Handbook of Bioenergy Crop Plants
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Chemical Engineering for Bioenergy Plants

Publication details
David R. Shonnard, Michael J. Brodeur-Campbell, Abraham R. Martin-Garcia, Tom N. Kalnes
Published online on: 22 Mar 2012

How to cite :- David R. Shonnard, Michael J. Brodeur-Campbell, Abraham R. Martin-Garcia, Tom N. Kalnes. 22 Mar 2012, Chemical Engineering for Bioenergy Plants from: Handbook of Bioenergy Crop Plants CRC Press
Accessed on: 08 Sep 2023

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8 Chemical Engineering for Bioenergy Plants

Concepts and Strategies

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8.1 INTRODUCTION

Although global interest in liquid biofuels for transportation has recently increased, these fuels are not something new. Nearly a century ago automobiles were designed to run on gasoline, ethanol, and blends of these fuels; these were the forerunners of modern flexible-fueled vehicles. The motivation for biofuel use a century ago was different than today. Previously, biofuels were one of a diversity of fuel sources whereas in the modern era of petroleum, biofuels are meant to address a list of issues including global warming, rural economic development, domestic jobs, energy security, and balance of trade. The list of potential transportation biofuels today is much larger than in previous eras, mostly because of advances in biochemical and thermochemical processing technologies, which have also increased the list of possible biomass feedstocks that can be converted.

This chapter will first give a brief overview of the technologies for converting biomass feedstocks into usable liquid transportation fuels. After that will be an introduction into the main processing steps used in commercial practice and a review of current research and development in this field. Afterward, a short summary will give the current status for global biofuel production.

8.1.1 AN OVERVIEW OF BIOMASS-TO-BIOFUELS PROCESSING TECHNOLOGIES

Processing routes for conversion of biomass to biofuels has traditionally been organized into two categories depending on the agents for transformation and reaction conditions: biochemical and thermochemical. Biochemical conversion processes use biological catalysts (e.g., enzymes) at mild temperatures to produce sugars from the original biomass and then microorganisms to ferment sugars into oxygenated biofuels. The choice of microorganism should take into account the types of sugars to be fermented and the desired fermentation products. For example, hydrolysis of woody biomass will yield a mixture of five- and six-carbon sugars, but not many microorganisms are able to readily ferment five-carbon sugars. Recent advances in metabolic engineering of microorganisms have created unique metabolic pathways within microorganisms so that mixtures of sugars obtained from lignocellulosic biomass can be fermented into oxygenated biofuels (e.g., ethanol and butanol) but more recently into true hydrocarbon fuels. Thermochemical conversion processes use chemical catalysts and are, for the most part, carried out at higher temperatures and pressures. These reactions exhibit much shorter reaction times than biochemical conversion processes, but selectivity to a particular biofuel product is not as specific as for biochemical conversions.

Figure 8.1 is an overview diagram showing the main conversion steps for conventional biofuels (such as ethanol from starch crops and cane, biodiesel from triglycerides in soybeans) and for
advanced biofuels. In both cases, biomass feedstock is first converted into an intermediate product through initial reaction or separation steps. The intermediates are then transformed to final biofuel product and co-products through additional reaction and separation steps. The vast majority of global production is conventional biofuels [2008 data, 18.7 billion gallons ethanol/year, 4.4 billion gallons biodiesel/year (EIA 2010)]. Dry and wet mill corn ethanol facilities produce an intermediate glucose sugar product and a final product of ethanol plus dry distiller grains solids (DDGS), which is marketed as an animal feed. The overall fermentation reaction is given by $\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 2 \text{C}_2\text{H}_5\text{OH} + 2 \text{CO}_2$.

Two carbons from the sugar molecule are emitted as carbon dioxide, but the energy content of the two ethanol molecules is substantially higher than the sugar feedstock. Process energy for corn ethanol production is typically from natural gas for steam production and electricity is from the local grid. Because of the importing of these energy resources, corn ethanol has a relatively large fossil energy demand (ratio of fossil energy required for all processing steps per unit of energy in ethanol produced) of approximately 0.5–0.8 (Wu et al. 2006; Shapouri et al. 2010). Current (as of 2010) production rates of corn grain ethanol in the United States are approximately 50% that of global production at 12 billion gallons/year (RFA 2010), and from sugar cane in Brazil it is approximately 8 billion gallons ethanol/year (EIA 2010). Biodiesel is a methyl ester of fatty acids derived from plant oils. The biodiesel reaction can be simply described as triglyceride + methanol → 3 fatty acid methyl esters + glycerol (CH$_3$OH–CHOH–CH$_2$OH). Methanol is almost always produced from natural gas (fossil origin), and co-products of biodiesel production include glycerol and a residue from the oil extraction step (soymeal for example), which is often marketed as animal feed. The key intermediate is a plant oil obtained from the oil extraction step.

Advanced biofuels take advantage of the most plentiful biomass resource on Earth, lignocellulosic (woody) feedstocks, and of unconventional plant oils and algae. Processing routes for advanced

**FIGURE 8.1** Processing routes for conventional and advanced biofuels.
biofuels are more complicated than for starch ethanol and biodiesel, and less is known about the costs and environmental impacts of these biofuels. This is because very few demonstration- or commercial-scale facilities exist for these biofuels at this time, yet this situation may soon change because of recent industry and government initiatives in research and commercial development. For example, as of 2010 there are 26 cellulosic ethanol facilities in various stages of construction in the United States with capacities ranging from a low of 20,000 gallons/year to 100 million gallons/year (RFA 2010). Additionally, in the United States, demonstration-scale facilities of similar scale are in the planning and construction phase for production of some other types of advanced biofuels (Figure 8.1).

The remaining sections of this chapter describe some of the main features of conventional and advanced biofuel technologies. Technological barriers are discussed and recent approaches to overcome them are presented. The chapter ends with a discussion of the relative advantages and disadvantages of each conversion technology from cost and environmental impact perspectives.

8.2 PLANT OILS: CONVERSION TO BIODIESEL AND HYDROCARBONS

8.2.1 INTRODUCTION TO THE PROCESSING CONCEPTS

This section focuses on the conversion of plant-derived oils to distillate transportation fuels. Two distinctly different processing pathways are commercially available: (1) base-catalyzed transesterification of triacylglycerol (TAG)-rich feedstocks with methanol to produce fatty acid methyl esters (FAME), referred to as biodiesel; and (2) catalytic reaction of TAG and free fatty acid (FFA)-rich feedstocks with hydrogen to produce hydrocarbon-based fuels such as hydrotreated renewable diesel (HRD) and hydrotreated renewable jet (HRJ) fuel. Biodiesel can also be produced from FFA-rich feedstocks using a more severe acid-catalyzed esterification process.

To date, most of the existing capacity for producing diesel fuel from plant oils has centered on biodiesel. Although its use in blends with petroleum diesel is already widespread, there are some limitations to biodiesel that may ultimately limit its future use. These limitations include fuel storage stability, cold flow properties in winter climates, and high solvency that can lead to engine compatibility issues. The implementation of an ASTM specification for biodiesel (ASTM D6751-09) has helped to overcome issues related to fuel contamination with methanol, glycerol, and partially converted glycerides and fatty acids. To minimize the chance of engine problems, some car manufacturers have recommended capping the amount of biodiesel in petroleum blends at approximately 5% (McCormick 2009).

In the hydprocessing pathway to biofuels, plant oils can be processed in pure form or co-processed with petroleum feedstock. HRD and HRJ are hydrocarbon liquids produced from plant oil feedstock using advanced hydprocessing technology. Their physical properties (e.g., viscosity, flash point, distillation, freeze point) are similar to petroleum-derived fuels and their chemical composition is similar to paraffin-rich Fischer–Tropsch (FT)-derived fuels (Koers et al. 2009). Because these fuels are fully deoxygenated, they have excellent storage stability and can be used in any proportion with existing petroleum fuels.

Although commercial production of hydrocarbon-based biofuels is not yet widespread, sufficient production capacity has been brought on stream to demonstrate fuel quality and compatibility with existing engine technology. A significant increase in the HRD and HRJ production rate is expected over the next 3–5 years.

A more detailed discussion of the chemistry and processing steps for each processing pathway is provided in the paragraphs that follow. Process yields and conversion efficiencies are compared as well as fossil fuel and total energy requirements. A discussion of the current state of commercialization is also provided, including a brief discussion of sustainable feedstock selection.
8.2.2 Process Descriptions

A simplified diagram of a modern biodiesel production plant is provided in Figure 8.2. Dry, refined plant oil is subjected to a two-stage transesterification reaction. Fresh and recycled methanol in excess of stoichiometric requirements are fed to the mix tank, where an alkali catalyst such as sodium hydroxide is added. The mixture is fed along with the oil to a first-stage esterification reactor, which is typically heated by a steam coil. Effluent from the first stage is separated in a settling tank, with the upper phase going to the second-stage esterification reactor and the lower phase routed to methanol recovery. Additional methanol and catalyst are fed to the heated second-stage reactor and the effluent is sent to a second separator. The lower phase from the second separator can be recycled to the first reaction stage or sent to the glycerine recovery whereas the ester phase is sent to a water wash column for removal of water-soluble impurities. The water phase is routed to a methanol recovery column where excess methanol is recovered, dried, and recycled to the first reaction stage. After drying, a biodiesel product can be recovered from crude feedstock at a yield of approximately 96%. Co-product crude glycerol and a wastewater stream containing soaps and neutralized catalyst are recovered.

An example of an advanced hydroprocessing technology is the UOP/ENI Ecofining™ process. A simplified block flow diagram of the process is provided in Figure 8.3 (Kalnes et al. 2008).

**FIGURE 8.2** A modern biodiesel production facility.

**FIGURE 8.3** Advanced process for HRD and HRJ production. (Kalnes, T., Marker, T., and Shonnard, DR., Biofuels Technol Quart, 2008, available at www.biofuels-tech.com.)
Similar to biodiesel plants, a pretreatment step is typically required to remove insoluble materials and trace metals, and two reaction stages are used. Unlike base-catalyzed transesterification, hydroprocessing is robust to high concentrations of FFAs, thus allowing other lower-cost materials such as tallow oil and waste greases to also be used as feedstock. Advanced hydroprocessing also produces a low-cloud-point product that can be used neat or blended with petroleum diesel without limitation.

In the Ecofining process, pressurized feedstock is mixed with recycled hydrogen and then sent to a multistage adiabatic catalytic hydrodeoxygenation reactor (R1) where the feedstock is saturated and completely deoxygenated. A vapor–liquid separator is used to recover excess hydrogen, and gas recycle to R1 is set to achieve a minimum hydrogen partial pressure. Conversion of feed is complete, and the volumetric yield of deoxygenated hydrocarbon products is greater than 100%. Selectivity to diesel boiling-range paraffin is very high. The primary deoxygenation reaction byproducts are propane, water, and carbon dioxide.

The effluent from R1 is separated to remove carbon dioxide, water, and low-molecular-weight hydrocarbons. The resultant diesel is mixed with additional recycle gas and then routed to a catalytic hydroisomerization reactor (R2) wherein a branched paraffin-rich diesel fuel is produced. In this manner, the cold flow properties of the diesel are adjusted to meet required specifications. The isomerization reaction is selective and consumes very little hydrogen.

Isomerized product is separated from excess hydrogen in a conventional gas/liquid separator. After purification, the excess hydrogen is recycled back to both reactors to maintain the minimum required hydrogen partial pressure. Make-up hydrogen is added to the process to balance chemical consumption and solution losses. The liquid product is sent to the product recovery section of the process where conventional distillation steps are used to separate co-products such as propane and naphtha.

Table 8.1 contrasts Ecofining™ inputs and outputs to those of conventional biodiesel production (Kalnes et al. 2007). The Ecofining process for producing HRD (green diesel) operates at conditions similar to a petroleum hydrodesulfurization unit and integrates well within existing petroleum refineries. If required, a portion of the light fuel co-product can be steam-reformed to generate all of the hydrogen consumed in the process (Kalnes et al. 2007). Estimates of fossil energy demand (FED), cumulative energy demand (CED), and life-cycle greenhouse gas (GHG) emissions for biodiesel and HRD produced in the UOP/ENI Ecofining process, green diesel (GD), are compared to petroleum diesel in Table 8.2.

### TABLE 8.1
Comparison of Biodiesel and HRD Process Inputs and Outputs

<table>
<thead>
<tr>
<th></th>
<th>Ecofining Green Diesel</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt% vol%</td>
<td>wt% vol%</td>
</tr>
<tr>
<td><strong>Feeds</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vegetable oil</td>
<td>100 100</td>
<td>100 100</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1.5–3.8 0–2 &lt;1–7</td>
<td>10 11 10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chemicals¹</td>
</tr>
<tr>
<td><strong>Products</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>5 9</td>
<td>96 100</td>
</tr>
<tr>
<td>Butane</td>
<td>0–2 0–3</td>
<td>10 7</td>
</tr>
<tr>
<td>Naphtha</td>
<td>&lt;1–7 1–10</td>
<td></td>
</tr>
<tr>
<td>Green diesel</td>
<td>75–85 88–99</td>
<td></td>
</tr>
</tbody>
</table>

¹ Chemicals include sodium hydroxide (NaOH) and an acid to neutralize the products.
Three renewable feedstocks are considered in Table 8.2: soybean oil, rapeseed oil, and tallow. It can be seen that plant-derived fuels exhibit a higher CED and lower FED when compared with petroleum diesel. The higher CED is due to the additional energy required to cultivate, harvest, and transport the feedstock. Because carbon dioxide (CO₂) generated in the combustion of biomass-derived fuel is considered carbon neutral, their FED and GHG emissions are significantly lower than petroleum diesel for all of the biofuels. For tallow, a waste material derived from meat production, the CED is lower than that for petroleum diesel. As a waste, this feedstock is free of the upstream energy burdens assigned to the primary meat product.

It is important to note that land-use change (LUC) effects are not included in the GHG emissions shown in Table 8.2. Although LUC GHG impacts can be negative or positive, depending on the prior condition of the land, controversial indirect land-use change (ILUC) impacts often consider a worst-case scenario in which food crop conversion to energy crop production leads to rainforest destruction. Long-term concerns associated with diverting food crops to fuel production or carbon-rich forests to cultivated land has shifted the commercial focus away from first-generation feedstocks like soybean and rapeseed oil and toward next-generation (inedible) oils such as jatropha and camelina, which can be intercropped, grown on marginal land, or grown as a rotation crop (Shonnard et al. 2009). Ultimately, algae could become the major source of TAG-rich feedstock for biofuel production.

### 8.2.3 Current State of Commercialization

The production of biodiesel is widespread, with most of the existing production capacity located in Europe, mainly Germany and France. In 2007, total world biodiesel production was approximately 5–6 million tons, with 4.9 million tons processed in Europe (of which 2.7 million tons was from Germany) and most of the rest from the United States (NBB 2008). For comparison, total world production of vegetable oil for all purposes in 2005–2006 was approximately 110 million tons, with approximately 34 million tons each of palm oil and soybean oil (FEDIOL 2008). A significant increase in the production of biodiesel is expected over the next few years in South America. Table 8.3 provides an estimate of existing and future biodiesel capacity in countries with large production rates (Thurmond 2008).

There are numerous biodiesel technology providers, and the required process scheme is strongly dependent upon feedstock properties. Special pretreatment or acid-catalyzed esterification is required for feeds (such as tallow) containing significant amounts of FFAs.

Although not as widespread, hydroprocessing for the production of renewable transportation fuels is also a commercial technology practiced in existing petroleum refineries. Several commercial facilities for HRD production are in operation or in later stages of design and construction. These include the NExBTL process (Neste Oy), Synfining process (Syntroleum), and Co-processing (Petrobras and ConocoPhillips) as well as the UOP/ENI Ecofining and UOP Renewable Jet Fuel process. Table 8.4 provides a partial summary of feedstocks, plant locations, production capacity, and approximate startup date. Over 800 million gallons/year (~3 million tons) of production capacity is expected to be on stream before 2012.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Petroleum Diesel FED, MJ/MJ</th>
<th>SBO Biodiesel</th>
<th>RSO Biodiesel</th>
<th>Tallow Biodiesel</th>
<th>Tallow GD</th>
</tr>
</thead>
<tbody>
<tr>
<td>FED, MJ/MJ</td>
<td>1.25</td>
<td>0.41</td>
<td>0.34</td>
<td>0.41</td>
<td>0.37</td>
</tr>
<tr>
<td>CED, MJ/MJ</td>
<td>1.27</td>
<td>1.53</td>
<td>1.42</td>
<td>1.88</td>
<td>1.82</td>
</tr>
<tr>
<td>GHG gCO₂-eq/MJ</td>
<td>85</td>
<td>48</td>
<td>40</td>
<td>46</td>
<td>41</td>
</tr>
</tbody>
</table>

SBO, soybean oil; RSO, rapeseed oil; GD, HRD from UOP/ENI ecofining process.
Most of the early units to come on stream (ConocoPhillips, PetroBras, and BP Australia) co-processed small percentages of fats and oils in existing petroleum HDS units. The remaining units are advanced hydroprocessing technologies designed to process feedstock that is 100% renewable fat and oil. Although the social, economic, and regulatory issues associated with expanded production of HRD and HRJ are outside of the scope of this chapter, it is crucial that future commercialization efforts focus on sustainable methods of producing feedstock.

To support this effort, industry participants including commercial airlines have formed a consortium that have set criteria that are complementary to emerging internationally recognized standards such as those being developed by the Roundtable on Sustainable Biofuels. These criteria are

- Feedstock sources should be developed in a manner that is noncompetitive with food and in which biodiversity impacts are minimized. In addition, the cultivation of those plant sources should not jeopardize drinking water supplies.
- Total life-cycle GHG emissions from plant growth, harvesting, processing, and end use should be significantly reduced compared with those associated with hydrocarbon fuels from fossil sources.

### TABLE 8.3

<table>
<thead>
<tr>
<th>Country</th>
<th>EU</th>
<th>Germany</th>
<th>United States</th>
<th>Canada</th>
<th>South America</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary feed</td>
<td>85% rapeseed</td>
<td>Rapeseed</td>
<td>Soybean</td>
<td>Canola</td>
<td>Soybean</td>
</tr>
<tr>
<td>Percent crop to fuels</td>
<td>N20%</td>
<td>N13%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2005 operating units</td>
<td>137</td>
<td>110</td>
<td>4</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>New units planned</td>
<td>179</td>
<td>250</td>
<td>30</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>2005 capacity, MGPY</td>
<td>960</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2006 capacity, MGPY</td>
<td>900</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>“2010” capacity, MGPY</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* million gallons per year

### TABLE 8.4

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Location</th>
<th>Producer</th>
<th>Technology</th>
<th>Mgal/Year</th>
<th>Start-Up</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jatropha</td>
<td>Portugal</td>
<td>GALP</td>
<td>Ecofining</td>
<td>95</td>
<td>2011</td>
</tr>
<tr>
<td>Mixed</td>
<td>Italy</td>
<td>Eni Spa</td>
<td>Ecofining</td>
<td>95</td>
<td>2012</td>
</tr>
<tr>
<td>Palm oil</td>
<td>Finland</td>
<td>Neste</td>
<td>NExBTL</td>
<td>56</td>
<td>2008</td>
</tr>
<tr>
<td>Palm oil</td>
<td>Singapore</td>
<td>Neste</td>
<td>NExBTL</td>
<td>264</td>
<td>2011</td>
</tr>
<tr>
<td>Animal fats</td>
<td>Louisiana, United States</td>
<td>Dynamic Fuels</td>
<td>Bio-SynFining</td>
<td>75</td>
<td>2010</td>
</tr>
<tr>
<td>Mixed/petroleum</td>
<td>Brazil</td>
<td>PetroBras</td>
<td>H-Bio</td>
<td>NA</td>
<td>2006</td>
</tr>
<tr>
<td>Mixed/petroleum</td>
<td>Ireland</td>
<td>ConocoPhillips</td>
<td>ConocoPhillips</td>
<td>14</td>
<td>2006</td>
</tr>
<tr>
<td>5% tallow</td>
<td>Australia</td>
<td>BP</td>
<td>Co-processing</td>
<td>34</td>
<td>2008</td>
</tr>
</tbody>
</table>

NA, not applicable.

* Neste Oil Company

* Syntroleum

* Eni/UOP

* estimated from press releases

* PetroBras and ConocoPhillips are co-processing vegetable oil (soy, sunflower, palm, animal fat, etc.)
• In developing economies, development projects should include provisions or outcomes that improve socioeconomic conditions for small-scale farmers who rely on agriculture to feed themselves and their families and that do not require the involuntary displacement of local populations.

• High conservation value areas and native ecosystems should not be cleared and converted for fuel plant source development.

Current and future producers are targeting sustainable production scenarios that, in addition to minimizing impact on LUC and food and water resources, provide an energy alternative that is economically competitive with current petroleum-based fuels. Market growth will require a coordinated effort between feedstock producers, refiners, and industry regulators to ensure that environmental impacts are minimized.

If done responsibly, increasing HRD and HRJ usage in the transportation sector can significantly reduce GHG emissions as well as diversify energy sources, enhance energy security, and stimulate the rural agricultural economy.

8.3 THERMOCHEMICAL CONVERSION OF PLANT WOODY BIOMASS

Archeological findings show the first evidence of thermochemical processing of woody biomass by humans to have occurred approximately 1.9 million years ago, the first controlled use of fire by humans approximately 400,000 years ago, and charcoal production and controlled burns some tens of thousands of years ago (Bowman 2009). Although the above examples are thermochemical reactions, this review will focus on more advanced thermochemical processing routes to upgrade woody biomass into liquid transportation and gaseous energy products.

The second major platform covered in this review is for conversion of woody biomass into biofuels and high-value chemicals through the use of thermochemical processing steps conducted at high temperature and pressure, often in the presence of chemical catalysts. Gasification and pyrolysis of wood are the two most important thermochemical processing routes. In both cases, wood is thermally decomposed into intermediate compounds of small molecular weight relative to the starting polymeric carbohydrate and lignin wood fractions. The predominant products of gasification constitute a synthesis gas, whereas in pyrolysis, depending on reaction conditions, the major products could be a crude bio-oil, a synthesis gas, or a solid carbonaceous char. The following sections will introduce these major thermochemical processing platforms, present the main features of reaction chemistries, and estimate energy efficiencies from conversion.

8.3.1 GASIFICATION-BASED CONVERSION OF PLANT BIOMASS

Gasification of woody biomass provides a means for production of renewable energy products, notably synthesis gas for liquid fuels production, fuel gas for heat or power applications, and hydrogen for fuel cells. Figure 8.4 shows a process flow diagram for gasification of woody feedstocks for production of these three main energy products. Wood chips are transferred to a storage operation, and upon entering the process pass through a size reduction step before gasification.

Gasification is a partial oxidation/thermal decomposition reaction carried out at high temperature (600–900°C) in the presence of a gasification medium (air, oxygen, steam) to yield a synthesis gas containing major products carbon monoxide (CO), H₂, CO₂, and H₂O but with significant amounts of minor products, mainly ash, ammonia, hydrogen sulfide (H₂S), tars, and particulate char (Torres et al. 2007) as well as trace contaminants such as hydrogen cyanide (HCN), halogens [e.g., hydrogen chloride HCl], alkali metals, and other metals (Pb, As, Hg) (NSF 2008). These minor products, or impurities, must be removed (gas cleanup) before using the synthesis gas for electricity generation, heat production, or catalytic conversion to the high-value fuels and chemicals, as shown in Figure 8.4. For example, (1) tars can coat surfaces within downstream processes and
interfere with rotating power generation equipment, (2) ammonia and other nitrogen-containing gases will be converted to oxides of nitrogen (NOₓ) in engines or turbines, and (3) H₂S poisons catalysts and ammonia blocks catalyst active sites and therefore both must be removed.

Conversion to fuels and chemicals (CO hydrogenation in Figure 8.4) occurs in the presence of specific metal catalysts and requires unique ratios of CO to H₂ to form the different fuel and chemical products. The CO/H₂ ratio can be adjusted through a catalytic water gas shift reaction in which CO is combined with H₂O to form additional H₂ and CO₂. Other approaches are possible to adjust the final CO/H₂ ratio, including the use of methane in a steam-reforming reaction (\( \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2 \)) or a H₂-selective membrane separation step. Depending on application, separation of final products and co-products is accomplished through distillation, membranes, and other devices.

### 8.3.1.1 Gasification of Biomass

Gasification of biomass can be carried out in several reactor configurations. Biomass chips can be introduced at the top of the reactor to be contacted with a co-current or countercurrent stream of the gasification medium (air, oxygen, and water vapor). Another configuration utilizes a bubbling or circulating fluidized bed reactor in which heat is transferred by a circulating stream of solid media such as sand. The gasification product composition is dependent on process conditions, gasification medium, and feedstock type, but with CO/H₂ ratio usually less than 1 and with a heating value between 5 and 15 MJ/Nm³ (Nm³ is normal cubic meter). Thus, biomass-derived synthesis gas is considered a low to medium fuel gas compared with natural gas (35 MJ/Nm³).

The gasification reaction itself is endothermic and requires a source of external heat. Volatile matter from heating of biomass is initially oxidized forming CO₂ and H₂O and releasing heat, which leads to further volatilization of biomass and H₂O. Partial oxidation and thermal decomposition reactions also take place leading to the product mixture discussed in Section 8.3.1.

Ash from the biomass is mostly bound up with particulate char and can be separated easily from the gas product using filtration or other means. The char can be oxidized yielding additional process heat or partially oxidized with O₂ or reformed with H₂O to increase carbon conversion in synthesis gas. Tars are high-molecular-weight aromatic hydrocarbons and must be removed to protect
downstream equipment and catalysts. Tar formation in the gasifier can be minimized by increasing the O₂-to-fuel ratio, raising gasification temperature, or using low-cost dolomite (CaMg(CO₃)₂) which acts as a base catalyst in steam reforming (CₙHₘ + H₂O → nCO + ((m/n)/2 + 1) H₂) of tars. For example, Gil et al. (1999) showed that addition of dolomite to a biomass gasifier decreased tars from approximately 20 to 2 g tar/Nm³, but was accompanied by higher production of dolomite attrition dust. Higher gasifier temperatures have disadvantages that lead to decreased carbon yield in syngas or with higher slag production (NSF 2008). Even with prevention steps in the gasifier, aftertreatment is required to reduce tars to tolerable levels, as discussed in the next section. Other minor products such as H₂S and ammonia are derived from biomass-bound S and N and their concentrations in gasifier effluent are feedstock dependent for the most part.

8.3.1.2 Synthesis Gas Clean-Up from Biomass Gasifier

Tars are produced at levels between 10,000 and 20,000 mg/Nm³ under typical biomass gasifier operating conditions (Torres et al. 2007; NSF 2008). Tars are best removed using steam-reforming (Ni catalyst) or cracking (dolomite, carbonate, or Ni catalysts) reactions, but cracking requires higher temperatures (900°C) than normally achieved at gasifier exit (<800°C) and Ni catalysts can be poisoned by low amounts of H₂S. Tar concentrations as low as 2 mg/Nm³ were observed over a 50-h trial when dolomite was used in the gasifier followed by two reactors containing Ni catalyst to remove tar (Caballero et al. 2000). However, a recent review concludes that no tar removal process has demonstrated long-term performance at a gasifier’s normal exit temperature of less than 800°C (NSF 2008).

Ammonia is produced at levels between 2000 and 4000 ppmv in a biomass gasifier (Torres et al. 2007) and is removed through decomposition to N₂ and H₂ using supported Ni, Ru, and Fe catalysts, but carbides and nitrides of W, V, and Mo can also be used. Much attention has been given to NH₃ decomposition in synthesis gas in the presence and absence of H₂S (Jothimurugesan and Gangwal 1998). NH₃ can be effectively removed with commercial reforming catalysts at 650°C, but removal of H₂S below 10 ppmv is required.

Because sulfur content of biomass is relatively low compared with other solid gasification feedstocks, the H₂S (and COS-carbonyl sulfide) concentration is normally between 20 and 600 ppmv in biomass gasifier outlets (Torres et al. 2007). But this H₂S concentration is too high to avoid poisoning of Ni catalysts for tar and ammonia removal, and although higher temperature operation can mitigate this S poisoning effect in Ni catalysts, sintering/deactivation of catalyst and materials-of-construction issues become important (NSF 2008). The most feasible option for sulfur removal is to use a high temperature adsorbent/regeneration process using ZnO, but Zn ferrites and Zn titanates are also effective.

\[
\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O} \quad \text{(adsorption step)} \quad (8.1)
\]

\[
\text{ZnS} + 3/2 \text{O}_2 \rightarrow \text{ZnO} + \text{SO}_2 \quad \text{(regeneration step)} \quad (8.2)
\]

Although gasification hot gas clean-up processes have been extensively studied in the past, significant research and development is needed to overcome barriers to commercialization of biomass gasification (Torres et al. 2007).

8.3.1.3 Water–Gas-Shift Reaction

The water–gas-shift (WGS) reaction is used to adjust the CO/H₂ ratio in synthesis gas by the mechanism:

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad (8.3)
\]

Commercial catalysts are available for WGS reactions in the temperature ranges of low (225–250°C, Cu–Zn), medium (350–375°C, Co–Mo sulfide form), and high (450–475°C, Fe–Cr). Because the
Cu–Zn catalysts require very low H₂S concentrations (<60 ppbv) and the Co-Mo catalyst tolerates very high H₂S concentrations (several thousands of parts per million by volume), perhaps the best catalyst for WGS reactions for biomass synthesis gas is the Fe–Cr catalyst, which can tolerate moderate H₂S levels of 50–100 ppmv. At this high temperature, remaining tars might continue in the vapor rather than deposit on the catalyst surface.

8.3.1.4 CO Hydrogenation Reaction

The final step in production of fuels and chemicals from biomass is the CO hydrogenation reaction. Conversion to hydrocarbons, alcohols, and other organic compounds is dependent on catalyst type, CO/H₂ ratio, and other reaction conditions. Fischer–Tropsch synthesis (FTS) converts CO and H₂ to gaseous and liquid hydrocarbons through a highly exothermic polymerization mechanism. FTS reaction begins with adsorption and dissociation of CO and H₂ on active sites on the catalyst surface (NSF 2008). A single C atom and multiple H atoms combine on a single active site to initiate chain growth of the hydrocarbon. Further chain growth occurs when adjacent intermediates combine in a C–C bond. Chain termination occurs when an adjacent adsorbed H combines with the growing chain to form a terminal C–H bond. The likelihood of chain growth is governed by the Anderson-Schultz-Flory chain growth probability, \( \alpha \), which is dependent on catalyst type, promoters present in the catalyst, and reaction conditions (Bartholomew and Farrauto 2006). Products ranging from C₁ to C₆₀+ can be achieved, and the actual distribution of carbon number in the hydrocarbon products is dependent on \( \alpha \), with high values of \( \alpha > 0.9 \) being preferred for liquid hydrocarbon products.

Common catalysts for FTS include those based on Fe and Co. Iron-based FTS catalysts are favored for converting low H₂/CO (0.6–1), non-WGS synthesis gas from biomass because these catalysts also exhibit significant WGS activity. Cobalt-based catalysts are used on higher H₂/CO (2.0–2.2) synthesis gas from WGS biomass synthesis gas. Co catalysts achieve much higher activities compared to Fe (5–10 times higher), and Co catalysts are more selective to higher-molecular-weight hydrocarbons (NSF 2008).

Gasoline products are favored in the high-temperature (HT) FTS range of 300–350°C, whereas diesel and jet fuel are prominent in the low-temperature (LT) FTS at 200–250°C. In a large biorefinery based on FTS, LT and HT reactors would be in operation along with refinery-type FTS liquid and wax upgrading steps (oligomerization, catalytic reforming, hydrotreating, and hydrocracking/hydroisomerization) and separations. Furthermore, aromatic content of the FTS jet fraction must be increased to provide desired properties, such as low freeze point (–47°C).

Because of the exothermic FTS reaction, the reactor design must remove heat effectively to avoid catalyst thermal degradation and maintain product selectivity. A thorough review of FTS reactor configurations is available in Bartholomew and Farrauto (2006), but the choices are between tubular fixed-bed reactors (TFBRs), fluidized bed reactors, and slurry bubble column reactors (SBCRs). SBCRs are reported to have advantages over TFBRs because of the simplicity, lower cost, higher volumetric productivity, heat removal efficiency, and more favorable catalyst productivities and handling. However, recent improvements of TFBR designs achieve performance similar to large SBCRs, as reported by Hoek and Kersten (2004).

Interest in alcohols as transportation fuels stems from their favorable engine performance and lower emissions compared with hydrocarbon fuels (Verbeek and Van der Weide 1997; Phillips and Reader 1998; NSF 2008). A blend of 10% ethanol in petroleum gasoline decreases GHG emissions, lowers CO and particulate emissions, and increases octane rating (NSF 2008). Dimethyl ether (DME) produced from methanol is reported to decrease particulate and NOₓ emissions (Sorenson and Mikkelsen 1995), and DME can easily form blends with petroleum diesel.

Methanol production from synthesis gas is practiced commercially and occurs at high pressure (50–80 atm) and at 225–250°C in the presence of Cu–Zn catalyst with nearly 100% selectivity, but with low conversions, and with a requirement of syngas recycling (Bartholomew and Farrauto 2006). Other catalysts are also used (silicoaluminophosphate) at similar temperatures with similarly
high selectivity (Williams et al. 1995; Shonnard et al. 2006). Presence of a small amount of CO₂ (4% vol.) helps productivity because the reaction mechanism is thought to involve hydrogenation of CO₂. Cu–Zn catalysts are very susceptible to poisoning by sulfur and arsine in syngas, thus requiring gas clean-up. Methanol synthesis is carried out in various reactor configurations, as discussed in Bartholomew and Farrouto (2006).

Higher alcohols are also produced by catalytic conversion of syngas; for example, producing the octane enhancer methyl tertbutylether (MTBE) from methanol and isobutanol. One alcohol of interest is ethanol, the direct synthesis of which from synthesis gas can be accomplished using a rhodium- or copper-based catalyst. Hu et al. (2007) report ethanol selectivity of more than 50% using an Rh catalyst at high pressure but with low conversion. Side reaction byproducts include methane, C₂–C₅ alkanes and alkenes, and low-molecular-weight oxygenated organics. A few pilot-scale processes for higher alcohol synthesis are in place, but no commercial facilities currently exist (NSF 2008).

Although catalytic CO hydrogenation reactions have been investigated in the past, and there is commercial production of select products, there is a need for further catalyst and reactor innovation. A comprehensive list of research recommendations leading to improved commercial production from catalytic CO hydrogenation is included in a recent benchmark study (NSF 2008).

8.3.2 Pyrolysis-Based Conversion of Plant Biomass

Pyrolysis is a thermal depolymerization and molecular fragmentation process carried out in the absence of oxygen (or air) and at moderate temperature (~450–700°C) (Mohan et al. 2006). These thermal reactions occur in stages, each corresponding to higher reaction severity, in which increasing severity refers to longer reactor residence times and higher reaction temperatures. Primary reactions at low severity yield gases (CO₂, CO, H₂O), organic vapors, and liquid products. Secondary reactions act on primary products decomposing larger molecules into low-molecular-weight gaseous and liquid species as well as char (a carbonaceous solid). Tertiary reactions further the degradation process to produce synthesis gas (CO₂, CO, H₂O, H₂) and soot (NSF 2008). Three primary co-products are present at the reactor exit: synthesis gas (CO, CO₂, H₂O), bio-oil, and char. The proportion of each of these is dependent on reaction severity.

A process flow diagram showing pyrolysis-based conversion of woody biomass into liquid transportation fuel is shown in Figure 8.5. In a sand fluidized bed pyrolysis reactor (a common configuration), char and gaseous co-product generated in the pyrolysis reaction are combusted in an integrated recycle vessel to maintain the sand at the required pyrolysis reactor temperature. Liquid bio-oil from the pyrolysis unit is then subjected to hydrotreating and hydrocracking catalytic reactions. Gaseous products from the hydrotreater can be converted to hydrogen and CO₂ using a steam reformer and gas shift reactor. Heavy oil product from the hydrotreater will feed a hydrocracker reactor to generate additional light oil components. The light oil products are then separated into different product blends such as gasoline, diesel, and, potentially, aviation fuel.

The following sections describe the processing steps in more detail and provide information on the properties and stability of pyrolysis bio-oil.

8.3.2.1 Pyrolysis Reactions

Pyrolysis reactions on biomass feedstocks have been carried out under various temperature regimes and in the presence of different solvents (see Mohan et al. 2006, Table 8.5). Carbonization occurs when biomass is heated slowly over several days at approximately 400°C, yielding charcoal as the main product, but also significant amounts of gas (CO₂, H₂O, CO). Conventional pyrolysis features biomass residence times of between 5 and 30 min, a slow heating rate, and 600°C temperature in which the products include synthesis gas, bio-oil, and char. Fast pyrolysis produces mostly bio-oil by using high heating rates, short residence times of 0.5–5 s, and temperatures of 425–650°C and it produces mostly bio-oil, but small amounts of synthesis gas and char. Ultrapyrolysis produces mostly gaseous products and chemicals through very high heating rates, high temperatures of
approximately 1000°C, and ultrashort residence times (< 0.5 s). Vacuum pyrolysis, similar to fast pyrolysis, produces predominantly bio-oil at 400°C, with a 2- to 30-s residence time, and medium heating rate. Hydropyrolysis uses water as a reducing reaction medium to convert woody biomass to bio-oil (mostly at < 500°C), using a high heating rate and a 10-s residence time. Because water is the reaction medium, hydropyrolysis has the advantage that it can accept biomass with field moisture without a drying step. Methanol is used as the reaction medium in methanol pyrolysis, but the main products are chemicals rather than fuels, and reactor conditions include a high heating rate, a residence time of less than 10 s, and temperatures of more than 700°C.

8.3.2.2 Fast Pyrolysis

Because the main focus of this volume is energy products, fast pyrolysis and utilization of bio-oil in energy and fuels applications will be covered in more detail, whereas additional information on other aspects of pyrolysis can be found in several excellent reviews (Bridgewater and Peacocke 2000; Mohan et al. 2006) and the references listed therein. Fast pyrolysis achieves high yields of bio-oil from biomass and lower recoveries of synthesis gas and char by carefully controlling the reaction environment. Typical yields for fast pyrolysis are bio-oil (60–75%), synthesis gas (10–20%), and char (15–25%). A further analysis of bio-oil reveals that water comprises approximately 20–30% by weight, the remaining being oxygenated organic compounds of varying molecular weight. Organic compounds in bio-oil from the carbohydrate fraction of wood are more water soluble, whereas those from lignin are considered more hydrophobic and are higher in molecular weight (NSF 2008). Requirements for fast pyrolysis are rapid heat transfer rates; a finely ground dry (5%) moisture biomass feedstock to achieve high heat transfer and reaction rates; and rapid cooling of pyrolysis vapors and aerosols to avoid degradation, dehydration, and fragmentation.

8.3.2.3 Properties of Pyrolysis Bio-Oil

Before discussing conversion of pyrolysis bio-oil into liquid transportation fuels or the use of bio-oil in heat or power applications, it is necessary to describe the chemical nature and properties of bio-oil.
because these will determine the processing steps needed for upgrading. In addition to H₂O content, which was described earlier, fast pyrolysis bio-oil is composed of the following classes of oxygenated organic compounds in descending order of occurrence (Bridgewater et al. 2001): pyrolytic lignin, 15–25%; aldehydes (formaldehyde, acetaldehyde, hydroxyacetaldehyde, and glyoxal), 10–20%; carboxylic acids (formic, acetic, propionic, and butyric, etc.), 10–15%; carbohydrates (cellobiosan, levoglucosan, and oligosaccharides); 5–10%; phenols (phenol, cresols, guaiacols, and syringols), 2–5%; alcohols (methanol and ethanol), 2–5%; ketones (acetol and cyclopentanone), 1–5%; and furfurals, 1–4%. The key challenge in upgrading these compounds to hydrocarbon transportation fuels is efficient de-oxygenation through hydrotreating, but to limit consumption of hydrogen, saturation of aromatic rings should be avoided (NSF 2008).

Properties of pyrolysis bio-oil and comparisons to petroleum heavy fuel oil are shown in Table 8.5. The ranges of property values in this table are a compilation from a wide diversity of biomass feedstocks, such as hardwoods, softwoods, bark, bagasse, straw, oil seed feedstocks, microalgae, and other sources (Mohan et al. 2006). Additional factors that affect the bio-oil properties listed in Table 8.5 are reaction temperature (400–650°C) and reaction residence time (0.3 s to 30 min).

8.3.2.4 Stability of Bio-Oil

Diebold (2000) reviewed reactions occurring in pyrolysis bio-oil during long-term storage and provided recommendations on improving storage stability. Reactions during aging of bio-oil appear to be catalyzed by organic acids (low pH) and elements found in char. These aging reactions result in changes to the molecular weight distribution of the bio-oil components, increase in bio-oil viscosity, and phase separation of higher-molecular-weight oligomers and polymers. Oxygen from air reacts with organics in bio-oil to form peroxides that catalyze polymerization of olefins and addition of mercaptans to olefins. Organic acids react with alcohols to form esters and water, and aldehydes react with components in bio-oil such as water, alcohols, other aldehydes, phenolics, and proteins to form hydrates, ethers, resins, oligomers, and dimers. In addition, olefins polymerize to form

---

**TABLE 8.5**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Fast Pyrolysis Bio-Oil</th>
<th>Petroleum Heavy Fuel Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-oil yield, % by weight of biomass</td>
<td>17–75</td>
<td>NA</td>
</tr>
<tr>
<td>Water content, % by weight of bio-oil</td>
<td>0–40</td>
<td>0.1</td>
</tr>
<tr>
<td>pH</td>
<td>2.3–5.5</td>
<td>NA</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.91–1.29</td>
<td>0.94</td>
</tr>
<tr>
<td>Elemental composition, % by weight</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>46–78</td>
<td>85</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5–12</td>
<td>11</td>
</tr>
<tr>
<td>Oxygen</td>
<td>11–47</td>
<td>1</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0–10</td>
<td>0.3</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Trace</td>
<td>0.5–3.0</td>
</tr>
<tr>
<td>Ash</td>
<td>Trace–1.5</td>
<td>0–0.1</td>
</tr>
<tr>
<td>Viscosity, centistokes at 50°C</td>
<td>1–50</td>
<td>50</td>
</tr>
<tr>
<td>Higher heating value, MJ/kg</td>
<td>14–41</td>
<td>40</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>–36 to 25</td>
<td>–18</td>
</tr>
<tr>
<td>Solids, % by weight</td>
<td>0.2–3</td>
<td>1</td>
</tr>
<tr>
<td>Stability</td>
<td>Poor</td>
<td>Good</td>
</tr>
</tbody>
</table>


NA, not applicable.
oligomers and polymers. The addition of methanol or ethanol to fast-pyrolysis bio-oil at the 10 wt% level was found to be effective in largely retarding these reactions (Diebold and Czernik 1997). Furthermore, elimination of contact with air, addition of antioxidants, and mild hydrogenation are effective measures to increase storage stability of pyrolysis bio-oils.

8.3.2.5 Catalytic Upgrading of Pyrolysis Bio-Oil

Pyrolysis bio-oil has limited applications as a fuel other than direct combustion in furnaces to provide heat or power. As a result, bio-oil must be upgraded to serve as fuel in vehicular transportation. The goal of upgrading is to increase volatility through molecular-weight reduction, enhance storage stability, and eliminate oxygen to raise product fuel heating value. Catalytic upgrading using hydrogen is accomplished using two main methods: hydroprocessing and catalytic cracking. These upgrading reactions are similar in nature to hydrotreating reactions that occur in conventional petroleum refinery processes. The advantage of producing hydrocarbon fuels from pyrolysis bio-oils, similar to FT reactions of biomass gasification synthesis gas, is the compatibility of the final fuel product with distribution infrastructure in pipelines and with conventional and high-efficiency engines.

Recent reviews have appeared on upgrading pyrolysis bio-oils to liquid hydrocarbon fuels through hydrotreatment and hydrocracking (Furimsky 2000; Huber et al. 2006; Elliott 2007). In hydroprocessing, oxygen is removed from compounds in pyrolysis bio-oils through reactions with hydrogen to produce water plus hydrocarbons, which can be isolated as immiscible separate phases. Various heterogeneous catalyst materials to carry out hydroprocessing reactions on bio-oils include sulfide catalysts found in the petroleum refining industry and precious metal catalysts.

The use of acidic cracking catalysts is well known in petroleum refining to reduce molecular weight and convert fuel components to more aromatic structures. When these catalysts are applied to pyrolysis bio-oils, similar results are observed, but with high levels of coke formation. Zeolitic acid catalysts, such as HZSM-5, yield high ratios of aromatic to aliphatic compounds and have been used to crack the product of pyrolysis bio-oil hydrotreatment. This yields a 5:1 ratio of aromatic to aliphatic product with 30–50% conversion to coke. Coke is burned to recover catalyst and generate process heat. However, a continuing challenge is achieving a good heat balance (NSF 2008).

Long-term catalyst stability and life has not been demonstrated in pyrolysis bio-oils that have been catalytically upgraded. Currently the longest test lasted 8 days before significant hydrotreating catalyst deactivation was observed. Deactivation of cracking catalysts has limited in-process life to only a few cycles in recent experiments. Catalyst deactivation has been attributed to the presence of water on oxide structures of catalysts and to the presence of trace contaminants such as minerals in biomass feedstocks, but the actual mechanisms are not currently well understood (NSF 2008).

8.3.2.6 Power Uses of Pyrolysis Bio-Oil

Pyrolysis bio-oil can be combusted similarly to fossil fuels in boilers, gas turbines, and diesel engine power applications. Co-firing with coal, natural gas, and fuel oil are also options for utilization of bio-oil as a renewable feedstock. Bio-oil has an advantage compared with wood chips and pellets because of its wider application in co-firing applications, which allows easier adaptation to higher-efficiency power generation (conventional natural gas) and advanced power (combined cycle power). A review of pyrolysis bio-oil power generation can be found in a recent publication by Czernik and Bridgewater (2004), showing that bio-oil can be successfully used as boiler fuel and in diesel engine and gas turbine applications.

8.4 BIOCHEMICAL CONVERSIONS PLANT WOODY BIOMASS

Biochemical conversion of lignocellulosic biomass to fuels and other chemicals generally focuses primarily on the isolation of sugars in their monomeric form from hemicellulose and
The four main processing steps are mechanical size reduction, chemical pretreatment, enzymatic hydrolysis, and fermentation. Although mechanical size reduction has obvious effects on downstream equipment and processes and may come before or after chemical pretreatment, the focus of this chapter will be on the remaining three steps: pretreatment, enzymatic hydrolysis, and fermentation.

8.4.1 Overview of Biochemical Conversion Processes

The purpose of pretreatment and enzymatic hydrolysis is to fractionate and recover monomeric sugars from lignocellulosic biomass, whereas fermentation takes those sugars and converts them into valuable products. Cellulose is a linear homopolymer of the six-carbon sugar glucose. Hemicellulose is a branched heteropolymer of five- and six-carbon sugars, primarily xylose, arabinose, galactose, glucose, and mannose. Six-carbon (hexose) sugars are readily fermented by many microorganisms, whereas the five-carbon (pentose sugars) are fermented by only a few native strains (Mosier et al. 2005). Figure 8.6 shows the major unit operations found in a biochemical conversion process for production of ethanol or other fermentation products from woody biomass.

Pretreatment serves two basic purposes: it begins the process of breaking down the more-easily hydrolyzable (mostly hemicellulose) sugars, and it opens up the structure of the lignocellulosic biomass to make the cellulose more accessible for enzymatic hydrolysis. Pretreatment must also preserve the hemicellulose sugars, limit the formation of degradation products, and make it easier to reduce biomass particle size (Mosier et al. 2005).

Separate hydrolysis and fermentation (SHF) is when enzymatic hydrolysis takes place separately from fermentation. However, certain processes can be consolidated in different configurations with some advantages. Simultaneous saccharification and fermentation (SSF) is the term for hydrolysis taking place in the presence of fermenting microorganisms. This reduces the effect of product inhibition during hydrolysis as the fermenting organisms consume the products (sugars) as they are produced If pentose and hexose sugars are being fermented in the same vessel as enzymatic hydrolysis, it is known as simultaneous saccharification and co-fermentation (SSCF). This can be done with a mixed culture of organisms that can ferment five- and six-carbon sugars, or with a single organism that can utilize all sugars.

Ultimately, genetic engineering maybe able to produce custom organisms capable of converting raw biomass into value-added product without pretreatment or enzymatic hydrolysis. This goal is known as consolidated bioprocessing (CBP). SSF and SSCF are preferred to SHF, because minimizing unit operations leads to lower costs. They are generally viewed as realistic near-term possibilities, whereas CBP is a longer-term goal (Mosier et al. 2005; Lynd et al. 2002; Wright 1988).

8.4.2 Pretreatment Hydrolysis Conversions

Pretreatment is among the most costly steps in processing cellulosic biomass, and it has effects on upstream (size reduction) and downstream (enzymatic hydrolysis) processes. For example, more efficient pretreatment can lead to lower enzyme loading requirements for enzymatic hydrolysis. Therefore, the interactions between pretreatment and enzymatic hydrolysis are of critical importance (Mosier et al. 2005; Wyman et al. 2005b). Several pretreatment technologies are available; however, their relative attributes differ. Table 8.6 shows several of the most promising biomass pretreatment methods along with their advantages and disadvantages.

In general, low pH treatments give liquid fractions containing most of the hemicellulose sugars and a solid residue containing most of the cellulose and lignin. High pH conditions remove lignin while leaving a solid residue that contains most of the cellulose and hemicellulose. Although AFEX (ammonia fiber explosion) is a high pH treatment, it does not generate a liquid stream, and therefore essentially 100% of the feedstock is recovered as dry matter with a disrupted structure suitable for
FIGURE 8.6  Process diagram for biochemical conversions of plant woody biomass.
### TABLE 8.6
Promising Biomass Pretreatment Technologies

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low pH Treatments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dilute acid, co-current</td>
<td>0.5–3% sulfuric acid, 130–200°C, 3–15 atm, 2–30 min, 10–40 wt% solids</td>
<td>Monomeric hemicellulose sugars, increases cellulose hydrolysis to near 100%</td>
<td>Costly materials of construction, high operating pressures, hydrolysate conditioning (neutralization required)</td>
</tr>
<tr>
<td>Dilute acid, flow-through</td>
<td>0–0.1% sulfuric acid, 190–200°C, 20–24 atm, 12–24 min, 2–4 wt% solids</td>
<td>Enhances hemicellulose and lignin removal</td>
<td>Challenging to implement commercially, high water use results in high energy requirements</td>
</tr>
<tr>
<td>Hot water/steam autolysis</td>
<td>Hot water, 160–190°C, 6–14 atm, 10–30 min, 5–30 wt% solids</td>
<td>No chemical additions, low capital and operation cost</td>
<td>Incomplete hydrolysis of hemicellulose</td>
</tr>
<tr>
<td>High pH Treatments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AFEX/FIBEX</td>
<td>Anhydrous ammonia, 70–90°C, 15–20 atm, 5 min, 60–90 wt% solids</td>
<td>Lower-cost vessels, hydrolysate conditioning unnecessary</td>
<td>Incomplete hydrolysis of hemicellulose</td>
</tr>
<tr>
<td>ARP</td>
<td>10–15 wt% ammonia, 150–170°C, 9–17 atm, 10–20 min, 15–30 wt% solids</td>
<td>Enhances cellulose digestion, lignin removal</td>
<td>Less effective at softwood pulps</td>
</tr>
<tr>
<td>Lime</td>
<td>0.05–0.15 g Ca(OH)₂/g biomass, 70–130°C, 1–6 atm, 1–6 hours, 5–20 wt% solids</td>
<td>Low temperature, atmospheric pressure; low-cost and inherently safe materials</td>
<td>Longer reaction times required</td>
</tr>
<tr>
<td>Solvent Pretreatments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organosolv</td>
<td>50–80% methanol or ethanol, 180–210°C, approximately 1 h, 2 wt% solids</td>
<td>Easy solvent recovery, lignin isolated as a solid, carbohydrates isolated as a syrup</td>
<td>Complicated washing arrangements, higher energy costs, explosion hazards</td>
</tr>
<tr>
<td>Ionic Liquids</td>
<td>5 wt% solids 130–150°C</td>
<td>Nonflammable, low vapor pressure, high recoverability</td>
<td>Expensive, large antisolvent requirement, little known about long-term prospects</td>
</tr>
</tbody>
</table>

enzymatic hydrolysis. Furthermore, high pH conditions can reduce subsequent cellulase loading requirements for enzymatic hydrolysis, provided that hemicellulase activity is present in sufficient quantity during the enzymatic hydrolysis. Flow-through pretreatments can remove as much as 75% of the lignin in addition to the hemicellulose, leaving behind mostly cellulose in the solids. (Wyman et al. 2005a) A detailed discussion of pretreatment technologies follows.

8.4.2.1 Low pH Pretreatments

8.4.2.1.1 Dilute Acid

Strong acids at 0.5–3 wt% and 130–200°C will hydrolyze most hemicellulose into soluble sugars as well as disrupting and removing some lignin. Dilute acid pretreatment removes and recovers hemicellulose sugars as monomers and increases glucose yields from cellulose to near 100%, but requires costly construction materials, high operating pressures, and neutralization and conditioning of the hydrolyzate before fermentation.

8.4.2.1.2 Hot Water/Steam Autolysis

Hot water under pressure without the addition of acid will hydrolyze hemicellulose in a process similar to a dilute acid co-current pretreatment. Water under pressure has a lower pH, penetrates cell walls, dissolves hemicellulose and some lignin, directly breaks hemiacetal linkages, and catalyzes the breakage of other linkages through released organic acids. This process has lower capital and operating costs, reduces corrosion, and requires no chemical additions compared with dilute acid, but it suffers from the disadvantage of incomplete hydrolysis of hemicellulose and requires hemicellulases later on.

8.4.2.2 High pH Pretreatments

8.4.2.2.1 AFEX/Fiber Extrusion

AFEX is a batch process. The continuous process is called FIBEX (fiber extrusion). This is a dry-to-dry process that produces no liquid stream but a solid and a vapor phase, and it produces no hydrolysis products but only physical disruption of the biomass for increased enzymatic hydrolysis. Biomass is incubated with anhydrous ammonia at elevated temperatures. Rapid depressurization volatilizes ammonia for recovery and increases biomass surface area for enzymatic hydrolysis. Little lignin is removed, but lignin structure is modified, thus diminishing interference with enzymatic hydrolysis. AFEX can be performed in lower-cost vessels than those required for dilute acid pretreatment. The hydrolyzate is compatible with fermentation without conditioning, and it decrystallizes the cellulose, thus increasing downstream enzymatic hydrolysis. Most hemicellulose is recovered as oligomers, which require important hemicellulases in the enzymatic hydrolysis for efficient sugar recovery.

8.4.2.2.2 Ammonia Recycle Percolation/Soaking in Aqueous Ammonia

Ammonia recycle percolation (ARP) is a process in which aqueous ammonia is passed over biomass at elevated temperatures and pressures. Ammonia swells biomass, depolymerizes lignin, and breaks lignin–hemicellulose bonds. A lower-cost alternative is soaking in aqueous ammonia (SAA), which treats biomass in a batch reactor at 25–60°C under atmospheric pressure. ARP enhances cellulose digestion, reduces nonproductive binding of cellulase enzymes, and improves microbial activity, largely because of the removal of lignin, but it is less effective at treating softwood pulps.

8.4.2.2.3 Lime

Typical conditions are 0.1 g lime plus 5 g water per gram biomass. Additional water has little effect on the process. Temperatures can vary from 25 to 130°C, corresponding to treatment times ranging from weeks to hours. For high-lignin materials, additional lignin removal can be accomplished through the addition of oxygen or air. Because this is a low temperature pretreatment, biomass can be treated without a pressure vessel. Approximately 33% of lignin is removed and 100% of acetyl...
groups are removed. It is low cost and uses inherently safe materials, but it requires extremely long reaction times.

8.4.2.3 Solvent Pretreatments

8.4.2.3.1 Organic Solvents

Biomass is treated with an ethanol:water or methanol:water solvent to remove 70–90% of the lignin in the aqueous phase. The solvent is then recovered by distillation, and the condensed black liquor is diluted with water to precipitate lignin. The solvent can also contain a catalyst composed of acids, bases, or mineral salts. Solvents are easy to recover, and lignin is isolated as a solid, whereas carbohydrates are produced as syrup. However, pretreated solids must be washed with solvent before water washing, requiring complicated washing arrangements and higher energy costs. Organic solvents also have to be tightly controlled because of fire and explosion hazards.

8.4.2.3.2 Ionic Liquids

Ionic liquids are salts in which the ions are only loosely coordinated, resulting in a liquid at or near room temperature. Some ionic liquids have been shown to be a good solvent for cellulose, disrupting the crystalline structure, then precipitating out amorphous cellulose after the addition of an antisolvent. Although expensive, ionic liquids have many advantages such as recoverability, low vapor pressure, and nonflammability. Research into ionic liquid pretreatments is still at an introductory stage.

An economic analysis performed by Eggeman et al. (2005) found that major economic effects on plant operations from pretreatment include yield of five- and six-carbon sugars, solids concentration (and subsequent ethanol concentration), enzyme loading, and hemicellulase activity. There is little overall economic differentiation among the pretreatment technologies; low-cost pretreatment reactors were often counterbalanced by higher costs associated with catalyst or product recovery. The process was modeled using ASPEN Plus 10 and implemented in four parts: (1) capital cost estimate, (2) operating cost estimate (in which feed pricing was assumed to be $35/dry t, enzyme pricing is assumed to be $0.15/gallons of ethanol), (3) revenue (from ethanol sales and electricity sales at a price of $0.04/kW-h), (4) and discounted cash flow (2.5 years construction, 0.5 years start-up, and 20 years operation with cash flows discounted at 10%/year). Ethanol pricing is done on a rational pricing basis in which the minimum ethanol selling price (MESP) to achieve a zero net present value is determined. The MESP for the listed pretreatment technologies ranges from $1.34 (dilute acid) to $1.67 (hot water).

8.4.3 Enzymatic Hydrolysis of Cellulose and Hemicellulose

After pretreatment, a solid residue remains that contains cellulose, plus varying amounts hemicellulose and lignin depending on the pretreatment strategy used. Cellulose, and any hemicellulose that may be present, is then hydrolyzed to monomeric sugars for fermentation. The enzymatic hydrolysis step provides the greatest opportunity for biomass ethanol production to be cost-competitive with that of other liquid biofuels (Mosier et al. 2005). SHF is more costly than SSF for several reasons, an important one being that using SSF eliminates the cost of a reaction vessel and reduces the enzyme loading necessary because fermentation consumes the glucose product, which is a strong inhibitor of further enzymatic hydrolysis.

8.4.3.1 Cellulases

Cellulose degrading enzymes are classified by sequence homology into families 1, 3, 5–9, 12, 44, 45, 48, 61, and 74 of the glycoside hydrolases. On the basis of modes of action, they can be classified into three groups: exo-1,4-β-d-glucanases (cellbiohydrolases, EC 3.2.1.91), endo-1,4-β-d-glucanases (endoglucanases, EC 3.2.1.4), and β-glucosidases (EC 3.2.1.21) (McFarland et al. 2007).
In natural systems, these enzymes work synergistically to rapidly break down cellulose into glucose for metabolism. Endoglucanases cleave cellulosic bonds at random, mostly amorphous regions in the cellulose chain, thereby producing more chain ends for cellobiohydrolase attachment. Cellobiohydrolases produce cellobiose and some cellotriose from mostly crystalline regions of cellulose, attaching to chain ends and working progressively along the cellulose chain. The product of this action, cellobiose, is a strong inhibitor of cellobiohydrolase activity. β-glucosidases work on the soluble cellobiose and cellotriose products, breaking them into glucose monomers. All of these enzymes can be produced as complexed enzyme (attached to the surface of the cell) or noncomplexed (released into the environment) according to species (Lynd et al. 2002). To function effectively, cellulolytic enzymes must be able to associate with the insoluble substrate, disrupt the structure, and guide a single polymer chain through the catalytic domain (Eijsink et al. 2008).

Cellulase activity can be determined on several different substrates, natural and artificial, each with its own advantages and disadvantages. Table 8.7 provides a summary of many of the potential substrates. Filter paper is readily available and has a well-established assay method. Avicel can be used to effectively measure exoglucanase activity because it is largely crystalline with a low degree of polymerization. Carboxymethylcellulose (CMC) can be used to measure endoglucanase activity, but methylation blocks progressive action of exoglucanases. Lignocellulosic biomass is a heterogeneous matrix of diverse linkages of polysaccharides and aromatic compounds, and hydrolysis of such biomass is much more complex than for pure cellulose. Activities determined for enzymes on pure cellulose do not necessarily correlate with activities on biomass (King et al. 2009).

**TABLE 8.7**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Detection</th>
<th>Enzymes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Soluble</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Short chain (low DP celldextrins)</td>
<td>RS, HPLC, TLC</td>
<td>Endo, Exo, BG</td>
</tr>
<tr>
<td>Radiolabeled celldextrins</td>
<td>TLC plus liquid scintillation</td>
<td>Endo, Exo, BG</td>
</tr>
<tr>
<td>b-methylumbelliferyl-oligosaccharides</td>
<td>Fluorophore liberation, TLC</td>
<td>Endo, Exo, BG</td>
</tr>
<tr>
<td>β-nitrophenol-oligosaccharides</td>
<td>Chromophore liberation, TLC</td>
<td>Endo, Exo, BG</td>
</tr>
<tr>
<td>CMC, HEC</td>
<td>RS, viscosity</td>
<td>Endo</td>
</tr>
<tr>
<td>Dyed CMC</td>
<td>Dye liberation</td>
<td>Endo</td>
</tr>
<tr>
<td><strong>Insoluble</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cotton, microcrystalline cellulose (Avicel), Valonia cellulose, bacterial cellulose</td>
<td>RS, TSS, HPLC</td>
<td>Total, Endo, Exo</td>
</tr>
<tr>
<td>Amorphous cellulose</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PASC, alkali-swollen cellulose, RAC</td>
<td>RS, TSS, HPLC, TLC</td>
<td>Total, Endo, Exo</td>
</tr>
<tr>
<td>Dyed cellulose</td>
<td>Dye liberation</td>
<td>Total, Endo, Exo</td>
</tr>
<tr>
<td>Fluorescent cellulose</td>
<td>Fluorophore liberation</td>
<td>Total, Endo</td>
</tr>
<tr>
<td>Chromogenic and fluorephoric derivatives</td>
<td>Chromophore liberation</td>
<td>Endo</td>
</tr>
<tr>
<td>TNP-CMC</td>
<td>Fluorophore liberation</td>
<td>Endo, Total</td>
</tr>
<tr>
<td>Fluram-cellulose</td>
<td>HPLC, RS</td>
<td>Total</td>
</tr>
<tr>
<td>Pretreated biomass</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


RS, reducing sugars; TSS, total soluble sugars; HPLC, high-performance liquid chromatography; TLC, thin layer chromatography; HEC, hydroxyethylcellulose; PASC, phosphoric acid swollen cellulose; RAC, regenerated amorphous cellulose.
Reaction conditions for cellulose hydrolysis are frequently in the ranges of 40–50°C, acetate or citrate buffer pH 4.8–5, 15–60 FPU/g-glucan plus excess β-glucosidase, 1–20 wt% solids, 24- to 72-h reaction time.

8.4.3.2 Hemicellulases

Hemicellulose degrading enzymes act specifically on the hemicellulose. Because hemicellulose is a branched heteropolymer, many different hemicellulases are required for efficient enzymatic hydrolysis. Hemicellulases include the xylanases (E.C. 3.2.1.8), β-mannanases (EC 3.2.1.78), α-L-arabinofuranosidases (EC 3.2.1.55) and α-L-arabinanases (EC 3.2.1.99), α-D-glucuronidases (E.C. 3.2.1.139), β-xylosidases (EC 3.2.1.37), xylan esterases (EC 3.1.1.72), and eruloyl esterases (EC 3.1.1.73) (Shallom and Shoham 2003).

8.4.4 Fermentation of Biomass-Derived Sugars to Biofuels

8.4.4.1 Overview of Fermentation-Based Conversions

Fermentation refers to the anaerobic conversion by microorganisms of substrates into products such as acetone, 2-propanol, butanol, hydrogen, methanol, and hydrocarbons chains. Amongst the potential products that could be obtained from fermentations, this chapter focuses mainly on ethanol obtained from five- and six-carbon sugars. Traditional sources of sugars for ethanol production such as corn, sugarcane, and sugarbeets are mostly composed of disaccharides or polysaccharides of six-carbon sugars, but the most abundant feedstocks for ethanol production, lingocellulosic materials, contain six-carbon sugars as well as five-carbon sugars in considerable amounts. The nature of having five- and six-carbon sugars in these feedstocks raises the need of acquiring or developing one or more organisms, or a mixture thereof, to release and ferment these sugars sequentially or simultaneously. The main source of six-carbon sugars, specifically glucose, is cellulose (Zaldivar et al. 2001). Hemicellulose is the source of five-carbon sugars such as arabinose and xylose as well some six-carbon sugars, such as glucose, mannose, and galactose (Badal 2003). Glucose, the main component of cellulose, and xylose, the main component of hemicellulose, are the most abundant carbohydrates on Earth (Zaldivar et al. 2001; Badawl 2003). As stated previously, these carbohydrates can be fermented into several products. The biochemical reactions that summarize their biosynthesis are shown in Table 8.8. Biochemical fermentation of five- and six-carbon sugars is presented in greater detail in the next sections.

8.4.4.2 Fermentation of Six-Carbon Sugars

The preferred biochemical substrate for obtaining energy in the cell is glucose. When glucose is used as a source of energy under anaerobic conditions, it undergoes a process called glycolysis. Glycolysis consists of a series of reactions that mainly produce adenosine triphosphate (ATP), which is the carrier and energy source of all biochemical processes inside of cells. Glucose fermentation or glycolysis consists in a series of ten reactions that break down this carbohydrate into two molecules of pyruvate, which could undergo subsequent reactions to finally obtain acetone, 2-propanol, ethanol (Hahn-Hägerdal et al. 1994; Ostergaard et al. 2000; Dien et al. 2003), and others compounds. Once that pyruvate is produced, it could undergo a series of transformations to acetone, 2-propanol, and ethanol. To produce ethanol, pyruvate is first decarboxylated by the enzyme pyruvate decarboxylase in the presence of magnesium(II) and thiamine pyrophosphate (TPP); as a product of this process, acetaldehyde (2C) is produced. Acetaldehyde is further reduced to ethanol by means of the enzyme alcohol dehydrogenase in the presence of NADH and H+. The overall process of ethanol production is given by the following reaction with a theoretical yield of 0.51 g of ethanol per gram of glucose (Nelson and Cox 2000):

\[
\text{Glucose} \rightarrow 2\text{[Ethanol]} + 2\text{CO}_2 + 2\text{H}_2\text{O} \quad (8.4)
\]

During the treatment of biomass for biofuel production, the six-carbon sugars mannose and glucose are also produced. Also the feedstock for biofuels production could contain fructose. All of
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<table>
<thead>
<tr>
<th>Product</th>
<th>Biochemical Reaction</th>
<th>Theoretical Yield (g product/g substrate)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butanol</td>
<td>C₆H₁₂O€ → C₄H₁₀O + 2CO₂ + H₂O</td>
<td>0.41</td>
<td>Nelson and Cox 2000; Liu et al. 2009</td>
</tr>
<tr>
<td>Acetone, hydrogen</td>
<td>C₆H₁₂O₆ + H₂O → C₃H₆O + 3CO₂ + 4H₂</td>
<td>0.32 for acetone, 0.04 for hydrogen</td>
<td>Nelson and Cox 2000; Liu et al. 2009</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₆H₁₂O₆ → 2C₃H₆O + 2CO₂</td>
<td>0.51</td>
<td>Nelson and Cox 2000; Liu et al. 2009</td>
</tr>
<tr>
<td>Butyric acid</td>
<td>C₆H₁₂O₆ → C₄H₄O₂ + 2CO₂ + 2H₂</td>
<td>0.49</td>
<td>Antonopoulou et al. 2008; Liu et al. 2009</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>C₆H₁₂O₆ + 2H₂O → 2CH₃COOH + 2CO₂ + 4H₂</td>
<td>0.66</td>
<td>Nelson and Cox 2000; Liu et al. 2009; Antonopoulou et al. 2008</td>
</tr>
<tr>
<td>Gasoline-like</td>
<td>Renewable sugars are metabolized into fatty acids, which are subsequently converted into hydrocarbons</td>
<td>Not available</td>
<td>LS9, Inc.</td>
</tr>
</tbody>
</table>

The carbohydrates mentioned before are metabolized as depicted in the previous section after some modifications, entering in the glycolysis cycle in different stages. Mannose, galactose, and fructose are phosphorylated and isomerized to fructose-6-phosphate, which is then fed to glycolysis.

### 8.4.4.3 Fermentation of Five-Carbon Sugars

Five-carbon carbohydrates such as xylose and arabinose are transferred into the cells of microorganisms and converted into xylulose, a five carbon sugar. Xylulose is then fed into the pentose phosphate pathway, where six units of xylulose are converted into five units of glucose, or its isomer fructose (McMillan 1993; Ostergaard et al. 2000; Jeffries and Jin 2004; Dmutruk et al. 2008), which are then fed to the glycolysis pathway. The intermediaries of this process are sedoheptulose, a seven-carbon carbohydrate, erythrose, a four-carbon carbohydrate, and glyceraldehyde. The six-carbon sugars are then fed to the glycolysis process. Overall the process of fermenting six units of xylose to ethanol, by means of the pentose phosphate pathway followed by glycolysis, is summarized by the following reaction with a theoretical yield of xylose to ethanol of 0.51 g of ethanol per g of xylose (McMillan 1993):

$$6[\text{Xylose}] \rightarrow 10[\text{Ethanol}] + 10\text{CO}_2 + 10\text{H}_2\text{O} \quad (8.5)$$

### 8.4.4.4 Fermentation of Five- and Six-Carbon Sugars to Ethanol and Other Biofuels

Ethanol production from lignocellulosic materials deals with the fermentation of xylose (derived from hemicelluloses) and glucose (mostly derived from cellulose). The fermentation of these sugars could be achieved separately or simultaneously. When the fermentation of xylose and glucose occurs in different vessels, it is possible to select a specific microorganism to ferment xylose and a specific microorganism to ferment glucose. When the fermentation is simultaneous, it is possible to achieve the fermentation of both carbohydrates by the use of a mixture of microorganisms or a single specially engineered microorganism (DOE 2006). Also, during the selection of the microorganisms, it is important to consider the technology used to make available the carbohydrates because of the possibility of generation of some inhibitors of fermentation. When lignocellulosic material is subjected to dilute acid hydrolysis at high temperature, furfural and 5-hydroxymethylfurfural are formed. *Saccharomyces cerevisiae* is inhibited by these compounds (Liu 2006). Table 8.9 shows information related to ethanol production from lignocellulosic materials.
### TABLE 8.9
Ethanol Production from Lignocellulosic Materials

<table>
<thead>
<tr>
<th>Microorganism</th>
<th>Substrate</th>
<th>Fermentation Type</th>
<th>Yield (g ethanol/g substrate)</th>
<th>Process Configuration</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Saccharomyces cerevisiae</em> Y-1528</td>
<td>Softwood-derived water-soluble fraction</td>
<td>Batch</td>
<td>0.47</td>
<td>Fermentation only</td>
<td>Keating et al. 2004</td>
</tr>
<tr>
<td><em>Saccharomyces cerevisiae</em> Tembec T1</td>
<td>Softwood-derived water-soluble fraction</td>
<td>Batch</td>
<td>0.44</td>
<td>Fermentation only</td>
<td>Keating et al. 2004</td>
</tr>
<tr>
<td><em>Candida shehatae</em> NCL-3501</td>
<td>Xylose in the range of concentrations from 10 to 80 g/L</td>
<td>Batch</td>
<td>0.40–0.43</td>
<td>Fermentation only</td>
<td>Abbi et al. 1996</td>
</tr>
<tr>
<td><em>Escherichia coli</em> FBR5</td>
<td>Sugars from wheat straw by lime pretreatment and enzyme hydrolysis</td>
<td>Batch</td>
<td>0.26</td>
<td>Simultaneous enzymatic hydrolysis and fermentation</td>
<td>Badal and Cotta 2007a</td>
</tr>
<tr>
<td><em>Escherichia coli</em></td>
<td>Alkaline peroxide pretreated rice hulls</td>
<td>Batch</td>
<td>0.49, 0.48</td>
<td>SHF, SSF</td>
<td>Badal and Cotta 2007b</td>
</tr>
<tr>
<td><em>Saccharomyces cerevisiae</em> and <em>Candida shehatae</em></td>
<td>Mixture of glucose at a concentration of 35 g/L and xylose at a concentration of 15 g/L</td>
<td>Continuous with immobilized microorganisms</td>
<td>0.48</td>
<td>Fermentation only</td>
<td>Lebeau et al. 1998</td>
</tr>
<tr>
<td>Recombinant xylose and cellooligosacharides-assimilating yeast strain$^a$</td>
<td>Sulfuric acid hydrolysate of lignocellulosic biomass with a concentration of total sugars of 73 g/L</td>
<td>Batch</td>
<td>0.41</td>
<td>Fermentation only</td>
<td>Katahira et al. 2006</td>
</tr>
<tr>
<td><em>Zymomonas mobilis</em></td>
<td>Corn stover</td>
<td>Batch</td>
<td>0.30</td>
<td>Co-current dilute acid prehydrolysis and enzymatic hydrolysis</td>
<td>Aden et al. 2002</td>
</tr>
</tbody>
</table>

$^a$ *Saccharomyces* strain with expression of xylose reductase and xylitol dehydrogenase from *Pichia stipitis*, xylulokinase from *Saccharomyces cerevisiae*, and β-glucosidase from *Aspergillus niger*. 

*β*-glucosidase from *Aspergillus niger*. 

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Utilizing mixtures of microorganisms or recombinant microorganisms (DOE 2006), together with enzyme technology for hydrolysis, can contribute to making cellulosic ethanol cost-effective (Solomon et al. 2007) and environmentally beneficial, because its energy output is greater that its energy input (Kemppainen and Shonnard 2005). For unit energy outputted from lignocellulosic material as ethanol, 14% of the energy must be added from fossil fuels, showing a global thermal efficiency of 86% (Kemppainen and Shonnard 2005). Because of the cost-effectiveness and thermal efficiency of cellulosic ethanol technology, there are presently four demonstration plants in operation, three in North America, and the other in Europe. Iogen, located in Ottawa, Canada, has operated since 2004 and has a production capacity of 3000 m³/year of ethanol using wheat, oat, and barley straw. Operating since 2007, ClearFuels Technology of Kauai, Hawaii in the United States has a production capacity of 11,400 m³/year of ethanol using bagasse and wood residues. Celunol, located in Jennings, LA, in the United States, processes bagasse and rice hulls and has produced 5000 m³/year of ethanol since 2007. Scheduled to open in 2009, Etek EtanolTeknik will have a capacity of producing 30,000 m³/year of ethanol from softwood residues of spruce and pine (Solomon et al. 2007).

As stated previously, several products, including biofuels, may be obtained through anaerobic degradation of glucose. The biofuels that could be produced in addition to ethanol are hydrogen and butanol. Antonopoulou and collaborators (2008) produced hydrogen from whey cheese, obtaining a yield of 0.9 mol per mol of glucose. Also, butanol has been produced achieving a yield of 0.4 g of butanol per gram of glucose (Lee et al. 2008). Other biofuels produced by fermentation of sugars are shown in Table 8.10.

### 8.4.4.5 Fermentation of Five- and Six-Carbon Sugars to Hydrocarbons and High-Value Products

The fermentation of five- and six-carbon sugars can produce hydrocarbon chains that could be used instead of gasoline and diesel and allow for the production of other high-value products such as solvents (acetone in Table 8.10), intermediaries to produce plastics, and sweeteners. Park and collaborators (2005) reported that *Vibrio furnissii* M1, when grown in a 50-mL scale with a carbon source of 3 mmol provided by glucose, xylose, starch, or sucrose, yielded between 10 and 27 mg of a mixture of alkanes and alkenes. The chain length of the alkanes and alkenes produced was in the range of C_{14}–C_{27}. LS9, Inc. of San Francisco, CA, produces gasoline-like hydrocarbons from renewable sugars. These sugars are first converted to fatty acids and subsequently to hydrocarbons by certain microorganisms. Roa-Engel and collaborators (2008) reported the

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<table>
<thead>
<tr>
<th>Microorganism</th>
<th>Product and Substrate</th>
<th>Fermentation Type</th>
<th>Yield (g product/g substrate)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Clostridium saccharoperbutylicum</em></td>
<td>Hydrogen from cheese whey</td>
<td>Batch</td>
<td>0.01</td>
<td>Antonopoulou et al. 2008</td>
</tr>
<tr>
<td><em>Clostridium beijerinckii</em></td>
<td>Butanol from glucose</td>
<td>Batch and continuous</td>
<td>0.40</td>
<td>Lee et al. 2008</td>
</tr>
<tr>
<td>NCIMB 8052</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Clostridium sp.</em></td>
<td>Hydrogen from wheat bran</td>
<td>Batch</td>
<td>0.01</td>
<td>Pan et al. 2008</td>
</tr>
<tr>
<td><em>Citrobacter sp.</em></td>
<td>Hydrogen from glucose</td>
<td>Batch</td>
<td>0.03</td>
<td>Oh et al. 2003</td>
</tr>
<tr>
<td><em>Clostridium sp.</em></td>
<td>Acetone and butanol from hydrolyzed agricultural waste</td>
<td>Continuous</td>
<td>For acetone 0.05 For butanol 0.09</td>
<td>Zverlov et al. 2006</td>
</tr>
</tbody>
</table>
production of fumaric acid by fermentation. Fumaric acid could be used as raw material for the polymer industry. This compound is produced from glucose, with a yield of 0.85 g per gram of glucose, by *Rhizopus* species. Also, through fermentation it is possible to produce succinic acid, which is a raw material involved in the making of surfactants, detergents, pharmaceuticals, and foods. Succinic acid is produced by *Actinobacillus succinogenes*. When this microorganism is grown on wheat flour, it produces 0.19 g of succinic acid per gram of substrate (Du et al. 2007). Polyhydroxyalkanoic acids and polyhydroxyalkanoates are biopolymers stored intracellularly as a energy source. These biopolymers present attractive properties in the fields of biodegradation and thermoplasticity. These biopolymers are produced by microorganisms such as *Pseudomonas guezenni* (Simon-Colin et al. 2008) and *Pseudomonas aeruginosa* ATCC 9027 (Rojas-Rosas et al. 2007) using glucose as carbon source. Finally, xylitol, a sweetener, is produced from xylose fermentation by *Candida tropicalis*. This microorganism yields 0.75 g of xylitol per gram of xylose (Kim et al. 2002). Xylitol possesses a higher sweetening power than sucrose and promotes oral health and prevents cavities.

### 8.5 COMPARISON OF ENERGY EFFICIENCIES AND COSTS OF BIOMASS PROCESSING TECHNOLOGIES

Technology energy efficiency and GHG emissions for biomass-derived energy products are of great interest to industry, policy-makers, and government regulators. Energy efficiency here is defined as the ratio of the energy content of the product electricity or biofuel to the energy content of biomass feedstock to the conversion process. GHGs include CO₂ released from the combustion of fossil carbon, nitrous oxide (N₂O), methane, solvents, and refrigerants.

For biofuels especially, GHG emissions over the product life-cycle are of interest to confirm the magnitude of reduction compared with conventional and next-generation fossil-derived fuels. For example, the U.S. Congress set Renewable Fuels Standards (RFS) for each year up to 2022 in the Energy Independence and Security Act (EISA) of 2007 (Congress 2007). The RFS calls for 36 billion gallons of renewable fuels to be produced by 2022, or approximately 25% of current gasoline consumption in the United States (Brodeur-Campbell et al. 2008). Advanced biofuels, according to EISA, are renewable fuels other than corn ethanol, for which the life-cycle emissions of GHG remain less than 50% of fossil gasoline baseline GHG emissions. Of the 36.0 billion gallons of renewable fuels in 2022, it will be required that 21.0 billion gallons be advanced biofuels. Cellulosic ethanol is the nearest to commercialization of the advanced biofuels technologies and is expected to provide a significant fraction of the 21 billion gallons of advanced biofuel mandated by the RFS. Alternatives to cellulosic ethanol exist, including biomass-to-liquid (BTL) diesel and importing ethanol from Brazil. The most likely fulfillment scenario includes a mixture of all of these options (DOE/EIA 2008).

Table 8.11 shows technology energy efficiency of several biomass-to-energy carrier technologies taken from a recent report (Shonnard et al. 2006; Shonnard and Koers 2009). For liquid and gaseous energy products, efficiencies range from 43 to 81% and electricity generation efficiencies are from 27.7 to 38%. Biomass-derived fuels are less efficient than fossil fuels, such as petroleum gasoline or diesel, the conversion efficiencies of which are approximately 80–90%. However, the life-cycle fossil energy savings of biomass-derived fuels are still very large because process energy is largely provided by the renewable biomass feedstock itself rather than from fossil resources (Kalnes et al. 2007; Koers et al. 2009). Thus, the lower technology energy efficiency of biofuels is compensated by substantial savings of fossil energy over the life-cycle.

### 8.6 CONCLUSIONS

The chemical engineering processing routes for converting bioenergy crop plants into liquid transportation fuels are quite diverse, as demonstrated by the broad range of processing technologies
presented in this chapter. Some of these processing technologies are being currently applied in the commercial production of biofuels, but most described here are still in the research and development (R&D) pipeline. However, most of the described chemical engineering technologies are being aggressively developed using R&D investments by government and industry sources. It is the opinion of the authors of this chapter that the future growth of a renewable liquid transportation biofuel industry will depend on the success of these R&D efforts, the goals of which are to increase conversion efficiencies and lower production costs. Commercial success will also depend on advancements in efficient and cost-effective production of bioenergy plant crops as described in other chapters in this handbook.

### Table 8.11

<table>
<thead>
<tr>
<th>Energy Carrier</th>
<th>Production Route</th>
<th>Biomass Resource</th>
<th>Total Investment 2005 $/kW</th>
<th>Technology Energy Efficiency (% LHV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>Combustion (direct, co-firing, gasification)</td>
<td>Any type of biomass, lignocellulosic is preferred</td>
<td>397–926</td>
<td>27.7&lt;sup&gt;a&lt;/sup&gt;, 32.5&lt;sup&gt;b&lt;/sup&gt;, 37&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Thermal conversion (gasification)</td>
<td>Any type of biomass, lignocellulosic is preferred</td>
<td>439–586</td>
<td>60&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Methanol</td>
<td>Thermal conversion (gasification)</td>
<td>Any type of biomass, lignocellulosic is preferred</td>
<td>647–732</td>
<td>55&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>FT liquids</td>
<td>Thermal conversion (gasification)</td>
<td>Any type of biomass, lignocellulosic is preferred</td>
<td>659–879</td>
<td>45&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ethanol from wood</td>
<td>Biochemical conversion (fermentation)</td>
<td>Lignocellulosic biomass</td>
<td>219–428</td>
<td>46&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ethanol from sugar</td>
<td>Biochemical conversion (fermentation)</td>
<td>Sugarcane</td>
<td>208–354</td>
<td>43&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Biodiesel RME</td>
<td>Mechanical/chemical (extraction)</td>
<td>Oily seeds</td>
<td>135–184</td>
<td>45&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Green diesel</td>
<td>Mechanical/chemical (extraction)/catalytic hydrotreatment</td>
<td>Algae, SBO, SFO, RSO, Jatropha, Camellina</td>
<td>170–230 (2008 $)</td>
<td>55–81&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>


<sup>a</sup> Original data given in €/kW. The 2003 average exchange rate of 1.15 was used to convert into 2003 U.S. dollars. Exchange rates were taken from http://epp.eurostat.cec.eu.int (accessed March 15, 2006). The quantities in 2003 U.S. dollars were updated to 2005 U.S. dollars using the harmonized Consumer Price Index.

<sup>b</sup> LHV, low heating value is defined as the amount of energy released when a fuel is burned completely in a steady-flow process and the products are returned to the state of reactants, except water, which remains in the vapor form. This efficiency is only for the manufacturing part of the energy product life-cycle.


REFERENCES


