub> [92,93].

### 1.22.7.2 Biomethanol Production

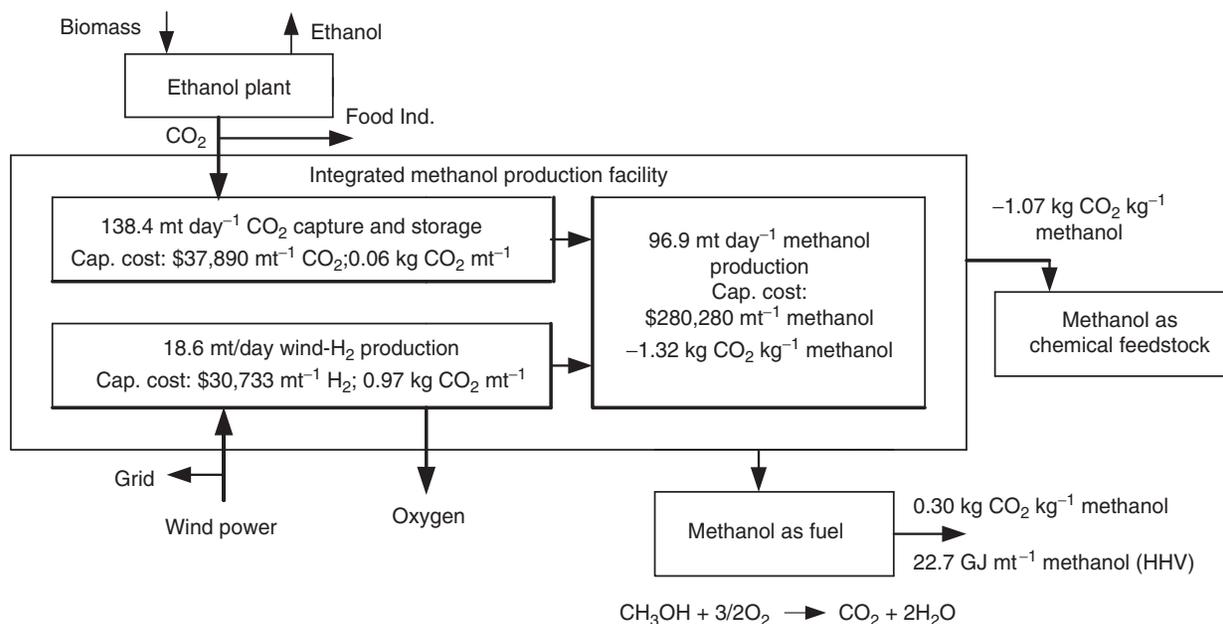
MeOH is produced almost exclusively by the ICI, the Lurgi, and the Mitsubishi processes. These processes differ mainly in their reactor designs and the way in which the produced heat is removed from the reactor. To improve their catalytic performance, the CuO/ZnO catalysts have been modified with various metals, such as chromium, zirconium, vanadium, cerium, titanium, and palladium [94,95]. During the synthesis these following reactions occur:



Only two of these reactions are linearly independent and their reaction rate equations can describe the kinetics of all the reactions [46,94].

Fig. 15 shows a process flow diagram to produce MeOH using hydrogen and CO<sub>2</sub>, which is designed and simulated using Aspen Plus software and the RK-SOAVE equation of state. Wind-based electrolytic H<sub>2</sub> and CO<sub>2</sub> supplied from an ethanol plant are used in the synthesis of MeOH. The plant uses 18.6 mt H<sub>2</sub> day<sup>-1</sup> and 138.4 mt CO<sub>2</sub> day<sup>-1</sup>, and produces 96.9 mt MeOH day<sup>-1</sup> at 99.5 wt% together with 55.0 mt day<sup>-1</sup> at 99 wt% of wastewater. Fig. 14 presents the process flow diagram for the MeOH plant using CO<sub>2</sub> and H<sub>2</sub>. The feedstock is at the conditions associated with typical storage, with H<sub>2</sub> at 25°C and 33 bar and CO<sub>2</sub> at -25.6°C and 16.422 bar (liquid phase) [46]. The ratio of H<sub>2</sub> to CO<sub>2</sub> is held at 3:1 to promote MeOH synthesis. In the feed preparation block, the renewable H<sub>2</sub> and CO<sub>2</sub> are compressed to 50 bar in a multistage compressor and pump, respectively, and mixed with the recycle stream S12 in mixer M101. Stream S1 is preheated in HX101 and E101 before being fed into the plug-flow reactor R101 where the MeOH synthesis takes place. Table 17 shows the stream table for the process shown in Fig. 14 [46,95].





**Fig. 15** Some economic and sustainability indicators in the integral methanol (MeOH) production facility. Reproduced from Matzen M, Alhajji M, Demirel, Y. Chemical storage of wind energy by renewable methanol production: feasibility analysis using a multi-criteria decision matrix. Energy 2015;93:343–53.

**Table 18** Sustainability metrics for the integral methanol (MeOH) plant

<i>Material intensity</i>	
CO <sub>2</sub> used/unit product	1.43
H <sub>2</sub> used/unit product	0.19
<i>Energy intensity</i>	
Net duty/unit product, MWh mt <sup>-1</sup>	0.39
Net duty cost/unit product, \$ mt <sup>-1</sup>	825.61
<i>Environmental impact</i>	
Total CO <sub>2e</sub> /unit product	- 1.07
Net carbon fee/unit product, \$ mt <sup>-1</sup>	- 2.11

Note: US-EPA-Rule E9-5711; fuel source: natural gas; carbon fee: \$2/mt CO<sub>2</sub>.

Source: Reproduced from Matzen M, Alhajji M, Demirel Y. Chemical storage of wind energy by renewable methanol production: feasibility analysis using a multi-criteria decision matrix. Energy 2015;93:343–53.

### 1.22.7.3 Biodimethyl Ether Production

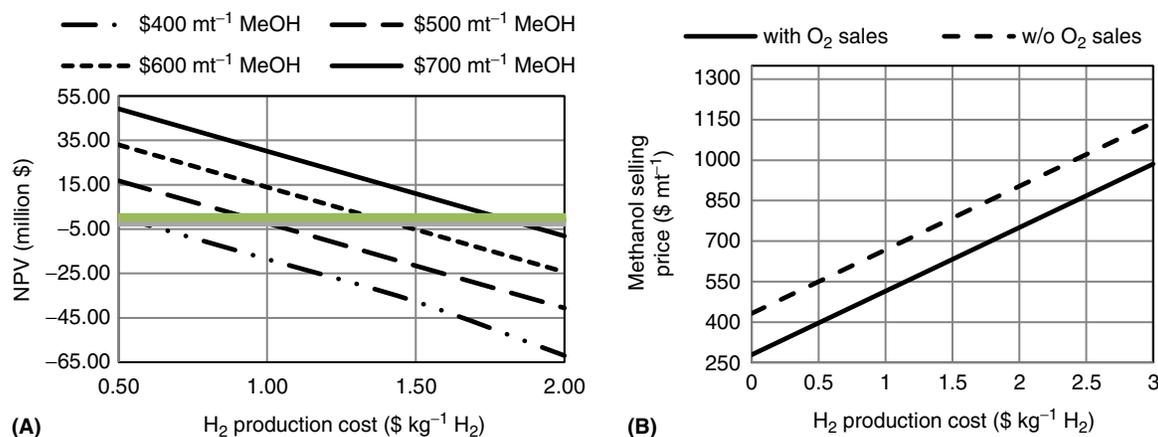
Biodimethyl ether can be produced from MeOH using wind power-based electrolytic hydrogen and CO<sub>2</sub> captured from an ethanol fermentation process. MeOH and DME from CO<sub>2</sub> hydrogenation may outperform conventional petroleum-based fuels, reducing GHG emissions 82%–86%, minimizing other criteria pollutants (SO<sub>x</sub>, NO<sub>x</sub>, etc.), and reducing fossil fuel depletion by 82%–91% [73,98].

Biodimethyl ether production was modeled in Aspen Plus using a previously simulated MeOH production facility (Fig. 18). The facilities use 18.6 mt of H<sub>2</sub> and 138.4 mt CO<sub>2</sub> per day. Biomethanol is produced at a rate of 96.7 mt/day (99.5 wt%) and DME is produced at a rate of 68.5 mt/day (99.6 wt%). Renewable MeOH and DME results were independently compared and this renewable process was also compared to conventional production routes. Results show that production of DME impacts the environment more than MeOH production. The largest environmental impact was found to be related to the fuel production stage for both fuels.

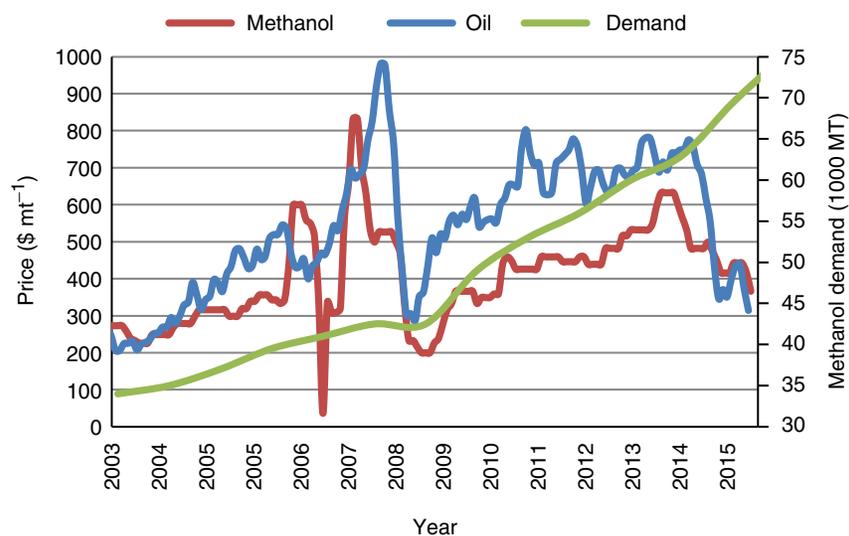
Nonnormalized indicators for the entire process can be found in Table 19. It should be noted that these values are strictly for the production stages of these chemicals (cradle-to-gate). Fuel combustion and the influence of using biogenic CO<sub>2</sub> are not accounted for [73].

### 1.22.7.4 Methyl Dodecanoate (Biodiesel)

Production of methyl dodecanoate (biodiesel) using lauric acid and MeOH with a solid acid catalyst of sulfated zirconia uses two distillation sequences where the reactive distillation and MeOH recovery columns are thermally coupled (Fig. 19). This sequence may consume less energy by allowing interconnecting vapor and liquid streams between the two columns to eliminate reboiler or



**Fig. 16** The influence of H<sub>2</sub> production cost on: (a) net present value at constant methanol (MeOH) price, (b) selling price of MeOH for NPV=0 with and without selling O<sub>2</sub> byproduct at \$100 mt<sup>-1</sup>. Reproduced from Matzen M, Alhajji M, Demirel Y. Chemical storage of wind energy by renewable methanol production: feasibility analysis using a multi-criteria decision matrix. *Energy* 2015;93:343–53; Methanex. Current posted prices. Available from: <https://www.methanex.com/our-business/pricing>; 2015 [accessed 09.07.15]; Chesko J. Methanol industry outlook [presentation slides]. Vancouver: Methanex; 2014.



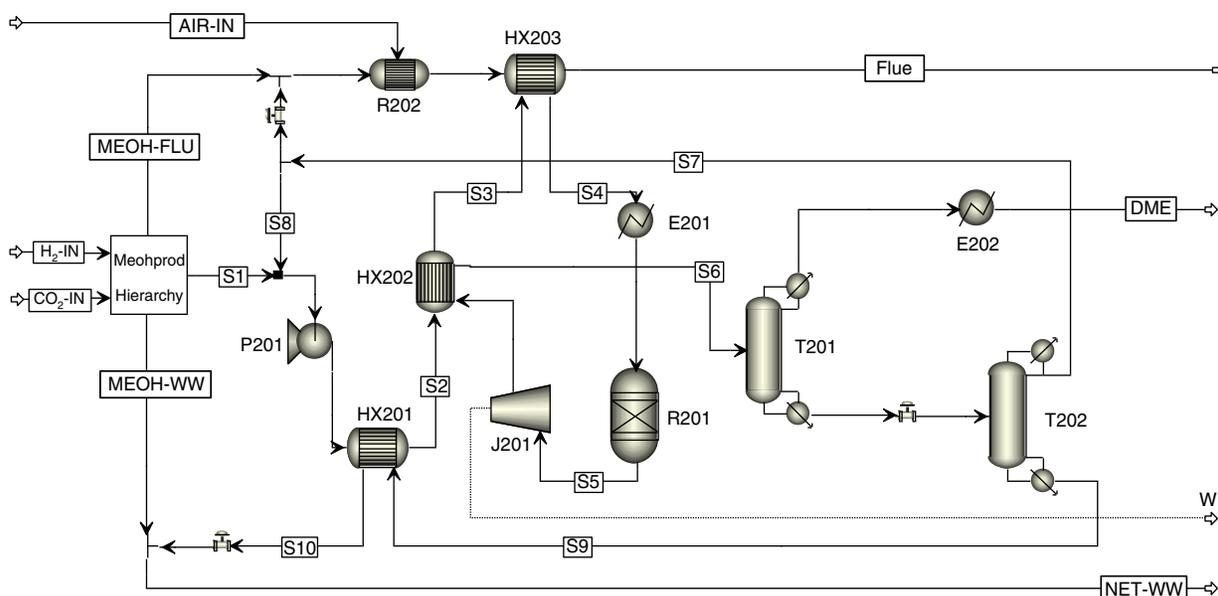
**Fig. 17** Methanol (MeOH) price and demand in recent history. Reproduced from Methanex. Current posted prices. Available from: <https://www.methanex.com/our-business/pricing>; 2015 [accessed 09.07.15]; Chesko J. Methanol industry outlook [presentation slides]. Vancouver: Methanex; 2014.

condenser or both [99]. **Table 20** summarizes the stream properties for the process shown in **Fig. 19**. Stream METH combined with stream S3B in mixer M101 is preheated to 110°C in heat exchanger HX102 before it is fed to the bottom of the reaction zone at stage 29 of RD101. The feeds enter at both ends of the reaction zone to maximize conversion [99]. The plant produces around 99.2 wt% of 21,527 kg h<sup>-1</sup> of methyl dodecanoate and dilute concentration of MeOH in water as summarized in **Table 20**.

Column T101 recovers MeOH from water and recycles. The column operates with 12 stages, with a kettle reboiler and a total condenser. The activity coefficient model of NRTL is used for predicting the equilibrium and liquid properties in column T101. The top product, stream S3A, containing mostly MeOH, is pressurized before it is recycled. The bottom product, stream WATA, is treated as a waste [99].

### 1.22.8 Future Directions

Biomass is a main component of the food supply chain, and also represents a stored renewable carbon and energy source. Therefore, it is a future challenge to increase the biofuel production from the second and third generations, and waste biomass feedstock resources. Improving the technologies of production and increasing the variety of value-added byproducts would be essential for the economic feasibility of the biofuel sector [89,99,100]. Biofuel share within the energy supply chain is still very



**Fig. 18** Process flow diagram for the backend dimethyl ether (DME) facility. Reproduced from Matzen M, Demirel Y. Methanol and dimethyl ether from renewable hydrogen and carbon dioxide: Alternative fuels production and life-cycle assessment. *J Cleaner Prod* 2016;139:1068–77.

**Table 19** Nonnormalized environmental impacts for mt of product (methanol (MeOH) or dimethyl ether (DME))

Indicator	MeOH	DME	Unit $mt^{-1}$ product
Global warming potential	0.30	0.53	mt CO <sub>2</sub> eq
Acidification potential	0.67	0.97	kg SO <sub>2</sub> eq
Photochemical oxidant formation	0.69	1.17	kg NMVOC eq <sup>a</sup>
Particulate matter (PM) formation	0.29	0.44	kg PM <sub>10</sub> eq
Human toxicity	0.10	8.18	kg 1,4-DB eq <sup>b</sup>

<sup>a</sup>NMVOC: nonmethane volatile organic compound.

<sup>b</sup>1,4-DB: 1,4 dichlorobenzene.

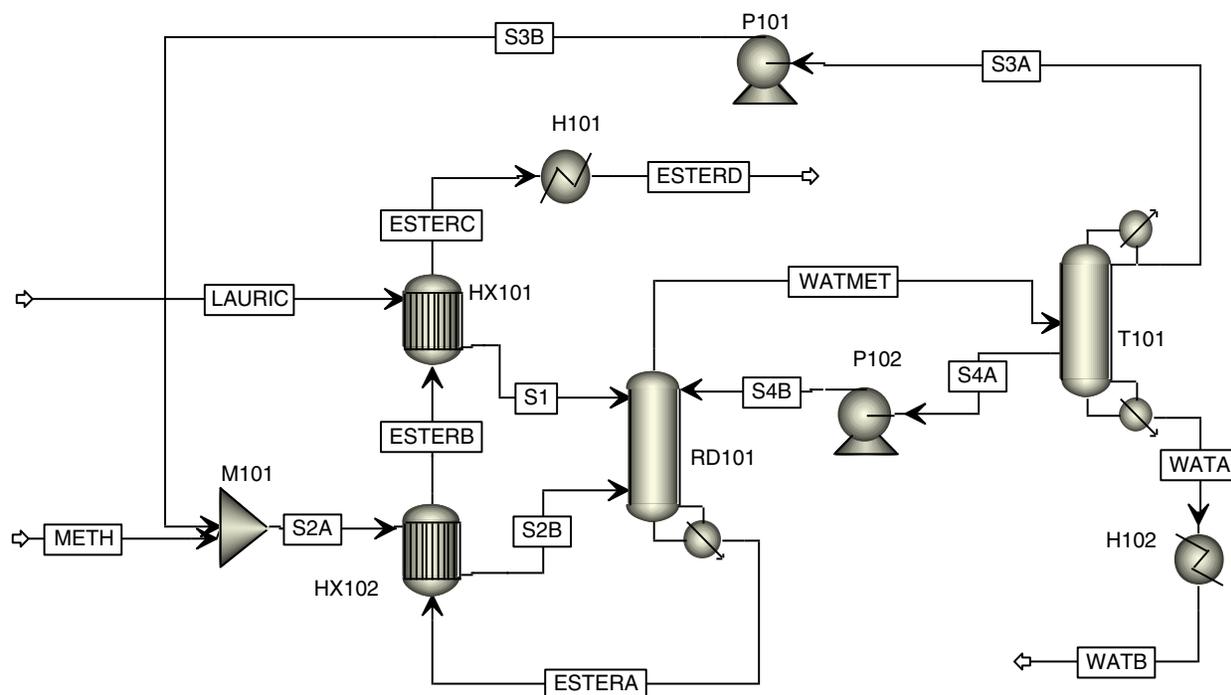
Source: Reproduced from Matzen M, Demirel Y. Methanol and dimethyl ether from renewable hydrogen and carbon dioxide: alternative fuels production and life-cycle assessment. *J Cleaner Prod* 2016;139:1068–77.

small and needs to be increased with improved technology and reduced unit cost of production. Within the biorefinery and multigeneration settings the unit cost of biofuels can be reduced, because the current cost of biofuels is not competitive enough with those of fossil fuels. Distributed versus centralized biorefinery concepts should also be fully analyzed for an optimum process setting for sustainable biofuel production, regional economic development, and environmental protection [55,87,101].

### 1.22.9 Closing Remarks

Biomass is a renewable carbon source with built-in energy storage, contrary to solar and wind energy sources. At the same time, biomass usage may compete with food production accompanied with land and water requirements. Compared with the fossil fuel, nuclear, and water resources, renewable resources are abundant and more uniformly distributed worldwide. Biomass feedstock as a renewable source may play an important role for sustainable energy supply and hence development. With around 5%–15% available cropland up to 6% displacement of fossil fuels may be possible [47]. Mainly the United States and European Union are setting ambitious production levels and leading in the research and development of biofuel conversion processes from various feedstocks to reduce the cost and increase the energy conversion efficiency. This may be encouraging for biofuel usage worldwide and may reduce the adverse effects of fossil fuels on climate change.

Production of biofuels depends on the availability and cost of biomass feedstock. Economic analyses estimate the cost of different types of biomass for producers as well as the cost of converting biomass to biofuel. The intersection of the newly emerging biofuel market with established markets in agriculture, forestry, water, and energy is causing substantial economic impacts on the prices of agricultural commodities, food, feedstuffs, forest products, fossil fuel energy, and land values because of the competition for feedstock created by increased production of biofuels.



**Fig. 19** Process flow diagram for biodiesel (methyl dodecanoate) production. Reproduced from Nguyen N, Demirel Y. Using thermally coupled reactive distillation columns in biodiesel production. *Energy* 2011;36:4838–47.

**Table 20** Stream properties of the thermally coupled design

	LAURIC	METH	ESTERD	WATMET	WATB
Mass flow (kg h <sup>-1</sup> )	20,032.14	3364.43	21,526.71	5036.00	1869.83
Temperature (°C)	25.00	25.00	25.00	155.50	25.00
Pressure (bar)	9.0	9.5	1.0	9.0	1.0
Vapor fraction	0	0	0	1	0
Enthalpy (kcal mol <sup>-1</sup> )	-176.42	-56.98	-159.90	-51.97	-68.30
Mass flow (kg h <sup>-1</sup> )					
Water	0.00E+00	0.00E+00	1.79E-01	1.93E+03	1.80E+03
Methanol (MeOH)	0.00E+00	3.36E+03	1.34E+02	3.06E+03	3.41E+01
Lauric acid	2.00E+04	0.00E+00	3.79E+01	9.99E+00	9.64E+00
Metester	0.00E+00	0.00E+00	2.14E+04	3.30E+01	2.90E+01
Mass fraction					
Water	0.0000	0.0000	0.0000	0.3838	0.9611
MeOH	0.0000	1.0000	0.0062	0.6076	0.0182
Lauric acid	1.0000	0.0000	0.0018	0.0020	0.0052
Metester	0.0000	0.0000	0.9920	0.0066	0.0155

Source: Reproduced from Nguyen N, Demirel Y, Using thermally coupled reactive distillation columns in biodiesel production. *Energy* 2011;36:4838–47.

## References

- [1] Jiang Y, Swinton SM. Market interactions, farmer choices, and the sustainability of growing advanced biofuels: a missing perspective? *Int J Sustain Dev World Ecol* 2009;16:438–50.
- [2] Dawson B, Spannagle M. *The complete guide to climate change*. London: Routledge; 2009.
- [3] Hahn-Hagerdal B, Galbe M, Gorwa-Grauslund MF, Liden G, Zacchi G. Bio-ethanol—the fuel of tomorrow from the residues today. *Trends in Biotechnol* 2006;24:549–56.
- [4] Klass DL. *Biomass for renewable energy, fuel, and chemicals*. San Diego: Academic Press; 1998.
- [5] Demirel Y. *Energy: production, conversion, storage, conservation, and coupling*. 2nd ed. London: Springer; 2016.
- [6] Gaur S, Reed T, Teed TB. *Thermal data for natural and synthetic fuels*. New York, NY: CRC Press; 1998.
- [7] Ptasiński KJ. *Efficiency of biomass energy: an exergy approach to biofuels, power, and biorefineries*. New York: Wiley; 2016.
- [8] BNDES/CGEE. *Sugarcane-based bioethanol, energy for sustainable development*. Rio de Janeiro: BNDES and CGEE; 2008.
- [9] Cherubini F. The biorefinery concept: using biomass instead of oil for producing energy and chemicals. *Energy Convers Manag* 2010;51:1412–21.

- [10] Liu G, Larson ED, Williams RH, Kreutz TG, Guo X. Making Fischer–Tropsch fuels and electricity from coal and biomass: performance and cost analysis. *Energy Fuels* 2011;25:415–37.
- [11] Huber GW, Corma A. Synergies between bio- and oil refineries for the production of fuels from biomass. *Agnew Chem Int Ed* 2007;47:7184–201.
- [12] Chen NY, Degnan JTF, Koenig LR. Liquid fuel from biomass: direct conversion of carbohydrates. *ChemTech* 1986;16:506–11.
- [13] Jae J, Tompsett GA, Foster AJ, *et al.* Investigation into the shape selectivity of zeolite catalysts for biomass conversion. *J Catal* 2011;279:257–68.
- [14] Kumar A, Nouredini H, Demirel Y, Jones DD, Hanna MA. Simulation of corn stover and distillers grains gasification with Aspen Plus. *Trans Am Soc Agric Biol Eng (ASABE)* 2009;52:1989–95.
- [15] Phillips S, Aden A, Jechura J, Dayton D, Eggeman T. Thermochemical ethanol via indirect gasification and mixed alcohol synthesis of lignocellulosic biomass, Technical report NREL/TP-510-41168; 2007.
- [16] Kumar A, Demirel Y, Jones DD, Hanna MA. Optimization and economic evaluation of industrial gas production and combined heat and power generation from gasification of corn stover and distillers grains. *Bioresour Technol* 2010;101:3696–701.
- [17] Manganaro J, Chen B, Adeosun J, *et al.* Conversion of residual biomass into liquid transportation fuel: an energy analysis. *Energy Fuels* 2011;25:2711–20.
- [18] van der Stelt MJC, Gerhauser H, Kiel JHA, Ptasinski KJ. Biomass upgrading by torrefaction for the production of biofuels: a review. *Biomass Bioenergy* 2011;35:3748–62.
- [19] Liu B-F, Ren N-Q, Vie G-J, *et al.* Enhanced biohydrogen production by the combination of dark-and photofermentation in batch culture. *Bioresour Technol* 2010;101:5325–9.
- [20] Zhou M, Yang J, Wang H, *et al.* Microbial fuel cells and microbial electrolysis cells for the production of bioelectricity and biomaterials. *Environ Technol* 2013;34:1915–28.
- [21] Mata-Alvarez J, Macé S, Llabrés P. Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. *Bioresour Technol* 2000;74:3–16.
- [22] Mythili R, Venkatchalam P, Subramanian P, Uma D. Production characterization and efficiency of biodiesel: a review. *Int J Energy Res* 2014;38:1233–59.
- [23] Patil PD, Gude VG, Reddy HK, Muppaneni T, Deng S. Biodiesel production from waste cooking oil using sulfuric acid and microwave irradiation process. *J Environ Prot* 2012;3:107–13.
- [24] Demirbas MF. Hydrogen from various biomass species via pyrolysis and steam gasification processes. *Energy Sources Part A* 2006;28:245–52.
- [25] Unruh D, Pabst K, Schaub G. Fischer–Tropsch syngas from biomass: maximizing carbon efficiency and hydrocarbon yield. *Energy Fuels* 2010;24:2634–41.
- [26] Acharya B, Dutta A, Basu P. Chemical-looping gasification of biomass for hydrogen-enriched gas production with in-process carbon dioxide capture. *Energy Fuels* 2009;23:5077–83.
- [27] Basu P. Biomass gasification and pyrolysis: practical design and theory. New York, NY: Academic Press; 2010.
- [28] Dutta A, Acharya B. Handbook of biofuel production-processes and technologies: production of bio-syngas and biohydrogen via gasification. Cambridge: Woodhead Publishing; 2011.
- [29] Moghtaderi B. Review of the recent chemical looping process developments for novel energy and fuel applications. *Energy Fuels* 2012;26:15–40.
- [30] Demirel Y, Matzen M, Winters C, Gao X. Capturing and using CO<sub>2</sub> as feedstock with chemical-looping and hydrothermal technologies and sustainability metrics. *Int J Energy Res* 2015;39:1011–47.
- [31] Das D, Veziroglu TN. Hydrogen production by biological processes: a survey of literature. *Int J Hydrogen Energy* 2001;26:13–28.
- [32] Turner JA. Sustainable hydrogen production. *Science* 2004;305:972–4.
- [33] Ptasinski KJ, Prins MJ, Pterik A. Exergetic evaluations of biomass gasification. *Energy* 2007;32:568–74.
- [34] Nguyen N, Sim J, Demirel Y. Bioethanol dehydration in thermally integrated extractive distillation columns. In: AIChE's annual meeting, Salt Lake City; 2010 November 7–12, 2010.
- [35] Patzek TW. A first-law thermodynamics analysis of the corn-ethanol cycle. *Natl Resources Res* 2006;15:255–70.
- [36] National Research Council. Renewable fuel standard: potential economic and environmental effects of U.S. biofuel policy, The National Academic Press. Available from: <http://nap.edu/13105>; 2011 [accessed 12.07.16].
- [37] NAS-NAE-NRC (National Academy of Sciences, National Academy of Engineering, National Research Council). Liquid transportation fuels from coal and biomass: technological status, costs, and environmental impacts. Washington, DC: National Academies Press, Available from: <https://www.nrel.gov/workingwithus/re-biofuels.html>. <http://www.alternative-energy-news.info/technology/biofuels/>; 2009 [accessed 12.07.16].
- [38] Blanco-Canqui H, Lai R. Crop residue removal impacts on soil productivity and environmental quality. *Crit Rev Plant Sci* 2009;28:139–63.
- [39] Nevoigt E. Progress in metabolic engineering of *Saccharomyces cerevisiae*. *Microbiol Mol Biol Rev* 2008;72:379–412.
- [40] Konda NVSNM, Singh S, Simmons BA, Klein-Marcuschamer DK. An investigation on economic feasibility of macroalgae as a potential feedstock for biorefineries. *BioEnergy Res* 2015;8:1046–56.
- [41] Zhang W. Automotive fuels from biomass via gasification. *Fuel Process Technol* 2010;91:866–76.
- [42] Ezeji TC, Qureshi N, Blaschek HP. Bioproduction of butanol from biomass: from genes to bioreactors. *Curr Opin Biotechnol* 2007;18:220–7.
- [43] Tao L, Tan ECD, McCormic R, *et al.* Techno-economic analysis and life-cycle assessment of cellulosic isobutanol and comparison with cellulosic ethanol and n-butanol. *Biofuels, Bioprod Biorefining* 2014;8:30–48.
- [44] Ptasinski KJ, Hamelinck C, Kerhof PJAM. Exergy analysis of methanol from the sewage sludge process. *Energy Convers Manag* 2002;43:1445–57.
- [45] Matzen M, Alhajji M, Demirel Y. Technoeconomics and sustainability of renewable methanol and ammonia productions using wind power-based hydrogen. *Adv Chem Eng* 2015;5:128.
- [46] Matzen M, Alhajji M, Demirel Y. Chemical storage of wind energy by renewable methanol production: feasibility analysis using a multi-criteria decision matrix. *Energy* 2015;93:343–53.
- [47] IEA, International Energy Agency. Technology roadmap: energy and GHG reductions in the chemical industry via catalytic processes. Available from: [http://www.iea.org/publications/freepublications/publication/Chemical\\_Roadmap\\_2013\\_Final\\_WEB.pdf](http://www.iea.org/publications/freepublications/publication/Chemical_Roadmap_2013_Final_WEB.pdf); 2013 [accessed 07.10.16].
- [48] Clausen LR, Houbak N, Elmegaard B. Technoeconomic analysis of a methanol plant based on gasification of biomass and electrolysis of water. *Energy* 2010;35:2338–47.
- [49] Hammond EG, Johnson LA, Su C, Wang T, White PJ. Soybean oil. In: Shahidi F, editor. *Bailey's industrial oil and fat products*. 6th ed. New York, NY: Wiley; 2005.
- [50] Nguyen N, Demirel Y. A novel biodiesel and glycerol carbonate production plant. *Int J Chem Reactor Eng* 2011;9:1–25.
- [51] Nguyen N, Demirel Y. Economic analysis of biodiesel and glycerol carbonate production plant by glycerolysis. *J Sustain Bioenergy Syst* 2013;3:209–16.
- [52] Berrios M, Martín MA, Chica AF, Martín A. Study of esterification and transesterification in biodiesel production from used frying oils in a closed system. *Chem Eng J* 2010;160:473–9.
- [53] Zabeti M, Daud WMAW, Aroua MK. Activity of solid catalyst for biodiesel production: a review. *Fuel Process Technol* 2009;90:770–7.
- [54] Kalnes TN, Koers KP, Marker T, Shonnard DR. A technoeconomic and environmental life cycle comparison of diesel to biodiesel and syndiesel. *Env Prog Sustain, Energy* 2009;28:11–20.
- [55] Harun R, Doyle M, Gopiraj R, *et al.* Process economics and greenhouse gas audit for microalgal biodiesel production. In: Lee JW, editor. *Advanced Biofuels and Bioproducts*. New York, NY: Springer; 2013. p. 709–44.
- [56] Barry A, Wolfe A, English C, Ruddick C, Lambert, D. National algal biofuels technology review. U.S. Department of Energy; 2016.
- [57] Zemke P, Wood B, Dye D. Technoeconomic analysis of algal photobioreactors for oil production. Utah State University. Available from: <http://www.nrel.gov/biomass/pdfs/zemke.pdf>; 2008 [accessed 20.07.16].
- [58] Wang D, Li Y, Hu X, Su W, Zhang M. Combined enzymatic and mechanical cell disruption and lipid extraction of green alga *Neochloris oleoabundans*. *Int J Mol Sci* 2015;16:7707–22.

- [59] Tevatia R, Allen J, Rudrappa D, *et al.* The taurine biosynthetic pathway of microalgae. *Algal Res* 2015;9:21–6.
- [60] Kütçük K, Tevatia R, Sorgüven E, Demirel Y, Özilgen M. Bioenergetics of growth and lipid production in *Chlamydomonas reinhardtii*. *Energy* 2015;83:503–10.
- [61] Tevatia R, Allen J, Blum P, Demirel Y, Black P. Modeling of rhythmic behavior in neutral lipid production due to continuous supply of limited nitrogen: mutual growth and lipid accumulation in microalgae. *Bioresour Technol* 2014;170:152–9.
- [62] Tevatia R, Demirel Y, Blum P. Kinetic modeling of photoautotrophic growth and neutral lipid accumulation in terms of ammonium concentration in *Chlamydomonas reinhardtii*. *Bioresour Technol* 2012;119:419–24.
- [63] Muylaert K, Beuckels A, Depraetere O, *et al.* Wastewater as source of nutrients for microalgae biomass production. In: Moheimani NR, Borowitzka MA, editors. *Biomass and Biofuels from microalgae*. New York, NY: Springer; 2015.
- [64] Roberts GW, Fortier M-OP, Sturm BSM, Stagg-Williams SM. Promising pathway for algal biofuels through wastewater cultivation and hydrothermal conversion. *Energy Fuels* 2013;27:857–67.
- [65] Li X, Mupondwa E. Life cycle assessment of camelina oil derived biodiesel and jet fuel in the Canadian Prairies. *Sci Total Environ* 2014;481:17–26.
- [66] Sandor D, Wallace R, Peterson S. Understanding the growth of the cellulosic ethanol industry, Technical report NREL/TP-150-42120; 2008.
- [67] Hall CAS, Lambert JG, Balogh SB. EROI of different fuels and the implications for society. *Energy Policy* 2014;64:141–52.
- [68] Gnansounou E, Dauriat A, Villegas J, Panichelli L. Life cycle assessment of biofuels: energy and greenhouse gas balances. *Bioresour Technol* 2009;100:4919–30.
- [69] Pradhan A, Shrestha DS, McAloon A, *et al.* Energy life cycle assessment of soybean biodiesel revisited. *Transaction ASABE* 2011;54:1031–9.
- [70] Pimantel D, Patzek TW. Ethanol production using corn, switchgrass, and wood; biodiesel production using soybean and sunflower. *Nat Resour Res* 2005;14:65–76.
- [71] EPA. Available from: <https://www.epa.gov/renewable-fuel-standard-program>; 2016 [accessed: 07.12.16].
- [72] Paping S, Chom-in T, Noksa-nga S, Malkul P. Life cycle energy efficiency of biodiesel production from palm oil in Thailand. *Energy Policy* 2010;38:226–33.
- [73] Matzen M, Demirel Y. Methanol and dimethyl ether from renewable hydrogen and carbon dioxide: alternative fuels production and life-cycle assessment. *J Cleaner Prod* 2016;139:1068–77.
- [74] NREL (National Renewable Energy Laboratory). U.S. life cycle inventory database. [www.nrel.gov](http://www.nrel.gov); <https://www.lcacommons.gov/nrel/search>; 2012 [accessed 12.07.16].
- [75] Babcock BA, Barr K, Carriquiry M. Cost and benefits to taxpayers, consumers, and producers from U.S. ethanol policies. Ames: Iowa State University Center for Agricultural and Rural Development; 2010.
- [76] Skinner KA, Leathers TD. Bacterial contaminants of fuel ethanol production. *J. Industrial Microbiology & Biotechnology* 2004;31:401–8.
- [77] Wallace R, Ibsen K, McAloon A, Yee W. Feasibility study for co-locating and integrating ethanol production plants from corn starch and lignocellulosic feedstocks NREL/TP-510-37092. U.S. Department of Agriculture and U.S. Department of Energy; 2005.
- [78] Gubicza K, Nieves IU, Sauges WJ, *et al.* Techno-economic analysis of ethanol production from sugarcane bagasse using a liquefaction plus simultaneous saccharification and co-fermentation process. *Bioresour Technol* 2016;208:42–8.
- [79] Anex RP, Aden A, Kazi FK, *et al.* Techno-economic comparison of biomass-to transportation fuels via pyrolysis, gasification, and biochemical pathways. *Fuel* 2010;89(1):S29–35.
- [80] La Rovere EL, Pereira AS, Simones AF. Biofuels and sustainable energy development in Brazil. *World Development* 2011;39:1026–36.
- [81] Aden A, Ruth M, Ibsen K, *et al.* Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover. Golden 2002;CO: National Renewable Energy Laboratory (NREL); 2002.
- [82] Galindo CP, Badr O. Renewable hydrogen utilisation for the production of methanol. *Energy Convers Manag* 2007;48:519–27.
- [83] Olah GA, Goeppert A, Surya GK. Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons. *J Org Chem* 2009;74:487–98.
- [84] French BC. Some considerations in estimating assembly cost functions for agricultural processing operations. *J Farm Econ* 1960;42:767–78.
- [85] Stone KC, Hunt PG, Cantrell KB, Ro KS. The potential impacts of biomass feedstock production on water resource availability. *Bioresour Technol* 2010;101:2014–25.
- [86] EIA (U.S. Energy Information Administration). Annual energy outlook 2010 – with projections to 2035. Washington, DC: U.S. Department of Energy; 2010.
- [87] The National Academies Press. Sustainable development of algal biofuels in the United States. Available from: <http://nap.edu/13437>; 2012 [accessed 15.07.16].
- [88] Naik SN, Goud VV, Rout PK, Dalai AK. Production of first and second generation biofuels: a comprehensive review. *Renew Sustain Energy Rev* 2010;14:578–97.
- [89] Chisti Y. Biodiesel from microalgae beats bioethanol. *Trends in Biotechnol* 2007;26:126–31.
- [90] Dincer I, Ratlamwala T. Development of novel renewable energy based hydrogen production systems: a comparative study. *Energy Convers Manag* 2013;72:77–87.
- [91] Norsk. Electrolyzer. (n.d.). Available from: [http://large.stanford.edu/courses/2010/ph240/pushkarev2/docs/norsk\\_electrolysers.pdf](http://large.stanford.edu/courses/2010/ph240/pushkarev2/docs/norsk_electrolysers.pdf); 2014 [accessed 10.02.16].
- [92] Mueller-Langer F, Tzimas E, Kaltschmitt M, Petevs S. Techno-economic assessment of hydrogen production processes for the hydrogen economy for the short and medium term. *Int J Hydrogen Energy* 2007;32:2810–3797.
- [93] Saur G. Wind-to-hydrogen project: electrolyzer capital cost study Golden, CO: National Renewable Energy Laboratory 2008 Available from: <http://www.nrel.gov/hydrogen/pdfs/44103.pdf>
- [94] Toyir J, Miloua R, Elkadri N, *et al.* Sustainable process for the production of methanol from CO<sub>2</sub> and H<sub>2</sub> using Cu/ZnO-based multicomponent catalyst. *Phys Proced* 2009;2:1075–9.
- [95] Li C, Yuan X, Fujimoto K. Development of highly stable catalyst for methanol synthesis from carbon dioxide. *Appl Catal A: Gener* 2014;469:306–11.
- [96] Methanex. Current posted prices. Available from: <https://www.methanex.com/our-business/pricing>; 2015 [accessed 09.07.15].
- [97] Chesko J. Methanol industry outlook [presentation slides]. Vancouver: Methanex; 2014.
- [98] Pontzen F, Liebner W, Gronemann V, Rothaemel M, Ahlers B. CO<sub>2</sub>-based methanol and DME – efficient technologies for industrial scale production. *Catal Today* 2011;171:242–50.
- [99] Nguyen N, Demirel Y. Using thermally coupled reactive distillation columns in biodiesel production. *Energy* 2011;36:4838–47.
- [100] Nguyen N, Demirel Y. Retrofit of distillation columns in biodiesel production plants. *Energy* 2010;35:1625–32.
- [101] Platon A, Kothandaraman G, Hsu DD, Dutta A. Techno-economic comparison of biomass-to transportation fuels via pyrolysis, gasification, and biochemical pathways. *Fuel* 2010;89:S29–35.

## Further Reading

- Sodamade A, Oyedepo TA, Bolaji OS. 2013. Fatty acids composition of three different vegetable oils (soybean oil, groundnut oil and coconut oil) by highperformance liquid chromatography. *Chem Mat Res* 2013;3:26–9.
- Van-Dal ES, Bouallu C. 2013. Design and simulation of a methanol production plant from CO<sub>2</sub> hydrogenation. *J Clean Prod* 2013;57:38–45.
- Weiduan S, Zhang J, Bingchen Z, *et al.* 1989. Kinetics of methanol synthesis in the presence of C301 Cu-based catalyst (i) intrinsic and global kinetics. *J Chem Ind and Eng (China)* 1989;4:248–57.

## Relevant Websites

- <https://www.chevron.com/stories/biofuels>  
Chevron.

<https://ec.europa.eu/energy/en/topics/renewable-energy/biofuels>  
European Commission.

<http://www.nationalgeographic.com/environment/global-warming/biofuel/>  
National Geographic.

<https://www.nrel.gov/workingwithus/re-biofuels.html>  
National Renewable Energy Laboratory (NREL).

<https://www.scientificamerican.com/article/the-next-generation-of-biofuels/>  
Scientific American.

<http://needtoknow.nas.edu/energy/energy-sources/emerging-technologies/biofuels/>  
The National Academics of Sciences, Engineering, Medicine.

<https://www.epa.gov/environmental-economics/economics-biofuels>  
United States Environmental Protection Agency (EPA).