Chapter 3
Biofuels

3.1 Introduction

Today's energy system is unsustainable because of equity issues as well as environmental, economic, and geopolitical concerns that have implications far into the future. Bioenergy is one of the most important components to mitigate greenhouse gas emissions and substitute for fossil fuels (Goldemberg 2000; Dincer 2008). Renewable energy is one of the most efficient ways to achieve sustainable development.

Plants use photosynthesis to convert solar energy into chemical energy. It is stored in the form of oils, carbohydrates, proteins, etc. This plant energy can be converted to biofuels. Hence biofuels are primarily a form of solar energy. For biofuels to succeed at replacing large quantities of petroleum fuel, the feedstock availability needs to be as high as possible.

In the context of climatic changes and of soaring prices for a barrel of petroleum, biofuels are now being presented as a renewable energy alternative. Presently, research is being done on microscopic algae, or microalgae, which are particularly rich in oils and whose yield per hectare is considerably higher than that of sunflower or rapeseed.

In recent years, recovery of liquid transportation biofuels from biorenewable feedstocks has became a promising method. The biggest difference between biorenewable and petroleum feedstocks is oxygen content. Biorenewables have oxygen levels of 10 to 44% while petroleum has essentially none, making the chemical properties of biorenewables very different from those of petroleum (Demirbas 2008; Balat 2009). For example, biorenewable products are often more polar and some easily entrain water and can therefore be acidic.

There are two global transportation fuels – gasoline and diesel fuel. The main transportation fuels that can be obtained from biomass using different processes are sugar ethanol, cellulosic ethanol, grain ethanol, biodiesel, pyrolysis liquids, green diesel, green gasoline, butanol, methanol, syngas liquids, biohydrogen, algae diesel, algae jet fuel, and hydrocarbons. Renewable liquid biofuels for transportation have recently attracted considerable attention in different countries around the world be-

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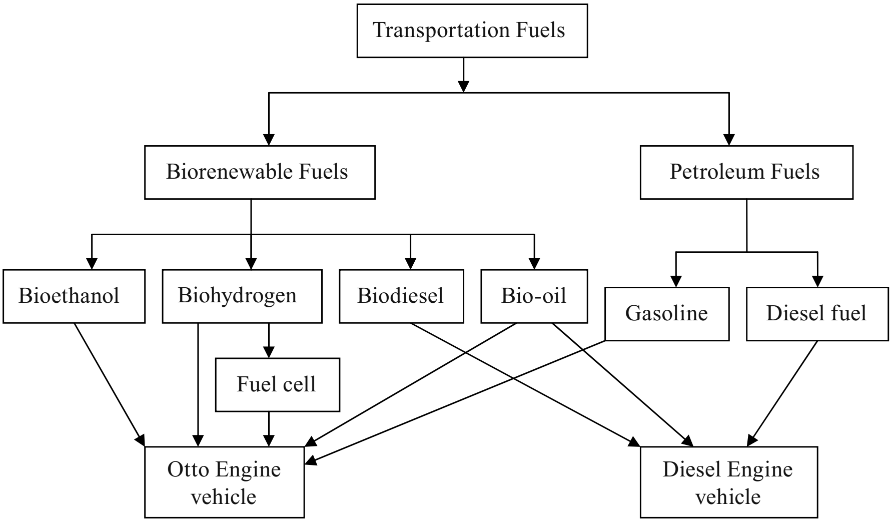

Figure 3.1 Petroleum- and biorenewable-based transportation fuels

cause of their renewability, sustainability, widespread availability, and biodegradability, as well as the benefits they bring with respect to regional development, rural manufacturing jobs, and reduction in greenhouse gas emissions (Demirbas 2008). Petroleum- and biorenewable-based transportation fuels are given in Figure 3.1.

The policy drivers for biorenewable liquid biofuels have been rural development and economic opportunities for developing countries (Keskin 2009). The European Union ranks third in biofuel production worldwide, behind Brazil and the USA. In Europe, Germany is the largest and France the second largest producer of biofuels.

The term modern biomass is generally used to describe traditional biomass use through efficient and clean combustion technologies and sustained supply of biomass resources, environmentally sound and competitive fuels, heat, and electricity using modern conversion technologies. As an energy source, biomass has two striking characteristics. First, biomass is the only renewable organic resource as well as one of the most abundant resources. Second, biomass fixes carbon dioxide in the atmosphere by photosynthesis. Direct combustion and cofiring with coal for electricity production from biomass holds great promise for the near future. Biomass thermochemical conversion technologies such as pyrolysis and gasification are certainly not the most important options at present; combustion is responsible for over 97% of the world's bioenergy production. Ethanol and fatty acid (m)ethylester (biodiesel) as well as diesel produced from biomass by Fischer–Tropsch synthesis (FTS) are modern biomass-based transportation fuels. Liquid transportation fuels can be economically produced by Biomass Integrated Gasification Fischer–Tropsch (BIG-FT) processes. Modern biomass produced in a sustainable way excludes traditional uses of biomass as fuel wood and includes electricity generation and heat production, as well as transportation fuels, from agricultural and forest residues and

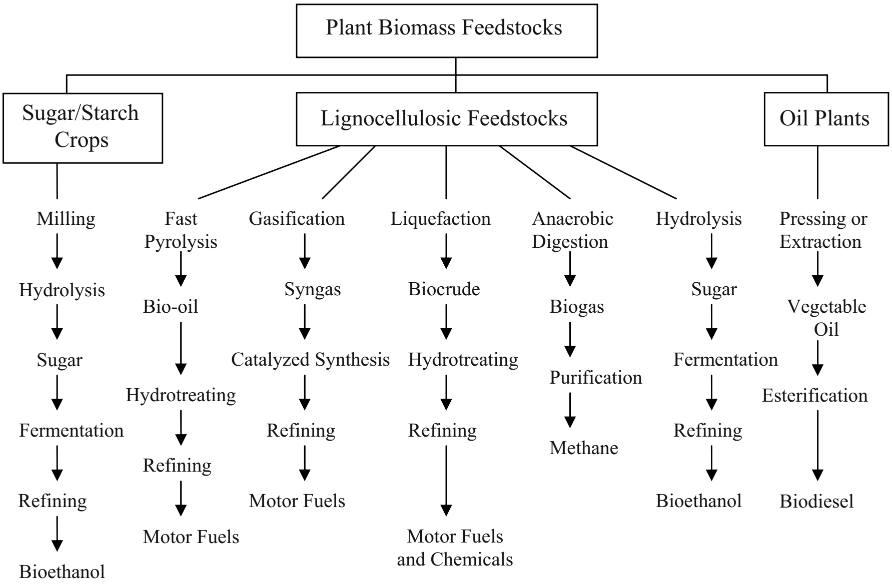

Figure 3.2 Overview of conversion processes of plant biomass feedstocks into biofuels

solid waste. On the other hand, "traditional biomass" is produced in an unsustainable way and is used as a noncommercial source – usually with very low efficiencies for cooking in many countries.

A biorefinery is an integrated plant producing multiple value-added products from a range of renewable feedstocks. This innovative approach responds to changing markets for traditional forest products as well as new products such as energy, chemicals, and materials. The range of feedstocks, processes, and potential products is large; each combination of feedstock, process, and product is characterized by its own unique combination of technical and economic opportunities, emerging technologies, and barriers. Figure 3.2 shows an overview of conversion routes of plant biomass feedstocks to biofuels.

3.2 Importance of Biofuels

Liquid biofuels will be important in the future because they replace petroleum fuels. The biggest difference between biofuels and petroleum feedstocks is oxygen content. Biofuels are nonpolluting, locally available, accessible, sustainable, and reliable fuel obtained from renewable sources. Biofuels can be classified based on their production technologies: first-generation biofuels (FGBs), second-generation biofuels (SGBs), third-generation biofuels (TGBs), and fourth-generation biofuels.

The FGBs refer to biofuels made from sugar, starch, vegetable oils, or animal fats using conventional technology. The basic feedstocks for the production of FGBs are often seeds or grains such as wheat, which yields starch that is fermented into bioethanol, or sunflower seeds, which are pressed to yield vegetable oil that can be used in biodiesel.

SGBs and TGBs are also called advanced biofuels. SGBs are made from nonfood crops, wheat straw, corn, wood, and energy crops using advanced technology. Algae fuel, also called algal oil or a TGB, is a biofuel from algae. Algae are low-input/high-yield (30 times more energy per acre than land) feedstocks to produce biofuels using more advanced technology. On the other hand, an emerging fourth-generation fuel is based on the conversion of vegetable oil and biodiesel into biogasoline using the most advanced technology.

The SGBs include renewable and green diesels. The former involves a technology that incorporates vegetable oils in the crude-oil-derived diesel production process to produce a renewable carbon-based diesel with no oxygen content and a very high cetane number, while the latter entails the production of middle distillate by means of Fischer–Tropsch (FT) catalysts, using synthesis gas produced by the gasification of biomass. FT-like catalysts (synthol process) can also produce ethanol and mixed alcohols.

There are some barriers to the development of biofuel production. They are technological, economic, supply, storage, safety, and policy barriers. Reducing these barriers is one of the driving factors in government involvement in biofuel and biofuel research and development. Production costs are uncertain and vary with the feedstock available. The production of biofuels from lignocellulosic feedstocks can be achieved through two very different processing routes: biochemical and thermochemical. There is no clear candidate for "best technology pathway" between the competing biochemical and thermochemical routes. Technical barriers for enzymatic hydrolysis include low specific activity of current commercial enzymes, high cost of enzyme production, and lack of understanding of enzyme biochemistry and mechanistic fundamentals.

The major nontechnical barriers are restrictions or prior claims on of land use (food, energy, amenity use, housing, commerce, industry, leisure or designations as areas of natural beauty, special scientific interest, etc.), as well as the environmental and ecological effects of large areas of monoculture. For example, vegetable oils are a renewable and potentially inexhaustible source of energy with energy content close to that of diesel fuel. On the other hand, extensive use of vegetable oils may cause other significant problems such as starvation in developing countries. The vegetable oil fuels were not acceptable because they were more expensive than petroleum fuels.

There are few technical barriers to building biomass-fired facilities at any scale, from domestic to around 50 MW, above which considerations of the availability and cost of providing fuel become significant. In general, however, the capacity and generating efficiency of biomass plants are considerably less than those of modern natural-gas-fired turbine systems. The main nontechnical limitations to investment in larger systems are economic, or in some countries reflect planning conditions and public opinion, where a clear distinction may not be made between modern effective biomass energy plant and older polluting incinerator designs.

The most important biorenewable liquid fuels are bioethanol and biodiesel. Bioethanol is a petrol additive/substitute. Biodiesel is a diesel alternative. Biorenewable fuels are safely and easily biodegradable and so are particularly attractive from an environmental perspective. Biodiesel, a biofuel that can directly replace petroleum-derived diesel without engine modifications, has gained a lot of attention due to its environmental and technological advantages.

Production of motor fuel alternatives from biomass materials is an important application area of biotechnological methods. Table 3.1 shows the potential and available motor fuels. Biorenewable sourced motor fuel alternatives are:

1. Gasoline-alcohol mixtures
2. Alcohol substituting for gasoline
3. Gasoline-vegetable oil mixtures
4. Diesel fuel-vegetable oil mixtures
5. Vegetable oil substituting for diesel fuel.

Table 3.1 Potential and available motor fuels

Fuel type	Available motor fuel
Traditional fuels	Diesel and gasoline
Oxygenated fuels	Ethanol 10% (E10), methanol, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary butyl alcohol (TBA), and tertiary amyl methyl ether (TAME)
Alternative fuels	Liquefied petroleum gases (LPG), ethanol, 85% (E85), ethanol, 95% (E95), methanol, 85% (M85), methanol, neat (M100), compressed natural gas (CNG), liquefied natural gas (LNG), biodiesel (BD), hydrogen, and electricity

In gasoline-alcohol mixtures ethanol and methanol are generally used, and in gasoline engine mixtures containing 20% or less alcohol by volume can be used without altering the construction of the engine. Because of the hygroscopic properties of ethanol and methanol, gasoline-alcohol mixtures are in fact ternary mixtures composed of gasoline-alcohol and water. In the evaluation of such mixtures as motor fuel, there is the phase separation problem, which depends on several factors. It is evident in the literature that numerous attempts have been made to overcome this problem (Mislavskaya *et al.* 1982; Osten and Sell 1983).

In gasoline-methanol mixtures containing 0.1% water i-propanol is added to the environment (medium) in order to decrease the phase separation temperature, and fuels containing different ratios of gasoline-methanol-i-propanol and water are composed that have proven to be stable in certain climatic conditions. An increase in the aromatic character of the gasoline, a decrease in the water content of the mixture, and an increase in the amount of the additive used results in a decrease in the phase separation temperature of the mixture. In gasoline-ethanol mixtures the additive used is also i-propanol. In gasoline-alcohol mixtures various additives like i-propanol, n-butanol, i-butanol, and i-amylalcohol are used.

3.3 Bioethanol

Ethanol (CH_5OH or EtOH) is a liquid biofuel that can be produced from several different biomass feedstocks and conversion technologies. Bioethanol is an attractive alternative fuel because it is a renewable bio-based resource and is oxygenated, thereby providing the potential to reduce particulate emissions in compression-ignition engines.

Ethanol can be made synthetically from petroleum or by microbial conversion of biomass materials through fermentation. In 1995, about 93% of the ethanol in the world was produced by the fermentation method and about 7% by the synthetic method. The fermentation method generally uses three steps: (1) the formation of a solution of fermentable sugars, (2) the fermentation of these sugars to ethanol, and (3) the separation and purification of the ethanol, usually by distillation.

Ethanol has a higher octane number, broader flammability limits, higher flame speeds, and higher heats of vaporization than gasoline. These properties allow for a higher compression ratio, shorter burn time and leaner burn engine, which lead to theoretical efficiency advantages over gasoline in an internal combustion engine. The disadvantages of ethanol include its lower energy density than gasoline (but about 35% higher than that of methanol), its corrosiveness, low flame luminosity, lower vapor pressure (making cold starts difficult), miscibility with water, and toxicity to ecosystems.

Because ethanol-based fuel contains oxygen (35% oxygen content), it can effectively reduce particulate matter emission in a diesel engine. Ethanol is appropriate for mixed fuel in gasoline engines because of its high octane number, and its low cetane number and high heat of vaporization impede self-ignition in diesel engines. The most popular blend for light-duty vehicles is known as E85, which contains 85% ethanol and 15% gasoline. In Brazil, bioethanol for fuel is derived from sugar cane and is used pure or blended with gasoline in a mixture called gasohol (24% bioethanol, 76% gasoline). In several states of the USA, a small amount of bioethanol (10% by volume) is added to gasoline; this is known as gasohol or E10. Blends having higher concentrations of bioethanol in gasoline are also used, e.g., in flexible-fuel vehicles (FFVs) that can operate on blends of up to 85% bioethanol – E85. Some countries have established biofuel programs on bioethanol-gasoline blends such as the USA (E10 and for flexible fuel vehicle [FFV] E85), Canada (E10 and for FFV E85), Sweden (E5 and for FFV E85), India (E5), Australia (E10), Thailand (E10), China (E10), Colombia (E10), Peru (E10), Paraguay (E7), and Brazil (E20, E25, and FFV any blend) (Kadiman 2005).

As biomass hydrolysis and sugar fermentation technologies approach commercial viability, advancements in product recovery technologies will be required. For cases in which fermentation products are more volatile than water, recovery by distillation is often the technology of choice. Distillation technologies that will allow the economical recovery of dilute volatile products from streams containing a variety of impurities have been developed and commercially demonstrated. A distillation system separates the bioethanol from water in the liquid mixture.

The first step is to recover the bioethanol in a distillation or beer column, where most of the water remains with the solid parts. The product (37% bioethanol) is then concentrated in a rectifying column to a concentration just below the azeotrope (95%). The remaining bottoms product is fed to the stripping column to remove additional water, with the bioethanol distillate from stripping being recombined with the feed to the rectifier. The recovery of bioethanol in the distillation columns in the plant is fixed at 99.6% to reduce bioethanol losses.

Bioethanol can be used directly in cars designed to run on pure ethanol or blended with gasoline to make "gasohol." Anhydrous ethanol is required for blending with gasoline. No engine modification is typically needed to use the blend. Ethanol can be used as an octane-boosting, pollution-reducing additive in unleaded gasoline.

Figure 3.3 shows the world production by country of ethanol between 1980 and 2008 (RFA 2009). Between 1991 and 2001, world ethanol production rose from around 16 billion liters a year to 18.5 billion liters. From 2001 to 2007, production is expected to have tripled, to almost 60 billion liters a year. Brazil was the world's leading ethanol producer until 2005, when US production roughly equaled Brazil's. The USA became the world's leading ethanol producer in 2006. China holds a distant but important third place in world rankings, followed by India, France, Germany, and Spain. Ethanol production by country in 2007 and 2008 is given in Table 3.2.

The continued increases in the price of crude oil in 2005 and 2006 resulted in a reversal of the traditional relationship between the price of biomass energy and that of crude oil, something not seen since the 1930s. As a consequence of the high prices of traded crude oil, many countries advanced their biofuel goals, and, in the case of Brazil and the USA, large production gains occurred.

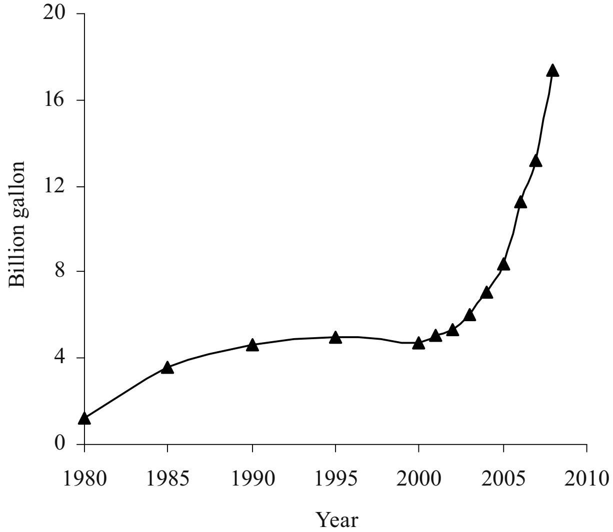

Figure 3.3 World production of ethanol, 1980–2008

Table 3.2 Ethanol production by country, 2007–2008 (millions of gallons, 1 gallon = 3.78 liters)

Country	2007	2008
USA	6,500	9,001
Brazil	5,020	6,473
European Union	571	734
China	487	502
Canada	212	238
Others	118	130
Thailand	80	90
Colombia	75	80
India	53	66
Australia	26	27
Turkey	16	18
Total	13,158	17,359

3.4 Biodiesel

Starting in the 1980s important progress has been made on evaluating some low-grade oils, oil production wastes, and residues as motor fuel (Pryor *et al.* 1983). But direct usage of vegetable oils causes a number of problems concerning the engine because of their high viscosity and the excessive carbonaceous deposits left in the cylinders and on the injector nozzles. Therefore, chemical conversion of vegetable oils was suggested. In order to lower the viscosities and flash points of vegetable oils, the transesterification method was applied, and it was reported that the alcoholysis products of soybean, sunflower, rapeseed, and used frying oils were proposed as diesel fuel alternatives.

The deregulation of domestic crude oil prices and the formation of OPEC have been largely responsible for high fuel prices. The farmer is highly dependent on diesel fuel for crop production. Alternative fuels such as vegetable oils could help ease the petroleum dependence of farmers. Recently, the demand for crude oil has decreased because of conservation practices but ultimately a liquid fuel resource problem exists (Pryor *et al.* 1983).

Vegetable oils with carbon chain lengths of between 16 and 22 carbon atoms are generally in the form of triacyl glycerides (TAG), which upon transesterification with methanol produce fatty acid methyl ester (FAME) as the precursor to biodiesel and glycerol as a byproduct. Vegetable oil (m)ethyl esters, commonly referred to as "biodiesel," are prominent candidates as alternative diesel fuels. The name biodiesel has been given to transesterified vegetable oil to describe its use as a diesel fuel. After FAME purification and testing for compliance with either EN 14214 or ASTM D6751 standards the product can be sold as biodiesel and used as blends – typically B5 (5% biodiesel) to B20, depending on the engine warranties.

Biodiesel is a mixture of methyl esters of long-chain fatty acids like lauric, palmitic, steric, oleic, etc. Typical examples are rapeseed oil, canola oil, soybean oil, sunflower oil, and palm oil and its derivatives from vegetable sources. Beef and sheep tallow and poultry oil from animal sources and cooking oil are also the sources of raw materials. The chemistry of conversion to biodiesel is essentially the same. Oil or fat reacts with methanol or ethanol in the presence of catalyst sodium hydroxide or potassium hydroxide to form biodiesel, (m)ethylesters, and glycerin. Biodiesel is technically competitive with or offers technical advantages over conventional petroleum diesel fuel. Biodiesel esters are characterized for their physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion, and volatility. Biodiesel fuels produce slightly lower power and torque, and higher fuel consumption than No. 2 diesel fuel. Biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content, and biodegradability. Some technical properties of biodiesels are shown in Table 3.3.

Table 3.3 Some technical properties of biodiesels

Common name	Bio-diesel or biodiesel
Common chemical name	Fatty acid (m)ethyl ester
Chemical formula range	C_{14}–C_{24} methyl esters or $C_{15-25}\,H_{28-48}\,O_2$
Kinematic viscosity range (mm^2/s at 313 K)	3.3–5.2
Density range (kg/m^3 at 288 K)	860–894
Boiling point range (K)	> 475
Flash point range (K)	428–453
Distillation range (K)	470–600
Vapor pressure (mm Hg, at 295 K)	< 5
Solubility in water	Insoluble in water
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy odor
Biodegradability	More biodegradable than petroleum diesel
Reactivity	Stable, but avoid strong oxidizing agents

Biodiesel is a synthetic diesel-like fuel produced from vegetable oils, animal fats, or waste cooking oil. It can be used directly as fuel, which requires some engine modifications, or blended with petroleum diesel and used in diesel engines with few or no modifications. At present, biodiesel accounts for less than 0.2% of the diesel consumed for transport (UN 2006). Biodiesel has become more attractive recently because of its environmental benefits. The cost of biodiesel, however, is the main obstacle to commercialization of the product. With cooking oils used as raw material, the viability of a continuous transesterification process and recovery of high-quality glycerol as a biodiesel byproduct are the primary methods to be considered for lowering the cost of biodiesel (Zhang *et al.* 2003). Table 3.4 shows the biodiesel production (2007) and production capacity (2008) of EU countries (EBB 2009). Figure 3.4 shows the world production of biodiesel between 1980 and 2008 (Demirbas 2008).

Between 1991 and 2001, world biodiesel production grew steadily to approx. 1 billion liters. Most of this production was in OECD Europe and was based on virgin vegetable oils. Small plants using waste cooking oils started to be built in

Table 3.4 Biodiesel production (2007) and production capacity (2008) of EU countries (millions of tons)

Country	2007 (production)	2008 (production capacity)
Germany	2,890	5,302
France	872	1,980
Italy	363	1,566
Spain	168	1,267
UK	150	726
Belgium	166	665
The Netherlands	85	571
Greece	100	565
Austria	267	485
Poland	80	450
Portugal	175	406
Bulgaria	9	215
Sweden	63	212
Slovakia	46	206
Czech Republic	61	203
Hungary	7	186
Finland	39	170
Lithuania	26	147
Denmark	85	140
Estonia	0	135
Latvia	9	130
Romania	36	111
Slovenia	11	67
Ireland	3	80
Malta	1	8
Cyprus	1	6
Luxembourg	0	0
Total	5,713	16,000

other OECD countries by the late 1990s, but the industry outside Europe remained insignificant until around 2004. Since then, governments around the world have instituted various policies to encourage development of the industry, and new capacity in North America, Southeast Asia, and Brazil has begun to come onstream at a brisk rate. As a result, between 2001 and 2007, biodiesel production will have grown almost tenfold, to 9 billion L (Demirbas 2008).

The advantages of biodiesel as diesel fuel are its portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content (Knothe *et al.* 2006; Demirbas 2008), higher cetane number, and higher biodegradability (Zhang *et al.* 2003). The main advantages of biodiesel given in the literature include its domestic origin, reducing the dependency on imported petroleum, biodegradability, high flash point, and inherent lubricity in the neat form (Knothe *et al.* 2005). The disadvantages of biodiesel are its higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide (NO_x) emissions, lower engine

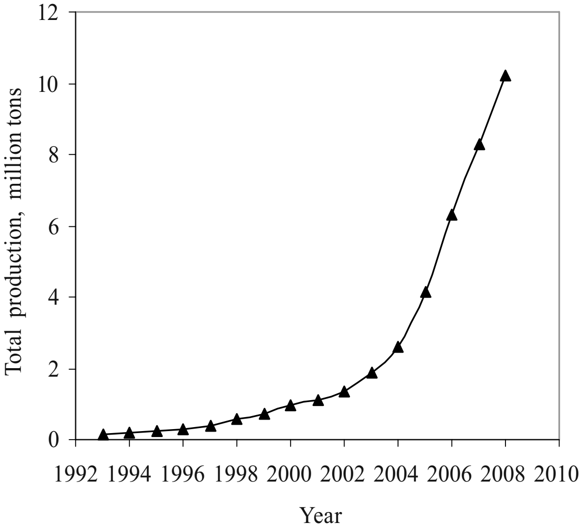

Figure 3.4 World production of biodiesel, 1980–2008

speed and power, injector coking, engine compatibility, high price, and higher engine wear.

The cost of feedstock is a major economic factor in the viability of biodiesel production. Using an estimated process cost (Note: all costs are given in US$), exclusive of feedstock cost, of $ 0.158/L ($ 0.60/gal) for biodiesel production, and estimating a feedstock cost of $ 0.539/L ($ 2.04/gal) for refined soy oil, an overall cost of $ 0.70/L ($ 2.64/gal) for the production of soy-based biodiesel was estimated (Haas *et al.* 2006). Biodiesel from animal fat is currently the cheapest option ($ 0.4 to $ 0.5/L), while traditional transesterification of vegetable oil is at present around $ 0.6 to $ 0.8/L (IEA 2007). Rough projections of the cost of biodiesel from vegetable oil and waste grease are, respectively, $ 0.54 to $ 0.62/L and $ 0.34 to $ 0.42/L. With pretax diesel priced at $ 0.18/L in the USA and $ 0.20 to 0.24/L in some European countries, biodiesel is thus currently not economically feasible, and more research and technological development will be needed (Bender 1999).

3.5 Bio-oil

The term bio-oil is used mainly to refer to liquid fuels from biorenewable feedstocks. Biomass is heated in the absence of oxygen, or partially combusted in a limited oxygen supply, to produce an oil-like liquid, a hydrocarbon-rich gas mixture and a carbon-rich solid residue. Pyrolysis dates back to at least ancient Egyptian times, when tar for caulking boats and certain embalming agents was made by pyrolysis. In the 1980s, researchers found that the pyrolysis liquid yield could be increased using fast pyrolysis where a biomass feedstock is heated at a rapid rate and the vapors produced are also condensed rapidly (Mohan *et al.* 2006).

In wood-derived pyrolysis oil, specific oxygenated compounds are present in relatively large amounts. A current comprehensive review focuses on the recent developments in wood/biomass pyrolysis and reports the characteristics of the resulting bio-oils, which are the main products of fast wood pyrolysis (Mohan *et al.* 2006). Sufficient hydrogen added to the synthesis gas to convert all of the biomass carbon into methanol carbon would more than double the methanol produced from the same biomass base.

The kinematic viscosity of pyrolysis oil varies from as low as 11 cSt to as high as 115 mm^2/s (measured at 313 K) depending on the nature of the feedstock, the temperature of the pyrolysis process, the thermal degradation degree and catalytic cracking, the water content of the pyrolysis oil, the amount of light ends that have collected, and the pyrolysis process used. Pyrolysis oils have water contents of typically 15 to 30 wt% of the oil mass, which cannot be removed by conventional methods like distillation. Phase separation may partially occur above certain water content levels. The water content of pyrolysis oils contributes to their low energy density, lowers the flame temperature of the oils, leads to ignition difficulties, and, when preheating the oil, can lead to premature evaporation of the oil and resultant injection difficulties. The higher heating value (HHV) of pyrolysis oils is below 26 MJ/kg (compared to 42 to 45 MJ/kg for conventional petroleum fuel oils). In contrast to petroleum oils, which are nonpolar and in which water is insoluble, biomass oils are highly polar and can readily absorb over 35% water (Demirbas 2007). Table 3.5 shows the fuel properties of diesel, biodiesel, and biomass pyrolysis oil.

The bio-oil from wood is typically a liquid, almost black through dark red brown. The density of the liquid is about 1,200 kg/m^3, which is higher than that of fuel oil

Table 3.5 Fuel properties of diesel, biodiesel, and biomass pyrolysis oil

Property	Test method	ASTM D975 (Diesel)	ASTM D6751 (biodiesel, B100)	Pyrolysis oil (bio-oil)
Flash point	D 93	325 K min	403 K	–
Water and sediment	D 2709	0.05 max %vol	0.05 max %vol	0.01–0.04
Kinematic viscosity (at 313 K)	D 445	1.3–4.1 mm^2/s	1.9–6.0 mm^2/s	25–1,000
Sulfated ash	D 874	–	0.02 max %wt	–
Ash	D 482	0.01 max %wt	–	0.05–0.01 %wt
Sulfur	D 5453	0.05 max %wt	–	–
Sulfur	D 2622/129	–	0.05 max %wt	0.001–0.02 %wt
Copper strip corrosion	D 130	No 3 max	No 3 max	–
Cetane number	D 613	40 min	47 min	–
Aromaticity	D 1319	–	35 max %vol	–
Carbon residue	D 4530	–	0.05 max %mass	0.001–0.02 %wt
Carbon residue	D 524	0.35 max %mass	–	–
Distillation temp (90% volume recycle)	D 1160	555 K min −611 K max	–	–

and significantly higher than that of the original biomass. Bio-oils typically have water contents of 14 to 33%wt, which cannot be removed by conventional methods like distillation. Phase separation may occur above certain water content levels. The higher heating value (HHV) is below 27 MJ/kg (compared to 43 to 46 MJ/kg for conventional fuel oils).

The bio-oil formed at 725 K contains high concentrations of compounds such as acetic acid, 1-hydroxy-2-butanone, 1-hydroxy-2-propanone, methanol, 2,6-dimethoxyphenol, 4-methyl-2,6-dimetoxyphenol, 2-cyclopenten-1-one, etc. A significant characteristic of bio-oils is the high percentage of alkylated compounds, especially methyl derivatives. As the temperature increases, some of these compounds are transformed via hydrolysis. The formation of unsaturated compounds from biomass materials generally involves a variety of reaction pathways such as dehydration, cyclization, Diels–Alder cycloaddition reactions, and ring rearrangement. For example, 2,5-hexandione can undergo cyclization under hydrothermal conditions to produce 3-methyl-2-cyclopenten-1-one with very high selectivity of up to 81% (An *et al.* 1997).

3.6 Biogas

Biogas can be obtained from several sources. There are a number of processes for converting biomass into gaseous fuels such as methane or hydrogen. One uses plant and animal wastes in a fermentation process leading to biogas from which the desired fuels can be isolated. This technology is established and in widespread use for waste treatment. Anaerobic digestion of biowastes occurs in the absence of air, the resulting gas, called biogas, is a mixture consisting mainly of methane and carbon dioxide. Biogas is a valuable fuel that is produced in digesters filled with feedstock like dung or sewage. The digestion is allowed to continue for a period of 10 d to a few weeks. A second process uses algae and bacteria that have been genetically modified to produce hydrogen directly instead of the conventional biological energy carriers. Finally, high-temperature gasification supplies a crude gas, which may be transformed into hydrogen by a second reaction step. This process may offer the highest overall efficiency.

Anaerobic digestion (AD) is a bacterial fermentation process that is sometimes employed in wastewater treatment for sludge degradation and stabilization. This is also the principal process occurring in the decomposition of food wastes and other biomass in landfills. The AD operates without free oxygen and results in biogas containing mostly CH_4 and CO_2 but frequently carrying other substances such as moisture, hydrogen sulfide (H_2S), and particulate matter that are generally removed prior to use of the biogas. The AD is a biochemical process for converting biogenic solid waste into a stable, humuslike product. Aerobic conversion uses air or oxygen to support the metabolism of the aerobic microorganisms degrading the substrate. Aerobic conversion includes composting and activated sludge wastewater treatment processes. Composting produces useful materials, such as mulch, soil additives and amendments, and fertilizers.

AD is known to occur over a wide temperature range from 283 to 344 K. It requires attention to the nutritional needs of the facultative and methanogenic bacteria degrading the waste substrates as well as maintenance of reasonable temperatures for those bacteria. The carbon/nitrogen (C/N) ratio of the feedstock is especially important. Biogas can be used after appropriate gas cleanup as a fuel for engines, gas turbines, fuel cells, boilers, industrial heaters, other processes, and the manufacture of chemicals. AD is also being explored as a route for direct conversion into hydrogen.

Cellulose and hemicelluloses can be hydrolyzed into simple sugars and amino acids that are consumed and transformed by fermentive bacteria. Lignin is refractory to hydrolysis and generally exits the process undigested. In fact, lignin may be the most recalcitrant naturally produced organic chemical. Lignin polymers are cross-linked carbohydrate structures with molecular weights on the order of 10,000 atomic mass units. As such, lignin can bind with or encapsulate cellulose, making that cellulose unavailable to hydrolysis and digestion. Lignin degradation (or delignification of lignocellulosics) in nature is due principally to aerobic filamentous fungi that decompose the lignin in order to gain access to the cellulose and hemicelluloses.

For anaerobic systems, methane gas is an important product. Depending on the type and nature of the biological components, different yields can be obtained for different biodegradable wastes. For pure cellulose, for example, the biogas product is 50% methane and 50% carbon dioxide. Mixed waste feedstocks yield biogas with methane concentrations of 40 to 60% (by volume). Fats and oils can yield biogas with 70% methane content.

Anaerobic digestion functions over a wide temperature range from the so-called psychrophilic temperature near 283 K to extreme thermophilic temperatures above 344 K. The temperature of the reaction has a very strong influence on the anaerobic activity, but there are two optimal temperature ranges in which microbial activity and biogas production rate are highest, the so-called mesophilic and thermophilic ranges. The mesophilic regime is associated with temperatures of about 308 K, a thermophilic regime of about 328 K. Operation at thermophilic temperature allows for shorter retention time and a higher biogas production rate; however, maintaining the high temperature generally requires an outside heat source because anaerobic bacteria do not generate sufficient heat. Aerobic composting can achieve relatively high temperatures (up to 344 K) without heat addition because reaction rates for aerobic systems are much higher than those for anaerobic systems. If heat is not conducted away from the hot center of a compost pile, then this could cause thermochemical reactions that might lead to spontaneous combustion if sufficient oxygen reaches the hot areas. Managed compost operations use aeration to provide oxygen to the bacteria but also to transport heat out of the pile. The molecular structure of the biodegradable portion of the waste that contains proteins and carbohydrates is first broken down through hydrolysis. The lipids are converted to volatile fatty acids and amino acids. Carbohydrates and proteins are hydrolyzed to sugars and amino acids. In acetogenesis, acid forming bacteria use these byproducts to generate intermediary products such as propionate and butyrate. Further microbial action results in the degradation of these intermediary products into hydrogen and acetate. Methanogenic bacteria consume the hydrogen and acetate to produce methane and carbon dioxide.

After the first 6 d of digestion, methane production from manure increases exponentially, after 16 d it reaches a plateau value, and at the end of day 20, the digestion reaches the stationary phase. For wheat straw and mixtures of manure and straw the rates of digestion are lower than that of manure.

The maximum daily biogas productions are between 4 and 6 d. During a 30-d digestion period, approx. 80 to 85% of the biogas is produced in the first 15 to 18 d. This implies that the digester retention time can be designed to 15 to 18 d instead of 30 d. For the first 3 d, methane yield is almost 0% and carbon dioxide generation is almost 100%. In this period, digestion occurs as fermentation to carbon dioxide. The yields of methane and carbon dioxide gases are 50/50 at day 11. At the end of day 20, digestion reaches the stationary phase. The methane content of the biogas is in the range of 73 to 79% for the runs, the remainder being principally carbon dioxide. During digestion, the volatile fatty acid concentration is lower and the pH higher. The pH of the slurry with manure increases from 6.4 initially to 6.9 to 7.0 at the maximum methane production rate. The pH of the slurry with wheat straw is around 7.0 to 7.1 at the maximum methane production rate.

The first methane digester plant was built at a leper colony in Bombay, India, in 1859 (Meynell 1976). Most of the biogas plants utilize animal dung or sewage. A schematic of biogas plant utilizing cow dung is illustrated in Figure 3.5 (Balat 2008). AD is a commercially proven technology and is widely used for treating high-moisture-content organic wastes including +80 to 90% moisture. Biogas can be used directly in spark-ignition gas engines (SIGEs) and gas turbines. Used as a fuel in SIGEs to produce electricity only, the overall conversion efficiency from biomass to electricity is about 10 to 16% (Demirbas 2006).

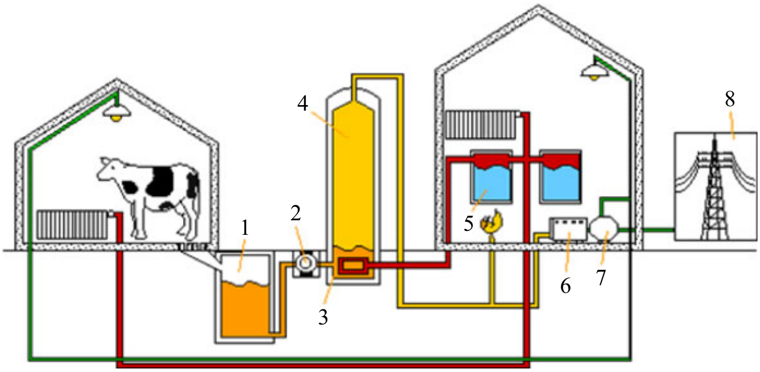

Figure 3.5 Biogas plant utilizing cow dung: 1. compost storage, 2. pump, 3. internal heater, 4. digester, 5. combustor, 6–8. power generator

3.7 Fischer–Tropsh Liquids from Biorenewable Feedstocks

Gasification followed by FTS is currently the most promising method for upgrading low-value coal and biomass to high-value liquid fuels and chemicals. The total biomass produced each year as waste material from agriculture and forest operations could be converted into roughly 40 billion gal/year of liquid fuels (roughly 25% of the current US gasoline usage).

Tijmensen *et al.* (2002) review the technical feasibility and economics of BIG-FT process and also point out the key R&D issues involved in the commercialization of this process. Boerrigter and den Uil (2002) give a similar review identifying a potential BIG-FT process configuration. The FTS for the production of liquid hydrocarbons from coal-based synthesis gas has been the subject of renewed interest for conversion of coal and natural gas to liquid fuels (Jin and Datye 2000).

Gasification is a complex thermochemical process that consists of a number of elementary chemical reactions, beginning with the partial oxidation of a biomass fuel with a gasifying agent, usually air, oxygen, or steam. The chemical reactions involved in gasification include many reactants and many possible reaction paths. The yield from the process is a product gas from thermal decomposition composed of CO, CO_2, H_2O, H_2, CH_4, other gaseous hydrocarbons, tars, char, inorganic constituents, and ash. The gas composition of product from biomass gasification depends heavily on the gasification process, the gasifying agent, and the feedstock composition. A generalized reaction describing biomass gasification is as follows:

$$\text{Biomass} + O_2 \rightarrow CO, CO_2, H_2O, H_2, CH_4 + \text{other (CHs)} + \text{tar} + \text{char} + \text{ash} \quad (3.1)$$

The relative amount of CO, CO_2, H_2O, H_2, and (CHs) depends on the stoichiometry of the gasification process. If air is used as the gasifying agent, then roughly half of the product gas is N_2.

Most biomass gasification systems utilize air or oxygen in partial oxidation or combustion processes. These processes suffer from low thermal efficiencies and low Btu gas because of the energy required to evaporate the moisture typically inherent in the biomass and the oxidation of a portion of the feedstock to produce this energy.

Syngas (a mixture of carbon monoxide and hydrogen) produced by gasification of fossil fuels or biomass can be converted into a large number of organic compounds that are useful as chemical feedstocks, fuels, and solvents. Many conversion technologies were developed for coal gasification but process economics have resulted in a shift to natural-gas-derived syngas. These conversion technologies successively apply similarly to biomass-derived biosyngas. Franz Fischer and Hans Tropsch first studied the conversion of syngas into larger, useful organic compounds in 1923 (Spath and Mann 2000).

The reasons for using biofuels are manifold and include energy security, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. Catalytic conversion will be a primary tool for industry to produce valuable fuels, chemicals, and materials from biomass platform chemicals. Catalytic conversion of biomass is best developed for synthesis gas, or syngas. Economic considerations dictate that the current production of liquid fuels from syngas translates into the use of natural gas as the hydrocarbon source. Biomass is the only renewable that can meet our demand for carbon-based liquid fuels and chemicals. Biofuels as well as green motor fuels produced from biomass by FTS are the most modern biomass-based transportation fuels. Green motor fuels are the renewable replacement for petroleum-based diesel. Biomass energy conversion facilities are important for obtaining bio-oil by pyrolysis. The main aim of FTS is the synthesis of long-chain hydrocarbons from a CO-H_2 gas mixture. The products from FTS are mainly aliphatic straight-chain hydrocarbons (C_xH_y). Besides the C_xH_y, branched hydrocarbons, unsaturated hydrocarbons, and primary alcohols are also formed in minor quantities. The FTS process is a process capable of producing liquid hydrocarbon fuels from biosyngas. The large hydrocarbons can be hydrocracked to form mainly diesel of excellent quality. The process for producing liquid fuels from biomass, which integrates biomass gasification with FTS, converts a renewable feedstock into a clean fuel.

FTS is a process for producing mainly straight-chain hydrocarbons from a syngas rich in CO and H_2. Catalysts are usually employed. Typical operating conditions for FTS are temperatures of 475 to 625 K and very high pressure depending on the desired products. The product range includes light hydrocarbons such as methane (CH_4) and ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), gasoline (C_5–C_{12}), diesel (C_{13}–C_{22}), and light waxes (C_{23}–C_{33}). The distribution of the products depends on the catalyst and the process conditions (temperature, pressure, and residence time). The syngas must have very low tar and particulate matter content.

The literature dealing with the actual conversion of biosyngas to fuels using FTS is smaller. Jun *et al.* (2004) report experimental results of FTS carried out using a model biosyngas. In his review on biofuels, Demirbas (2007) considers FTS using biosyngas as an emerging alternative.

FTS was established in 1923 by German scientists Franz Fischer and Hans Tropsch. It is described by the following set of equations (Schulz 1999):

$$n\mathrm{CO} + (n + m/2)\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_m + n\mathrm{H_2O} \tag{3.2}$$

where n is the average length of the hydrocarbon chain and m is the number of hydrogen atoms per carbon. All reactions are exothermic and the product is a mixture of different hydrocarbons where paraffin and olefins are the main constituents.

In FTS one mole of CO reacts with two moles of H_2 in the presence of a cobalt (Co)-based catalyst to yield a hydrocarbon chain extension (–CH_2–). The reaction of synthesis is exothermic ($\Delta H = -165$ kJ/mol):

$$\mathrm{CO} + 2\mathrm{H_2} \rightarrow \text{–}\mathrm{CH_2}\text{–} + \mathrm{H_2O} \qquad \Delta\mathrm{H} = -165\,\mathrm{kJ/mol} \tag{3.3}$$

The –CH_2– is a building block for longer hydrocarbons. A main characteristic regarding the performance of FTS is the liquid selectivity of the process (Stelmachowski and Nowicki 2003). When iron (Fe)-based catalysts are used in WGS reaction activity, the water produced in Reaction 3.2 can react with CO to form additional H_2. The reaction of synthesis is exothermic ($\Delta H = -204\,\text{kJ/mol}$). In this case a minimal H_2/CO ratio of 0.7 is required:

$$2CO + H_2 \rightarrow -CH_2- + CO_2 \qquad \Delta H = -204\,\text{kJ/mol} \tag{3.4}$$

The kind and quantity of liquid product obtained in FTS is determined by the reaction temperature, pressure and residence time, type of reactor, and catalyst used. Fe catalysts have a higher tolerance for sulfur, are cheaper, and produce more olefin products and alcohols. However, the lifetime of Fe catalysts is short and in commercial installations generally limited to 8 weeks (Davis 2002). Bulk Fe catalysts are the catalysts of choice for converting low H_2/CO ratio syngas produced by gasification of biomass or coal to fuels via FTS. These relatively low-cost catalysts have low methane selectivity and high WGS activity. However, development of a bulk Fe FTS catalyst that combines high FT activity, low methane selectivity, high attrition resistance, and long-term stability is still elusive and presents a widely recognized barrier to the commercial deployment of FTS for biomass conversion. The critical property determining the activity and deactivation of Fe catalysts for FTS appears not to be Fe in the metallic state but the carburized Fe surface.

The design of a biomass gasifier integrated with an FTS reactor must be aimed at achieving a high yield of liquid hydrocarbons. For the gasifier, it is important to avoid methane formation as much as possible and convert all carbon in the biomass to mainly carbon monoxide and carbon dioxide (Prins *et al.* 2004). Gas cleaning is an important process before FTS and is even more important for the integration of a biomass gasifier and a catalytic reactor. To avoid the poisoning of the FTS catalyst, tar, hydrogen sulfide, carbonyl sulfide, ammonia, hydrogen cyanide, alkali, and dust particles must be removed thoroughly (Stelmachowski and Nowicki 2003).

FTS has been widely investigated for more than 70 years, and Fe and Co are typical catalysts. Co-based catalysts are preferred because their productivity is better than that of Fe catalysts thanks to their high activity, selectivity for linear hydrocarbons, and low activity for the competing WGS reaction.

There has been increasing interest in the effect of water on Co FTS catalysts in recent years. Water is produced in large amounts with Co catalysts since one water molecule is produced for each C atom added to a growing hydrocarbon chain and due to the low WGS activity of Co. The presence of water during FTS may affect the synthesis rate reversibly as reported for titania-supported catalysts and the deactivation rate as reported for alumina-supported catalysts; water also has a significant effect on the selectivity for Co catalysts on different supports. The effect on the rate and on deactivation appears to depend on the catalyst system studied, while the main trends in the effect on selectivity appear to be more consistent for different supported Co systems. There are, however, also some differences in the selectivity effects observed. The present study deals mainly with the effect of water on the selectivity of alumina-supported Co catalysts, but some data on the activity change will also be reported. The results will be compared with those for other supported Co systems reported in the literature.

The activity and selectivity of supported Co FTS catalysts depends on both the number of Co surface atoms and on their density within support particles, as well as on transport limitations that restrict access to these sites. Catalyst preparation variables available to modify these properties include Co precursor type and loading level, support composition and structure, pretreatment procedures, and the presence of promoters or additives. Secondary reactions can strongly influence product selectivity. For example, the presence of acid sites can lead to the useful formation of branched paraffins directly during the FTS step. However, product water not only oxidizes Co sites, making them inactive for additional turnovers, but it can inhibit secondary isomerization reactions on any acid sites intentionally placed in FTS reactors.

Fe catalysts used commercially in FTS for the past five decades (Dry 2004) have several advantages: (1) lower cost relative to Co and ruthenium catalysts, (2) high WGS activity allowing utilization of syngas feeds of relatively low hydrogen content such as those produced by gasification of coal and biomass, (3) relatively high activity for the production of liquid and waxy hydrocarbons readily refined to gasoline and diesel fuels, and (4) high selectivity for olefinic C_2–C_6 hydrocarbons used as chemical feedstocks. The typical catalyst used in fixed-bed reactors is an unsupported Fe/Cu/K catalyst prepared by precipitation. While having the aforementioned advantages, this catalyst (1) deactivates irreversibly over a period of months to a few years by sintering, oxidation, formation of inactive surface carbons, and transformation of active carbide phases to inactive carbide phases and (2) undergoes attrition at unacceptably high rates in the otherwise highly efficient, economical slurry bubble-column reactor.

It is well known that the addition of alkali to iron causes an increase in both the 1-alkene selectivity and the average carbon number of produced hydrocarbons. While the promoter effects on iron have been thoroughly studied, few and, at first glance, contradictory results are available for Co catalysts. In order to complete the experimental data, the carbon number distributions are analyzed for products obtained in a fixed-bed reactor under steady-state conditions. Precipitated Fe and Co catalysts with and without K_2CO_3 were used.

Activated carbon (AC) is a high-surface-area support with the very unique property that its textural and surface chemical properties can be changed by an easy treatment like oxidation, and these changes affect the properties of the resultant catalysts prepared with AC.

Fe catalysts have a higher tolerance for sulfur, are cheaper, and produce more olefin products and alcohols. However, the lifetime of Fe catalysts is short and in commercial installations generally limited to 8 weeks. Co catalysts have the advantage of a higher conversion rate and a longer life (over 5 years). Co catalysts are in general more reactive for hydrogenation and therefore produce fewer unsaturated hydrocarbons and alcohols compared to Fe catalysts.

Low-temperature Fischer–Tropsch (LTFT) reactors, either multitubular fixed-bed (MTFBR) or slurry reactor (SR) operating at approx. 25 bar and 495 to 525 K, use a precipitated FE catalyst. High-temperature Fischer–Tropsch (HTFT) fluidized bed reactors, either fixed (SAS) or circulating (Synthol) operating at approx. 25 bar and

575 to 595 K, use a fused Fe catalyst. In their experiments with Fe for CO_2 hydrogenation, Riedel *et al.* (1999) found that alumina was the best support and potassium acted as a powerful promoter. Copper was added to the catalyst to enable its easy reduction. They report that the hydrocarbon distribution from the H_2/CO_2 and H_2/CO syngas is the same, but the reaction rate for CO_2 syngas was about 43% lower than that of the CO-rich syngas.

The Al_2O_3/SiO_2 ratio has a significant influence on Fe-based catalyst activity and selectivity in the process of FTS. Product selectivities also change significantly with different Al_2O_3/SiO_2 ratios. The selectivity of low-molecular-weight hydrocarbons increases and the olefin-to-paraffin ratio in the products shows a monotonic decrease with an increasing Al_2O_3/SiO_2 ratio. Table 3.6 shows the effects of the Al_2O_3/SiO_2 ratio on hydrocarbon selectivity (Jothimurugesan *et al.* 2000). Recently, Jun *et al.* (2004) studied FTS over Al_2O_3- and SiO_2-supported Fe-based catalysts from biomass-derived syngas. They found that Al_2O_3 as a structural promoter facilitated the better dispersion of copper and potassium and gave much higher FTS activity. Table 3.7 shows properties of FT diesel and No. 2 diesel fuels.

Biosyngas consists mainly of H_2, CO, CO_2, and CH_4. FTS has been carried out using a $CO/CO_2/H_2/Ar$ (11/32/52/5 vol.%) mixture as a model for biosyngas on coprecipitated Fe/Cu/K, Fe/Cu/Si/K, and Fe/Cu/Al/K catalysts in a fixed-bed reactor. Some performances of catalysts that depended on the syngas composition have also been presented (Jun *et al.* 2004). The kinetic model predicting product distribution is taken from Wang *et al.* (2003) for an industrial Fe-Cu-K catalyst.

Table 3.6 Effects of Al_2O_3/SiO_2 ratio on hydrocarbon selectivity

Hydrocarbon selectivities (wt%)	100Fe/6Cu/ 5K/25SiO_2 22SiO_2	100Fe/6Cu/ 5K/3Al_2O_3/ 20SiO_2	100Fe/6Cu/ 5K/5Al_2O_3/ 18SiO_2	100Fe/6Cu/ 5K/7Al_2O_3/ 15SiO_2	100Fe/6Cu/ 5K/10Al_2O_3/	100Fe/6Cu/ 5K/25Al_2O_3
CH_4	6.3	8.7	10.4	10.7	14.3	17.3
$C_{2–4}$	24.5	27.8	30.8	29.9	33.4	46.5
$C_{5–11}$	26.8	27.6	32.2	33.9	40.0	31.0
$C_{12–18}$	21.9	21.2	15.8	15.0	6.0	4.9
C_{19+}	20.5	14.4	11.0	10.6	6.1	0.4

Reaction condition: 523 K, 2.0 MPa, $H_2/CO = 2.0$, and Gas stream velocity: 2,000/h.

Table 3.7 Properties of Fischer–Tropsch (FT) diesel and No. 2 diesel fuels

Property	FT diesel	No. 2 petroleum diesel
Density, g/cm^3	0.7836	0.8320
Higher heating value, MJ/kg	47.1	46.2
Aromatics, %	0–0.1	8–16
Cetane number	76–80	40–44
Sulfur content, ppm	0–0.1	25–125

FTS for the production of transportation fuels and other chemicals from synthesis has attracted much attention due to the pressure from the oil supply. Interest in the use of Fe-based catalysts stems from its relatively low cost and excellent WGS reaction activity, which helps to make up the deficit of H_2 in the syngas from coal gasification (Wu *et al.* 2004; Jothimurugesan *et al.* 2000; Jun *et al.* 2004). Riedel *et al.* (1999) have studied the hydrogenation of CO_2 over both these catalysts. In the absence of any WGS reaction promoter like Mn, CO_2merely behaves as a diluting gas as it is neither strongly adsorbed nor hydrogenated on Co catalysts. When Mn is added to Co catalysts, reverse WGS is possible. The FT chain growth on Co occurs due to strongly adsorbed CO on the surface. With a low partial pressure of CO, these inhibitions are removed and the regime moves from an FT to a methanation regime, yielding more CH_4. It was observed that even when the r-WGS reaction was fast, the attainable CO concentration was not sufficient to attain an FT regime. It was hence concluded that CO_2 hydrogenation is not possible even with a hybrid Co catalyst containing a shift catalyst like Mn.

3.8 Biohydrogen

The combustion products of hydrogen when it is burned completely with air consist of water, oxygen, and nitrogen. However, it has been suggested that hydrogen is too valuable to burn. Laboratory tests conducted on internal combustion engines burning hydrogen demonstrate good performance (Berry *et al.* 1996). In comparison with an engine burning gasoline, the emission of nitrogen oxides is far less for the engine-fueled hydrogen. The product of hydrogen combustion with air is water vapor and negligible pollution when the peak temperature is limited. Some oxides of nitrogen (NO_x) are formed at very high combustion temperatures ($<$2,300 K); fortunately, the autoignition temperature of hydrogen is only 858 K.

Hydrogen has good properties as a fuel for internal combustion engines in automobiles. Some of the characteristic properties of a hydrogen–air mixture that can definitely influence engine design and performance are low ignition energy, low density, wide range of ignition limits, high diffusion speed, and high flame speed (Plass Jr. *et al.* 1990).

The main disadvantage of using hydrogen as a fuel for automobiles is the huge on-board storage tanks that are required because of hydrogen's extremely low density. Hydrogen may be stored on board a vehicle as compressed gas in ultra-high-pressure vessels, as a liquid in cryogenic containers, or as a gas bound with certain metals in metal hydrides.

Hydrogen is one of the most promising alternative energy technologies. Hydrogen can be generated in a number of ways, such as electrochemical processes, thermochemical processes, photochemical processes, photocatalytic processes, or photoelectrochemical processes (Momirlan and Veziroglu 1999, 2002). Biohydrogen production by anaerobic fermentation of renewable organic waste sources has been found to be a promising method for the recovery of bioenergy (Han and Shin 2004).

In this method, anaerobic bacteria use organic substances as the sole source of electrons and energy, converting them into hydrogen.

The use of hydrogen as a fuel for transportation and stationary applications is receiving much favorable attention as a technical and policy issue (Cherry 2004). Hydrogen gas is being explored for use in combustion engines and fuel-cell electric vehicles. It is a gas at normal temperatures and pressures, which presents greater transportation and storage hurdles than exist for liquid fuels. Several hydrogen technologies are under development; the most promising of these is the fuel cell. Fuel cells use hydrogen, oxygen, a catalyst, and an electrolytic solution to produce energy in the form of heat and electricity.

3.9 Other Liquid Biofuels

3.9.1 Glycerol-based Fuel Oxygenates for Biodiesel and Diesel Fuel Blends

Glycerol (1,2,3-propanetriol or glycerine) is a trihydric alcohol. It is a colorless, odorless, sweet-tasting, syrupy liquid. It melts at 291 K, boils with decomposition at 563 K, and is miscible with water and ethanol (Perry and Green 1997). The chemical formula for glycerol is $OH–CH_2–CH(OH)–CH_2–OH$. Glycerol is present in the form of its esters (triglycerides) in vegetable oils and animal fats.

Glycerol is a byproduct obtained during the production of biodiesel. As biodiesel production is increasing exponentially, the crude glycerol generated from the transesterification of vegetables oils has also been generated in large quantities (Pachauri and He 2006). With the increasing production of biodiesel a glut of glycerol has been created, causing market prices to plummet. This situation warrants finding alternative uses for glycerol. Glycerol is directly produced with high purity levels (at least 98%) by biodiesel plants (Ma and Hanna 1999; Bournay *et al.* 2005). Research efforts to find new applications of glycerol as a low-cost feedstock for functional derivatives have led to the introduction of a number of selective processes for converting glycerol into commercially valued products (Pagliaro *et al.* 2007). The principal byproduct of biodiesel production is crude glycerol, which is about 10 wt% of vegetable oil. For every 9 kg of biodiesel produced, about 1 kg of a crude glycerol byproduct is formed (Dasari *et al.* 2005).

Oxygenated compounds such as methyl tertiary butyl ether (MTBE) are used as valuable additives as a result of their antidetonant and octane-improving properties. In this respect, glycerol tertiary butyl ether is an excellent additive with a large potential for diesel and biodiesel reformulation.

Glycerol can be converted into higher-value products. The products are 1,3-propanediol, 1,2-propanediol, dihydroxyacetones, hydrogen, polyglycerols, succinic acid, and polyesters. The main glycerol-based oxygenates are 1,3-propanediol, 1,2-propanediol, propanol, glycerol tert-butyl ethers, ethylene glycol, and propylene glycol.

3.9.2 P-series Fuels

A P-series fuel is a unique blend of liquefied petroleum gas liquids, ethanol, hydrocarbons, and methyltetrahydrofuran (MeTHF). P-series fuels are blends of ethanol, MeTHF, and pentanes, with butane added for blends that would be used in severe cold-weather conditions to meet cold start requirements. P-series fuels are made primarily from biorenewable resources and provide significant emissions benefits over reformulated gasoline. A P-series fuel can be mixed with gasoline in any proportion and used in FFVs. P-series fuels are clear, colorless, 89- to 93-octane liquid blends that are formulated for use in FFVs. Like gasoline, low-vapor-pressure formulations are produced to prevent excessive evaporation during summer and high-vapor-pressure formulations are used for easy starting in the winter. P-series fuels are at least 60% nonpetroleum. They also have many environmental benefits. Because a majority of the components that make up P-series fuels come from domestically produced renewable resources, this alternative fuel promotes both energy security and environmental quality. P-series fuels could be 96% derived from domestic resources and could reduce fossil energy use by 49 to 57% and petroleum use by 80% relative to gasoline. Greenhouse gas emissions from the production and use of P-series fuels are substantially better than those from gasoline. Each unit of P-series fuel emits approx. 50% less carbon dioxide, 35% less hydrocarbons, and 15% less carbon monoxide than gasoline. It also has 40% less ozone-forming potential.

3.9.3 Dimethyl Ether

Dimethyl ether (DME or CH_3–O–CH_3), is a new fuel that has attracted much attention recently. Today DME is made from natural gas, but DME can also be produced by gasifying biomass. DME can be stored in liquid form at 5 to 10 bars pressure at normal temperature. A major advantage of DME is its naturally high cetane number, which means that self-ignition is easier. The high cetane rating makes DME most suitable for use in diesel engines, which implies that the high level of efficiency of the diesel engine is retained when using DME. The energy content of DME is lower than in diesel.

DME can be produced effectively from biosyngas in a single-stage, liquid-phase (LPDME) process. The origin of syngas includes a wide spectrum of feedstocks such as coal, natural gas, biomass, and others. Nontoxic, high-density, liquid DME fuel can be easily stored at modest pressures. The production of DME is very similar to that of methanol. DME conversion to hydrocarbons, lower olefins in particular, has been studied using ZSM-5 catalysts with varying SiO_2/Al_2O_3 ratios, whereas the DME carbonization reaction to produce methyl acetate has been studied over a variety of group VIII metal-substituted heteropolyacid catalysts.

3.9.4 Other Bio-oxygenated Liquid Fuels

Methanol and ethanol are not the only transportation fuels that might be made from wood. A number of possibilities exist for producing alternatives. The most promising bio-oxygenated fuels, and closest to being competitive in current markets without subsidy, are ethanol, methanol, ethyl-tert-butyl ether, and anti-methyl-tert-butyl ether. Other candidates include isopropyl alcohol, sec-butyl alcohol, tert-butyl alcohol, mixed alcohols, and tert-amylmethyl ether.

Another possibility for bio-oxygenated fuels is methanol. Methanol could conceivably be made from grain, but its most common source is natural gas. The use of natural gas is better for reducing carbon dioxide production in comparison to other fossil fuels, but the use of renewable fuels instead of natural gas would be better still. It can be made from coal or wood with more difficulty and lower efficiency than from natural gas. The cost of making methanol from natural gas is around US$ 0.40 per gallon. It could probably be sold as a motor fuel for about US$ 0.60 to $ 0.70 per gallon. This would be equivalent to gasoline selling at about US$ 0.92 to $ 1.03 per gallon. Methanol was once produced from wood as a byproduct of charcoal manufacture, but overall yields were low. To produce methanol from wood with a significantly higher yield would require production of synthesis gas in a process similar to that used for production of methanol from coal. Such processes for gasifying wood are less fully developed than the two-stage hydrolysis process for the production of ethanol.

A high octane rating is characteristic of all oxygenated fuels, including ethanol, methanol, ethyl-tert-butyl ether (ETBE), and MTBE. MTBE is made by reacting isobutylene with methanol. ETBE is made by using ethanol instead of methanol. Thus either ethanol or methanol from either grain or wood could be a factor in making tert-butyl ether octane enhancers. The characteristics of ethers are generally closer to those of gasolines than those of alcohols. Ethers are benign in their effect on fuel system materials and are miscible in gasoline; therefore, they are not subject to phase separation in the presence of water, as are methanol and ethanol.

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