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ETHANOL AND METHANOL FROM CELLULOSIC BIOMASS

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Cellulosic biomass includes agricultural and forestry wastes, municipal solid waste, and energy crops. Enough ethanol or methanol could be made from cellulosic biomass in countries such as the United States to replace all gasoline, thereby reducing strategic vulnerability and lowering trade deficits for imports. Direct alcohol blends and gasoline containing ethers of ethanol or methanol decrease emissions of carbon monoxide, and neat alcohols reduce smog. In addition, producing alcohol fuels from biomass that is grown sustainably does not contribute to the accumulation of carbon dioxide (CO_2) in the atmosphere. Significant progress has been made over the past few years in the technologies for converting biomass to ethanol or methanol. The simultaneous saccharification and fermentation (SSF) process is favored for producing ethanol from cellulose, because of its low cost potential. Technology has also been developed for converting hemicellulose into ethanol. Burning the remaining fraction—predominantly lignin—can provide enough heat and electricity for the conversion process and generate extra electricity for export. Developments in conversion technology have reduced the projected selling price of ethanol from about U.S.$45 per gigajoule ($0.95 per liter) ten years ago to only about $13 per gigajoule ($0.28 per liter) today.[1] For methanol production, improved gasification technology has been developed, and more economical syngas cleanup methods are available. The projected cost of methanol has been reduced from about $16 per gigajoule ($0.27 per liter) to less than $15 per gigajoule ($0.25 per liter) at present. Technical opportunities have been identified that could reduce the costs of ethanol and methanol produced from cellulosic biomass to levels competitive with gasoline ($0.21 per liter) derived from oil at $25 per barrel.

INTRODUCTION

Transportation issues

As underscored by political volatility in the Middle East, oil represents the most vulnerable component of the industrialized world's energy supply. For example, about 50 percent of all petroleum in the United States is imported, and imports have risen markedly over the past few years [1]. Because the Organization of Pe-

1. Pretax cost of production (COP), assuming a 12 percent discount rate.

troleum Exporting Countries (OPEC) controls about 75 percent of the world's oil reserves, petroleum imports will probably continue to rise in most countries unless alternatives are developed. Transportation fuels are almost totally derived from petroleum and are particularly vulnerable to disruptions. Moreover, imported petroleum accounted for about 40 percent of the balance-of-payments deficit for the United States in 1989 [2].

Much of the smog and carbon monoxide pollution in major cities is caused by automobiles [3]. In addition, global climate change may result from the accumulation of carbon dioxide (CO_2) in the atmosphere from burning petroleum and other fossil fuels [4].

Alcohols from cellulosic biomass

Ethanol and methanol are liquid fuels that can be readily substituted for gasoline in the transportation sector. Replacing gasoline with alcohol fuels produced from renewable sources of cellulosic biomass can improve energy security, reduce the balance-of-payments deficit, decrease urban air pollution, and reduce the atmospheric buildup of CO_2 [5–7]. However, it is necessary to reduce the cost of ethanol and methanol to the point that they can compete with gasoline without tax incentives, so that the benefits of these fuels can be realized.

Biomass types

Through photosynthesis, plants convert CO_2 and water into simple sugars. In plants such as sugarcane, solar energy is stored directly as the chemical energy of these sugars. In crops such as corn, the sugars are converted into starch. These sugars are also joined together to form the carbohydrate polymers cellulose and hemicellulose, which, together with lignin, provide structural support for the plant. In this way, the intermittent energy of the sun is captured in a solid material that can be burned directly to release the stored energy as heat, or thermally processed or biochemically transformed to produce liquid or gaseous fuels. Cellulosic biomass is the main constituent of most forms of plant matter and is much less expensive than cornstarch or sugar because it has no food value and costs less to produce.

Biomass availability

In the United States, researchers estimate that about 77 million hectares of land could be used to produce energy crops for the production of alcohol fuels. At an average productivity of 20 tonnes per hectare per year, about 1.5 billion tonnes of cellulosic biomass could be supplied annually [8]. When underused wood, agricultural residues, and municipal solid waste are included as well, about 2.3 billion dry tonnes of cellulosic biomass per year could be available at prices from \$20 to \$70 per dry tonne [5, 6]. These prices are equivalent to about \$1.10 to \$3.70 per gigajoule; in contrast, oil at \$25 per barrel costs about \$4.00 per gigajoule. This quantity of feedstock can generate more than 1 trillion liters of ethanol and methanol annually, more than enough to meet the total current U.S.

gasoline market of about 425 billion liters per year. Although these values are subject to significant uncertainty, they indicate that the resource base of renewable feedstocks is substantial while the cost is reasonable. Thus, cellulosic biomass is a promising feedstock for fuel alcohol production.

Fundamentals of ethanol production

Ethanol can be produced by biologically catalyzed reactions. In much the same way that sugars are fermented into beverage ethanol by various organisms including yeast and bacteria, sugars can be extracted from sugar crops, such as sugarcane, and fermented into ethanol. For starch crops such as corn, starch is first broken down to simple glucose sugars by acids or enzymes known as amylases. Acids or cellulase enzymes similarly catalyze the breakdown of cellulose into glucose, which can then be fermented to ethanol. The hemicellulose fraction of biomass breaks down into various sugars such as xylose in the presence of acids or enzymes known as xylanases; conventional organisms cannot ferment many of the sugars derived from hemicellulose into ethanol with reasonable yields. However, new technology has been developed to convert hemicellulose to ethanol.

Biological processing offers a number of advantages for converting biomass into biofuels. First, the enzymes used in bioprocessing are typically capable of catalyzing only one reaction, and so formation of unwanted degradation products and by-products is avoided. Additionally, biological transformations occur at near-ambient pressures and temperatures, so that the cost of containment is modest. Furthermore, materials not targeted for conversion can pass through the process unchanged and be used for other applications. Finally, biotechnology and bioprocessing are new and evolving areas with a demonstrated ability to dramatically alter a process and improve economics. Thus, former hurdles to developing cost-effective technologies for producing ethanol from cellulosic biomass may well be overcome.

Fundamentals of methanol production

Methanol is manufactured primarily by thermal processes, which occur at rapid rates. Methanol can be produced from fossil fuels such as natural gas, petroleum naphthas, and coal, and from biomass resources such as woody and herbaceous plants. In general, methanol production consists of three groups of chemical unit operations: 1) synthesis gas (syngas) generation, 2) syngas upgrading, and 3) methanol synthesis and purification. In the case of natural gas and naphtha, syngas generation consists of converting methane and light hydrocarbons to carbon monoxide (CO) and hydrogen (H_2) via steam reforming. In the case of coal and biomass, the solid feed is converted to syngas using gasification. For natural gas and naphtha systems, syngas upgrading consists primarily of CO_2 removal. For biomass and coal systems, the primary synthesis gas is either reformed or shifted to produce a syngas with low methane content and a proper H_2 to CO ratio. Carbon dioxide and sulfur compounds are removed before methanol synthesis. Commercial methanol synthesis operations involve react-

ing CO, H_2, and steam over a copper–zinc oxide catalyst in the presence of a small amount of CO_2 at temperatures of about 500 to 570 K and pressures of about 5.2 to 10.3 megapascals. The methanol synthesis reaction is equilibrium-controlled and excess reactants must be recycled to obtain economic yields. Thermal conversion methods can deal with a wide variety of biomass feedstocks, and methanol technologies are remarkably product specific. Improved gasification and gas conditioning technologies offer the potential to reduce methanol production costs.

ALCOHOLS AS FUELS

Alcohols may emerge as excellent alternative transportation fuels. They can be used in internal combustion engines as blends with gasoline, as neat fuels by themselves, or as oxygenated derivatives that are added to gasoline. Alcohols can also be employed in fuel cells.

Direct blends of ethanol and methanol with gasoline

Alcohol blends enable gasoline engines to run lean and reduce carbon monoxide emissions by 10 to 30 percent [9–12]. Alcohol also increases the octane of the gasoline with which it is blended. At a 10 percent blend with gasoline, ethanol increases the Reid vapor pressure[2] by about 3.4 kilopascals. Increasing vapor pressure increases evaporative emissions, while the addition of the oxygenate reduces tail pipe emissions of unburned hydrocarbons. Estimating the overall effect of ethanol blends on smog formation is complex, but modeling studies generally predict lower overall emissions with ethanol blends. Because methanol increases the Reid vapor pressure by about 10 kilopascals, methanol blends are not widely accepted in the United States, but are routinely used on a cosolvent basis in Europe at levels of up to 3 percent in gasoline [13]. In 1988 the worldwide use of methanol as a gasoline additive was 0.141 million tonnes [15].

Ethyl tertiary butyl ether (ETBE) and methyl tertiary butyl ether (MTBE) blends with gasoline

Alcohols are not fungible with gasoline: they do not ship and handle like other gasoline components. Therefore, they cannot be handled like conventional gasoline in common pipelines and tanks and are not swapped like normal gasoline [16]. This drawback can be overcome if ethanol and methanol are converted to fungible ether blend stocks. Ethanol or methanol can be reacted with isobutylene to form ethyl tertiary butyl ether (ETBE) or methyl tertiary butyl ether (MTBE), respectively, for blending with gasoline [17, 18]. Ethanol, methanol, ETBE, and

2. Reid vapor pressure is the pressure of a fuel mixture in a closed vessel with an air volume four times the volume of the liquid and heated to 38°C. Reid vapor pressure indicates the vapor-lock tendency of a fuel as well as explosion and evaporation hazards: ASTM D-323 [14]. Higher vapor pressure can improve cold starting of an engine but also increases emissions of unburned hydrocarbons that contribute to the formation of smog.

MTBE each contain one atom of oxygen per molecule, and addition of these alcohols or ethers to gasoline reduces CO emissions. However, because one molecule of the alcohol plus one molecule of isobutylene are needed to form one molecule of ether with no loss of oxygen, greater quantities of the ethers must be used to achieve the same blended oxygen content and equivalent alcohol use. For example, a 22 percent blend of ETBE and gasoline results in the same oxygen content and equivalent ethanol use as the direct addition of 10 percent ethanol to gasoline. MTBE is vapor-pressure neutral when blended with gasoline, while ETBE lowers the Reid vapor pressure of gasoline, thereby decreasing the release of smog-forming compounds.

MTBE is the major ether used by the refining industry because of its availability, pricing, fungibility, and its wide acceptance by consumers and the oil and automotive industries. MTBE is already an established gasoline component and has been in use since 1979 when it was approved by the U.S. Environmental Protection Agency (EPA) for unleaded gasoline [16]. Worldwide demand for MTBE was forecast at 2.8 million tonnes in 1990 and is expected to rise to about 8.5 million tonnes by the year 2000 [19]. Although ETBE is not yet a commercial product, substantial interest is mounting in its use [18].

Neat ethanol and methanol

Ethanol or methanol can be employed directly as a neat (close to 100 percent) fuel or hydrated ethanol (95 percent ethanol with 5 percent water), as it is in Brazil [5]. Using hydrated ethanol eliminates the cost of removing the final 5 percent water while providing better performance. Neat ethanol and methanol have many fuel properties that are desirable (see table 1). They provide superior efficiency and performance to gasoline in properly optimized engines because they require lower stoichiometric air/fuel ratios, have higher latent heats of vaporization, provide higher octane values, and have a lower flame temperature. Thus, ethanol and methanol are often preferred to gasoline for high performance automobile races such as the Indianapolis 500. The fact that the majority of new cars in Brazil run on neat ethanol clearly shows that it is a suitable fuel.

Currently, mixtures of 85 percent methanol and 15 percent gasoline (known as M85) or 85 percent ethanol and 15 percent gasoline (E85) are often preferred over pure alcohols for automotive use. The addition of gasoline increases the vapor pressure of the fuel enough to facilitate cold starting. Further engine development is needed to cold start engines with pure ethanol or methanol, particularly during winter months in colder climates.

Air quality problems associated with gasoline use in major cities throughout the world have reduced interest in gasoline options, such as the production of gasoline from methanol, in favor of new fuel and engine options. One of the important considerations favoring the use of neat alcohols is the air emission benefits they offer. Carbon monoxide emissions are similar for the combustion of neat ethanol, methanol, or gasoline in spark ignition engines. However, evaporative emissions during fueling and from the fuel system itself are less for the alcohols

than for gasoline due to the lower vapor pressure of the alcohols. In addition, several types of hydrocarbons and their partial combustion products escape in the engine exhaust of gasoline-powered vehicles. Although some of these organic compounds are toxic, a larger concern is the photochemical reaction of these materials in the atmosphere that increases local ozone concentrations, more commonly referred to as smog. On the other hand, the primary products from the

Table 1: Properties of methanol, ethanol, MTBE, ETBE, isooctane, and unleaded regular gasoline

Property	Methanol	Ethanol	MTBE	ETBE	Isooctane	Gasoline
Formula	CH_3OH	C_2H_5OH	$(CH_3)_3COCH_3$	$(CH_3)_3COC_2H_5$	C_8H_{18}	$C_4 - C_{12}$
Molecular weight	32.04	46.07	88.15	102.18	114	
Density *kg/m³ @ 298 K*	790	790	740	750	690	720–780
Air/fuel stoichiometric ratio						
Mole basis	7.14	14.29	35.71	42.86	59.5	
Mass basis	6.48	9.02	11.69	12.10	15.1	
Higher heating value *MJ/kg*	19.92	26.78	35.27	36.03	44.42	41.8–44.0
Lower heating value *MJ per liter*	15.74	21.16	26.10	27.02	30.65	31.4–33.0
RON	106	106		118	100	91–93
MON	92	89		102	100	82–84
(RON + MON)/2	99	98		110	100	88
Blending RON	135	114–141[a]	118	117–120[b]		
Blending MON	105	86–97[a]	101	101–104[b]		
(Blending RON + MON)/2	120	115	110	111	111	
Atmospheric boiling point *K*	337.8	351.6	328.6	344.8		
Heat of vaporization *MJ/kg*	1.1	0.84	0.34		0.41	
Flash point *K*	280	285	245			
Ignition point *K*	737	697	733			
Reid vapor pressure *kilopascals*						
Pure component		15.85		30.3		
Blending	214+	82.7–186	55.1	20.7–34.5		55.1–103.4
Water solubility *weight percent*						
Fuel in water	100	100	4.3	2	negligible	negligible
Water in fuel	100	100	1.4	0.6	negligible	negligible
Water azeotrope, (atm b.p.), *K*	(none)	351.4	325.4			
Water in azeotrope *weight percent*		4.4	3.2			

a. 10 percent blends.
b. Assumed 12.7 percent blend.

exhaust of an alcohol-fueled engine are unburned alcohol and aldehydes. The alcohols themselves have a lower photochemical reactivity to form ozone than the hydrocarbons associated with gasoline use, but the aldehydes (primarily formaldehyde for methanol combustion and acetaldehyde for ethanol use) are highly reactive. Nonetheless, combustion of ethanol or methanol is expected to contribute less to ozone formation than conventional gasoline when used in vehicles with equivalent emission controls.

Engines designed to run on alcohol emit less oxides of nitrogen (NO_x) because the alcohols burn at lower temperatures than gasoline, and NO_x emissions drop with decreasing temperature. However, as the engine compression ratio is increased to improve the efficiency of alcohol-fueled engine performance, NO_x emissions increase as well, negating much if not all of the NO_x benefit. Excessive NO_x is not a common problem in most cities, but it does contribute to smog formation. The benefits to be gained from the reductions in NO_x and hydrocarbon levels actually vary from city to city. Nevertheless, the consensus is that engines fueled with neat alcohols (including M85 and E85) will improve air quality, although the degree of improvement predicted is quite uncertain for existing atmospheric models [20].

Another plus for alcohols is their water solubility, which makes spills less environmentally threatening. In addition, ethanol has a relatively low toxicity, and both alcohols are readily biodegradable. The energy density of both alcohols is lower than that of gasoline. However, because of their higher octane, higher heat of vaporization, and other favorable properties, dedicated ethanol or methanol engines could achieve higher efficiencies than gasoline engines, thereby compensating for their lower volumetric energy content to some extent [21, 22].

Alcohol fuel cells

Alcohols could be used in fuel cells, devices in which fuel is electrochemically reacted with an oxidant. The fuel and oxidant are separated by an electrolyte that will readily transport ions but not electrons, and the electrons move through an external circuit as the reaction between the ions of fuel and oxidant occurs. Thus, chemical energy is converted into direct current electricity without first burning the fuel to produce heat, much like in a battery, except that the fuel and oxidant are supplied externally. The electricity produced can be used to power an electric motor for a vehicle.

Fuel cells offer a number of advantages compared with internal combustion engines. First, their emissions are several orders of magnitude less than for internal combustion engines, even when the latter are equipped with catalytic converters. Second, the efficiency of fuel use is at least two times greater for fuel cells than for gasoline-fueled, spark-ignited internal combustion engines and one and one half times that for diesel-fueled, compression-ignited engines, which reduces onboard fuel storage requirements. For example, methanol has an energy density deliverable to the wheels of 1,900 Wh per kilogram in a fuel cell versus 900 Wh per kilogram for gasoline in an internal combustion engine. For comparison, a lead

acid battery has an energy density of less than 40 Wh per kilogram, while advanced batteries are expected to have energy densities ranging from 100 to 200 Wh per kilogram [23]. Third, fuel cells are far quieter than internal combustion engines, producing only minor noise associated with the electrical control systems for conversion of direct to alternating current. Like battery-powered cars, fuel cell cars would have electric drive trains, but fuel-cell cars using methanol or ethanol do not require the long charge times characteristic of a battery but are refueled by simply refilling the tank, as with gasoline cars. Compared with internal combustion engine systems, fuel-cell systems would occupy more space and cost more, but the technology could be improved to overcome many, if not all, such problems [23].

Hydrogen can be used directly in fuel cells at high efficiency and with zero pollutant emissions. Moreover, hydrogen can be produced from a variety of renewable energy sources, including electrolytic hydrogen produced from wind or photovoltaic sources and biomass-derived hydrogen (see chapter 22: *Solar Hydrogen*), the latter using the same gasification technology as for making methanol from biomass [24]. However, the low volumetric energy density of hydrogen makes on-board storage difficult, and the lack of a gaseous fuel infrastructure complicates the process of introducing hydrogen as a fuel [23, 25].

Because they are liquids, methanol and ethanol could be introduced and stored much more easily than hydrogen, and methanol in particular has been extensively studied for fuel-cell applications. However, the alcohols are not particularly reactive with known catalysts in aqueous solutions, and large amounts of noble metal catalysts are required for fuel cells that use alcohol fuels directly. Because of the formation of carbon dioxide during oxidation of alcohols, fuel cells employing carbon dioxide–rejecting electrolytes must be used. Direct charging of fuel cells with methanol results in catalyst poisoning by partial oxidation products and unreacted alcohol [26, 27].

The problems posed by fuel cells fueled directly with alcohol can be overcome by reforming the alcohol over solid catalysts to form hydrogen and carbon dioxide. With steam reforming, the alcohol serves as a medium to facilitate the handling and storage of hydrogen fuel [25, 28]. Steam reforming results in a higher fuel-cell efficiency than for fuel cells fueled with alcohol directly. However, reformers start up and change output slowly [25].

To date, most attention has focused on methanol reformers, since methanol is relatively easy to reform, requiring modest temperatures (200 to 250°C) and low-cost (e.g., copper–zinc or copper–chromium) catalysts. In contrast, ethanol reformers have to operate at 500 to 600°C and employ more costly nickel catalysts.

For fuel cells that operate at sufficiently high temperatures, waste heat from the fuel cell could provide the heat for reforming. The phosphoric acid fuel cell (PAFC), which operates at about 200°C, is a good candidate for use with methanol, while the solid oxide fuel cell (SOFC), which operates at a temperature of 1,000°C, would be a good candidate fuel cell for ethanol.

The PAFC is a commercially ready technology, with a demonstrated long life and simple water management requirements. Its disadvantages are its high platinum loading, a slow start-up (about 15 minutes to reach 200°C), the sensitivity of its stack and component structures to shock and vibration, and its low power per unit weight and volume. Its low power density makes it an inappropriate candidate for automotive applications, although it might be useful in other transport areas, such as buses, trucks, trains, or ships. Although the SOFC would have high power density and no noble metal catalyst requirements, this technology is at a relatively early stage in its development.

At present, the most promising fuel cell for automotive applications is the solid polymer electrolyte fuel cell (SPEFC). It offers high power density, fast start-up times, ruggedness, and the potential for low cost in mass production. While SPEFCs have required high platinum catalyst loadings (which limits the potential for cost reduction), recent advances have reduced platinum loadings in laboratory fuel cells to low levels [29]. The SPEFC requires a good water management system to prevent the polymer membrane from drying out, and its intolerance of carbon monoxide limits its inherent compatibility for use with reformed alcohol fuels, but there are various strategies for meeting these challenges [25, 29–31].

Because of the low operating temperature of the SPEFC (about 80°C), some of the alcohol must be burned to provide the heat to operate the reformer. For this reason, and also because of the lower partial pressure of the hydrogen at the fuel cell's anode, a SPEFC operated on alcohol fuel would be less efficient than one operated on hydrogen. Despite this drawback, as well as the fact that hydrogen derived from biomass would probably be less costly delivered to the consumer than methanol from biomass, it is likely that on a life-cycle cost basis a SPEFC car operated on methanol from biomass would be less than one operated on biomass-derived hydrogen, if the hydrogen is stored on-board as a compressed gas, owing to the high cost of gaseous fuel storage (see chapter 22). Moreover, if the cost targets for SPEFCs are reached, a biomass-based, methanol-fueled SPEFC car could well be competitive with a gasoline-fueled internal combustion engine (ICE) car if oil sells for $25 a barrel (see chapter 22).

At present, the U.S. Department of Energy is supporting two fuel-cell projects: the Georgetown Bus Project, which uses a PAFC operated on reformed methanol [32, 33], and a project with the General Motors Company, which is to deliver a methanol-fueled SPEFC prototype automobile within five years [34].

Although fuel cells must be markedly improved before they can widely replace internal combustion engines in motor vehicles, their significantly improved emissions characteristics and high efficiency make them highly desirable.

The value of ethanol and methanol

For blending with gasoline, the following relationship expresses the additional price that a blending company could afford to pay for a fuel additive:

$$(P+\Delta p)f + P(1-f) = P+V \qquad (1)$$

in which P is the price of the base gasoline to which the agent is added, Δp is the amount over the base price the blender would be willing to pay for the fuel additive, V is the increase in value of the fuel with the additive, and f is the volume fraction of additive used. This expression is on a volumetric basis and neglects any change in volume when the two components are mixed (generally small) or any loss in energy content (also small) [35]. Based on this expression, the additional price Δp that can be paid for the fuel additive is:

$$\Delta p = \frac{V}{f} \tag{2}$$

In the case of ethanol, the 10 percent blend commonly used in the United States (known as gasohol) increases the octane level of regular unleaded gasoline to above that of midgrade. If midgrade is worth \$0.013 per liter more than regular (V in the above expressions), then according to the second equation, ethanol is worth \$0.13 per liter more than the base price of the gasoline to which it is added. For a base gasoline price of \$0.18 per liter, the blender would be willing to pay up to \$0.31 per liter for ethanol.

Currently, ethanol sells for about \$0.33 per liter in the United States. Thus, an additional federal excise tax exemption of \$0.013 per liter of 10 percent gasoline blend is used to encourage ethanol use, which translates into \$0.13 per liter of ethanol. When added to the \$0.31 per liter value of ethanol for blending, the total price one could afford to pay becomes \$0.44 per liter, well above the \$0.33 per liter selling price. Yet, ethanol is not widely blended with gasoline except in states with additional incentive programs.

This contradiction is partly due to the poor compatibility (fungibility) between ethanol and existing gasoline supplies, which causes problems with storage, transport in pipelines, and the effect of water on fuel properties. In addition, ethanol is typically blended with regular unleaded gasoline, and the vaporization characteristics and other fuel properties are different from typical gasoline [12]. Although the base gasoline formulation could be changed to compensate for these effects, the small companies that typically blend ethanol with gasoline are not equipped to make such adjustments, and the fuel that results can cause vapor lock and other problems in some engines. Consequently, ethanol blends are often viewed unfavorably by the public and must often be sold at lower prices than competing products. Another factor influencing the price differential is that ethanol is typically blended at the distributor's site, and the relationships above do not include the cost of blending equipment and additional storage vessels for the distributor.

For other fuel additives, such as MTBE, the picture is more complex because adjustments are made in the base gasoline composition. To simplify this analysis, if we consider the blending of MTBE with gasoline to have the same Δp as ethanol, then a blender would be willing to pay \$0.31 per liter for MTBE. Currently [36], MTBE sells for about \$0.25 per liter. In addition, MTBE is compatible

with the existing gasoline infrastructure for storage and transportation, can be manufactured and blended at the refinery site, does not change fuel properties noticeably, and has little negative publicity [37]. Consequently, MTBE is widely used in the United States without special tax considerations and is the basis for "reformulated" gasolines being marketed to reduce smog and carbon monoxide.

The price A that a consumer would be willing to pay for a neat alcohol fuel is given by:

$$A = \eta e P \tag{3}$$

where η is the relative efficiency of the alcohol as a fuel compared with the base fuel, e is the ratio of volumetric energy content of the alcohol fuel to that of the base fuel, and P is the price of the base fuel. The energy ratio e for methanol is about 0.50 and for ethanol the value is about 0.67 compared to gasoline (see table 1). Thus, if we assume no efficiency increase for the alcohols relative to gasoline, methanol must sell for only half the price of gasoline, and ethanol would have to sell for two-thirds the price of gasoline. Furthermore, ethanol is worth about 33 percent more than methanol. Yet, experience with the alcohols suggests that a 20 percent gain in engine efficiency can be obtained relative to gasoline in a well-designed engine [22, 38]. This improved efficiency is due to the greater octane, higher heat of vaporization, and other properties of ethanol and methanol. In this case, the price the consumer would be willing to pay for neat ethanol is 80 percent of that of gasoline; neat methanol is now worth 60 percent of the price of gasoline. Recent prices of gasoline, ethanol, and methanol [36] give a methanol-to-gasoline price ratio of about 80 percent and an ethanol-to-gasoline price ratio of 160 percent with natural gas and corn as the feedstocks, respectively. Thus, customers would prefer gasoline to either alcohol, if price is the only factor in their decision, and methanol from natural gas is now closer to being competitive with gasoline than ethanol derived from corn. For that reason, methanol is preferred over ethanol as a substitute for gasoline in programs such as the one being undertaken in California. Historically, however, prices exhibit substantial seasonal variation. In September 1990, U. S. Gulf Coast methanol prices (FOB barge) were \$0.09 per liter; in January 1991, they were \$0.16 per liter [39, 40]. Likewise, ethanol prices vary considerably both with season and with changes in gasoline prices. For example, ethanol prices in the United States fluctuated from about \$0.40 per liter in September 1990 to \$0.32 per liter in January 1991 [41, 42].

Currently, several major U.S. automobile manufacturers, such as Ford and General Motors, sell internal combustion engines that can use gasoline, methanol, ethanol, or any mixture of the three. The so-called flexible-fueled vehicles use fuel sensors to measure the composition of the fuel, and an on-board computer to adjust the air/fuel ratio and timing to ensure proper performance. However, some engine settings, such as the compression ratio, are not readily adjusted during operation and must be set to accommodate the generally poorer characteristics (such as lower octane) of gasoline compared with the alcohols. As a result, the alcohols achieve little, if any, performance advantage in these en-

gines. On the other hand, since ethanol and methanol perform about the same, inflexible settings in a dedicated alcohol engine could be optimized to achieve better efficiencies with either alcohol than with gasoline, and the fuel line sensor could be employed to adjust the air/fuel ratio and timing to accommodate either ethanol or methanol or mixtures of the two. Such engines are not much more expensive than conventional ethanol or methanol engines, and widespread use of this technology would allow motorists to readily switch between ethanol and methanol, based on price and regional availability. Thus, it appears that the market infrastructure could allow introduction of both fuels and accommodate differences in regional availability or preference for the two alcohols.

If alcohol fuel cells are successfully commercialized, the value of alcohols relative to gasoline in internal combustion engines might increase, owing to the higher overall efficiency of fuel cell vehicles. However, this value is determined not only by relative efficiencies but also by relative system capital and operating costs.

ETHANOL PRODUCTION

Ethanol has experienced several periods of strong demand over the years. It became important during World War I and World War II because petroleum products were scarce. In the 1930s, a blend of ethanol and gasoline was sold in several U.S. midwestern states, but because it could not compete with inexpensive domestic petroleum, its use soon ended. As energy prices rose in the 1970s, interest in ethanol as a transportation fuel was revived in the United States and Brazil. Although ethanol from sugar and corn can be produced commercially, the inexpensive conversion of cellulosic biomass to ethanol is still under development. Production of ethanol from sugar crops in Brazil is discussed in chapter 20: *The Brazilian Fuel-alcohol Program* and will not be considered further here.

Biomass composition

Carbohydrates, including sugars, are among the most abundant constituents of plants and animals and serve many vital functions. They provide energy and also form supporting tissues of plants and some animals. Carbohydrates are classified as mono-, di-, tri-, tetra-, and polysaccharides, depending on the number of sugar molecules that form them. Practically all natural monosaccharides contain five or six carbon atoms, known as pentoses and hexoses, respectively.

The disaccharide known as cane sugar, or sucrose, can be broken down into the six-carbon sugars glucose and fructose by hydrolysis. Sugarcane and other plants contain about 10 to 15 percent sucrose. About 70 percent of corn seed is the polysaccharide known as starch (see figure 1), which is a mixture of straight-chained and branched polymers of glucose with molecular weights ranging up to 1 to 2 million. Hydrolysis of starch by acids or enzymes known as amylases forms glucose sugar.

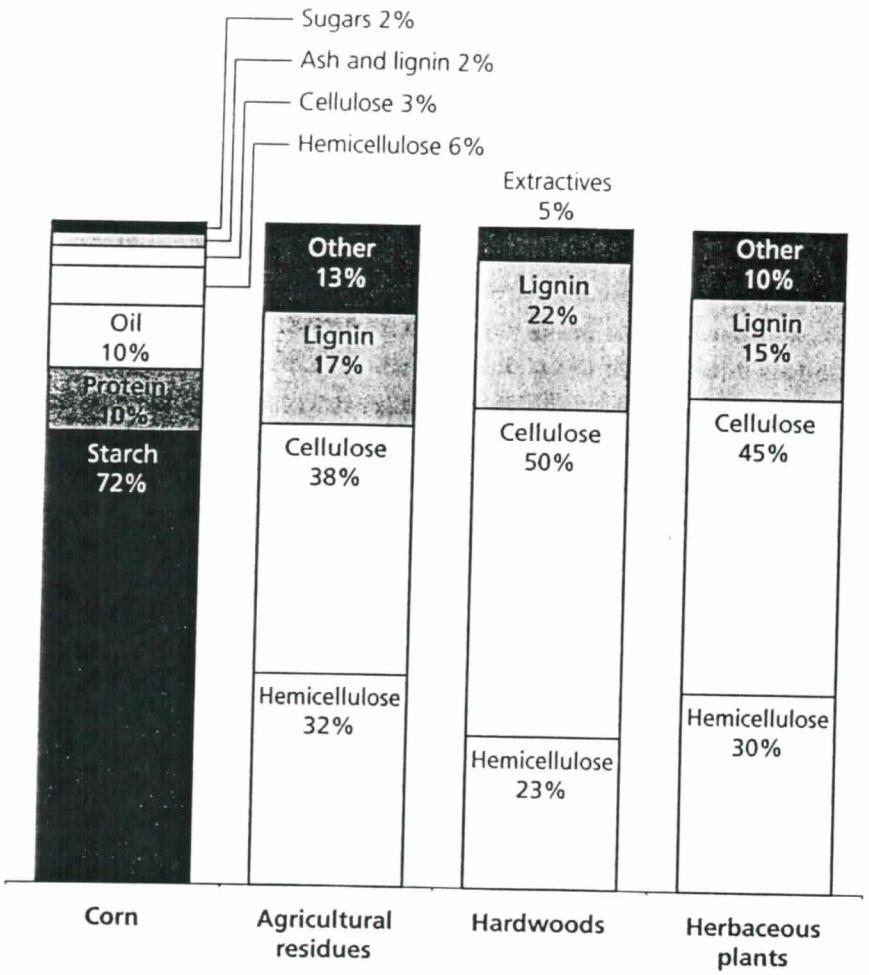

FIGURE 1: Starch crops, such as corn, are made up of about 70 percent starch. The remaining fraction is primarily protein, oil, cellulose, hemicellulose, and lignin. Cellulosic biomass consists of cellulose, hemicellulose, lignin, and some extractives as shown here for representative examples of agricultural residues (corn cobs), hardwood, and herbaceous plants.

Cellulosic biomass is actually a complex mixture of carbohydrate polymers known as cellulose and hemicellulose, plus lignin and a small amount of other compounds known as extractives. Examples include agricultural and forestry residues, municipal solid waste, herbaceous and woody plants, and underused standing forests. Cellulose is generally the largest fraction, representing about 40 to 50 percent of the material by weight (see figure 1); the hemicellulose portion represents 20 to 40 percent of the material. The remaining fraction is predominantly lignin with a lesser amount of extractives. The cellulose fraction is composed of glucose molecules bonded together in long chains that form a crystalline structure. The hemicellulose portion is made of long chains of different sugars and lacks a crystalline structure. For hardwoods, the predominant component of hemicellulose is xylose. Softwoods are generally not considered a viable feedstock for the dedicated production of energy in the near term because competition

from the paper industry and other markets makes softwoods too expensive. In addition, hardwoods are more amenable to the short-rotation production methods that offer the potential for the low costs vital for large-scale energy applications (see chapter 14: *Biomass for Energy: Supply Prospects*).

Ethanol from starch crops

Two processes are used to produce ethanol from corn and other starch crops in the United States: dry milling and wet milling. In dry milling, the feed material is ground mechanically and cooked in water to gelatinize the starch. Enzymes are then added to break down the starch to form glucose, which yeast ferments to ethanol. The fermentation broth passes through a series of distillation columns to recover a 95 percent ethanol/5 percent water mixture, which is then passed through additional distillation columns or molecular sieves to recover pure (close to 100 percent) ethanol. The solids from fermentation are recovered, dried, and sold as a cattle feed called distillers' dried grains and solubles (DDGS), which contain about 27 percent protein. In this process, about 440 to 460 liters of ethanol, 380 kilograms of DDGS, and 340 kilograms of carbon dioxide are produced per dry tonne of corn.

In wet milling, the insoluble protein, oil, fiber, and some solids are removed from the corn first, with only a slurry of starch fed to the ethanol production step. The enzymatic breakdown of starch, fermentation of glucose, and recovery of ethanol parallel those of the dry milling operation, but only the enzyme, unconverted starch, and yeast are left for recovery as a solid material following the wet milling process. About 37 kilograms of corn oil per dry tonne of corn are refined for human consumption. About 70 kilograms of a 60 percent protein product known as corn gluten meal are recovered per tonne of corn and sold for poultry feed. Also recovered prior to ethanol fermentation are 275 kilograms per tonne of corn of a 21 percent protein product used in cattle feed called corn gluten feed. During fermentation, about 440 liters of ethanol and 330 kilograms of carbon dioxide are produced per tonne of corn.

In 1987, fuel ethanol production from starch crops (primarily corn) provided gasohol equivalent to 8 percent of the U.S. gasoline market, up from less than 1 percent in 1981. Today about 7 million tonnes of corn are now used each year to provide more than 3 billion liters of anhydrous ethanol, (the equivalent of 0.06 exajoules), for 10 percent blends with gasoline [9]. There are about 50 fuel-ethanol manufacturing facilities in the United States using corn and other grains as feedstocks for ethanol production with about two-thirds of the ethanol production coming from wet milling and the remainder from dry milling operations [9]. However, ethanol from corn sells for between $0.29 per liter and $0.41 per liter and the price of corn at about $110 per tonne is too high to produce ethanol at prices competitive with gasoline at today's wholesale prices of $0.15 to $0.20 per liter, even with substantial coproduct credits [5]. Thus, relaxation of gasoline taxes is employed to encourage use of ethanol blends in the United States. The U.S. Department of Agriculture (USDA) estimates that an additional 15 to 19 bil-

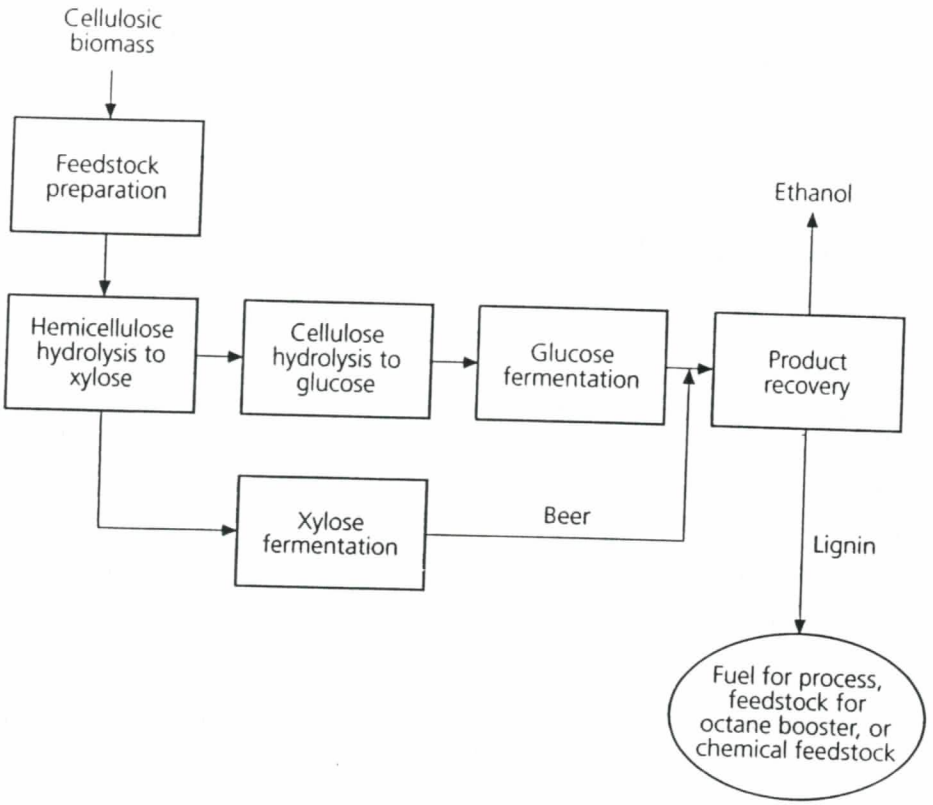

FIGURE 2: Process flow diagram for conversion of cellulosic biomass to ethanol.

lion liters of ethanol could be produced from 34 million tonnes of corn in the United States without jeopardizing agricultural resources and raising grain prices [43]. Thus, corn provides a valuable source of ethanol in the short run, but the increase in grain prices and the decrease in coproduct prices with increased production could hinder major displacement of gasoline by ethanol produced from corn.

Ethanol from cellulosic biomass

Various cellulosic feedstocks can be produced at costs much lower than the cost of growing corn and seemingly would be attractive for fuel production. However, these materials have evolved a natural resistance to decomposition that has ensured the survival of plant life. Thus, despite the low cost of the biomass substrate, the cost of biological conversion, until recently, has been too high to seriously consider economic application of cellulosic materials for biofuels production, but this situation is changing.

For production of ethanol, the cellulosic feedstock is first pretreated to reduce its size and open up the structure to facilitate conversion, as shown in figure 2. The cellulose fraction is hydrolyzed by acids or enzymes to produce glucose, which is subsequently fermented to ethanol. The soluble xylose sugars derived from hemicellulose are also fermented to ethanol, and the lignin fraction, which cannot be fermented into ethanol, can be used as fuel for the rest of the process,

converted into octane boosters, or used as a feedstock for the production of chemicals.

Acid-catalyzed processes

Several dilute acid hydrolysis pilot plants were constructed in Germany and the United States during wartime to produce ethanol as a petroleum substitute [44], but the economics were too unfavorable for continued postwar operation. Dilute acid–catalyzed processes are currently operated in the former Soviet Union for converting cellulosic biomass into ethanol and single-cell protein. Thus, acid-catalyzed processes provide a near-term technology for production of fuel-grade ethanol from cellulosic biomass, but the low yields of sugars from cellulose and hemicellulose (about 50 to 60 percent of the theoretical maximum) typical of dilute acid systems make them unable to compete with existing fuel options in a free market economy [45, 46]. Concentrated sulfuric or halogen acids achieve high yields (essentially 100 percent of theoretical). However, because low-cost acids (such as sulfuric) must be used in large amounts while more potent halogen acids are relatively expensive, recycling of acid by efficient, low-cost recovery operations is essential to achieve economic operation [47,48]. Unfortunately, the acids must also be recovered at a cost substantially lower than that of producing them from raw materials, which is a difficult requirement.

Enzymatic hydrolysis technologies

Enzymatic hydrolysis emerged from U.S. Army research during World War II aimed at finding ways to overcome microbial attack on the canvas (cellulosic) webbing and tents of soldiers stationed in the tropics. These studies in turn led to research on the possibility of promoting the decomposition of cellulose by a fungus responsible for the breakdown of cotton, now named *Trichoderma reesei*, in hopes of generating glucose syrups for application to food and then fuel ethanol production [49].

Enzyme-catalyzed processes offer several key advantages. They achieve high yields under mild conditions with relatively low amounts of catalyst. Moreover, enzymes are biodegradable and thus environmentally benign. Although the cost of ethanol produced from enzyme- and acid-catalyzed processes may be comparable at present, enzyme-catalyzed processes have tremendous potential for technology improvements that could bring the cost of ethanol down to levels competitive with those for petroleum-based fuels. Nonetheless, considerable improvement is required to achieve economic application of this technology.

Enzymatic processing steps

The following major steps are involved in converting cellulosic biomass into ethanol based on the application of enzymatic hydrolysis technology (see figure 3).

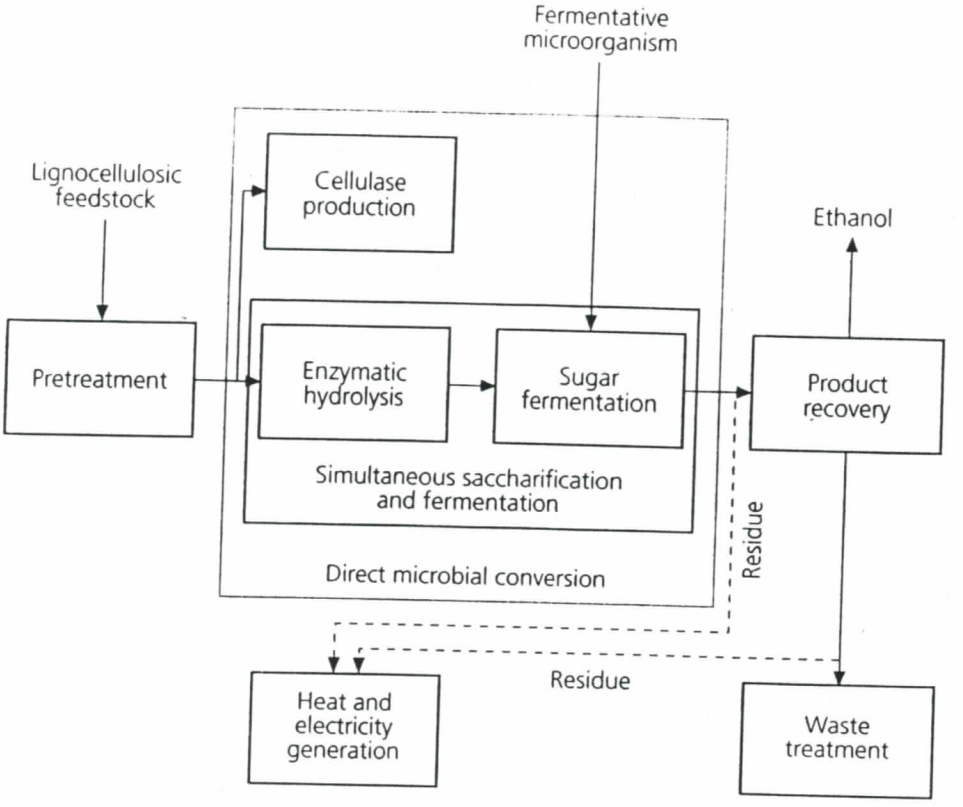

FIGURE 3: The separate steps of cellulose hydrolysis and glucose fermentation characteristic of the separate hydrolysis and fermentation (SHF) process are combined in the simultaneous saccharification and fermentation (SSF) configuration. Direct microbial conversion (DMC) takes this consolidation one step further by using organisms that can produce cellulase as well as ferment sugars, thereby eliminating the separate enzyme production step required for both SHF and SSF.

Pretreatment of cellulosic biomass

Cellulosic biomass is naturally resistant to enzymatic attack. A pretreatment step is required to overcome this resistance if the enzyme-catalyzed hydrolysis process is to proceed at a reasonable rate with the high yields vital to economic viability. The pretreatment step must facilitate conversion of both the cellulose and hemicellulose fractions of biomass into ethanol while minimizing the degradation of these fractions into compounds that cannot be fermented into ethanol. Several options have been considered for biomass pretreatment, including steam explosion, acid-catalyzed steam explosion, sulfur dioxide–catalyzed hydrolysis, treatment with organic solvents, base addition, and dilute acid. At this time, the dilute acid option appears to have the best near-term economic potential [50]. In this process, about 0.5 percent sulfuric acid is added to the milled feedstock, and the mixture is heated to around 140 to 160°C for 5 to 20 minutes. Under these conditions, most of the hemicellulose is hydrolyzed to form xylose, which is removed in solution, leaving a porous material of primarily cellulose and lignin that is

more accessible to enzymatic attack. The primary reaction, hydrolysis of hemicellulose to xylose, can be represented as:

$$(C_5H_8O_4)_n + nH_2O \xrightarrow{\text{acid}} nC_5H_{10}O_5$$

The xylose sugars released by this process can be fermented into ethanol. Pretreating various agricultural residues, short-rotation hardwoods, and herbaceous energy crops with dilute acids has consistently shown that the yield of glucose from the cellulose left in the solid correlates well with the degree of hemicellulose removal [51]. Pretreatment options that remove the lignin fraction may also be effective if an inexpensive system can be devised.

Cellulose hydrolysis and fermentation

In the cellulose hydrolysis step, cellulase enzymes catalyze the hydrolysis of cellulose to glucose sugars by the following reaction:

$$\underset{\text{cellulose}}{(C_6H_{10}O_5)_n} + \underset{\text{water}}{nH_2O} \xrightarrow{\text{cellulase}} \underset{\text{glucose}}{nC_6H_{12}O_6}$$

Yeast can then ferment the glucose into ethanol:

$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{yeast}} \underset{\text{ethanol}}{2C_2H_5OH} + \underset{\text{carbon dioxide}}{2CO_2}$$

Although almost half the weight of the glucose is lost to carbon dioxide, which has no heating value, about 96 percent of the heat of combustion of the cellulose is preserved in the ethanol product [5]. Thus, hydrolysis and fermentation efficiently convert the energy of a solid substrate into a more useful liquid form. A number of yeasts such as *Saccharomyces cerevisiae,* as well as the bacterium *Zymomonas mobilis,* are quite efficient ethanol formers with 92 to 95 percent or more of the glucose going to form ethanol by these reactions.

Although the individual steps for converting cellulosic biomass into liquid fuels can be conveniently isolated (see figure 2), these steps can be combined in various ways to minimize the overall conversion cost. The front-running integrated microbiology-based process configurations are described below.

Separate hydrolysis and fermentation (SHF). The SHF process uses distinct process steps for enzyme production, cellulose hydrolysis, and glucose fermentation (see figure 3) [52, 53]. The primary advantage of this configuration is that enzyme production, cellulose hydrolysis, and sugar fermentation can be treated separately, thus minimizing the interactions between these steps. However, cellulase enzymes are inhibited by the accumulation of sugars, and considerable effort is still needed to overcome this end-product inhibition, which impedes attainment of

reasonable ethanol concentrations at high rates and with high yields even at high enzyme loadings.

Simultaneous saccharification and fermentation (SSF). The sequence of steps for the SSF process is virtually the same as for SHF except that hydrolysis and fermentation are combined in one vessel (see figure 3) [54, 55]. The presence of yeast along with the enzymes minimizes accumulation of sugar in the vessel, and because the sugar produced during breakdown of the cellulose slows down the action of the cellulase enzymes, higher rates, yields, and concentrations of ethanol are possible for SSF than SHF at lower enzyme loadings. Additional benefits are that the number of fermentation vessels is cut in half, and that the presence of ethanol makes the mixture less vulnerable to invasion by unwanted microorganisms.

Direct microbial conversion (DMC). The DMC process combines enzyme production, cellulose hydrolysis, and sugar fermentation in one vessel [56–58]. In the most extensively tested configuration, two bacteria are employed to produce cellulase enzymes and ferment the sugars formed by the breakdown of cellulose and hemicellulose into ethanol. Unfortunately, the bacteria also produce a number of products in addition to ethanol, and yields are lower than for the SHF or SSF processes.

Of the alternatives, the SSF process has emerged as an especially promising route to low-cost fuel ethanol production within a reasonable time frame [50, 59].

Cellulase production

Several organisms, including bacteria and fungi, produce cellulase enzymes that can be used to hydrolyze cellulose into glucose [49, 50, 52, 53, 57, 58]. Currently, genetically altered strains of the fungus *Trichoderma reesei* are favored because of the relatively high yields, productivities, and activities of cellulase that are realized. The best performance is generally achieved in the fed batch mode of operation, in which cellulosic biomass is metered into the fermenter during the growth of the fungus and production of cellulase. Simple batch production of cellulase with addition of all ingredients at the beginning of the enzyme production cycle may be used with good results.

Hemicellulose conversion

The hemicellulose polymers in cellulosic biomass such as hardwood, agricultural residues, and herbaceous plants can be readily broken down during the pretreatment step to form xylose and other sugars. Several options have been considered for utilization of the sugars formed from hemicellulose.

In the presence of acid, the xylose can be reacted to form furfural, either during acid hydrolysis or after xylose recovery [46]. Furfural can be sold for use in

foundry and other applications, but the market would be quickly saturated by the volume of furfural that would accompany large-scale applications of fuel ethanol [60]. Anaerobic bacteria can convert xylose to methane gas, but methane is less valuable than ethanol.

Another avenue is to ferment xylose into ethanol, using strains of yeast such as *Candida shehatae, Pichia stipitis,* and *Pachysolen tannophilus* [61–64]. However, these strains require small amounts of oxygen in the fermentation broth to ferment xylose and typically cannot achieve high ethanol yields or rates or tolerate high ethanol concentrations [65]. Other microorganisms, such as thermophilic bacteria and fungi, can anaerobically ferment xylose into ethanol [6, 66–70]. Although ethanol tolerance, yields, and selectivity are historically low for those choices, some new evidence suggests such conclusions were premature for some bacteria [71]. The common bacterium *Escherichia coli* has been genetically engineered to produce large quantities of xylose isomerase enzyme. This enzyme can convert xylose into an isomer called xylulose, which many yeast can ferment into ethanol under anaerobic conditions [72–75]. By employing the enzyme and yeast together in one vessel, ethanol yields from xylose of 70 percent of theoretical have been achieved, but the need to provide the isomerase enzyme and adjust for differences in *p*H optima between the yeast and enzyme complicates the technology. In another approach, the genes from *Zymomonas mobilis* have been spliced into *E. coli* enabling it to ferment xylose directly into ethanol with high yields [76, 77]. However, further evaluation of the procedure is needed. The latter two options are favored for ethanol production at this time.

For xylose fermentation, the overall reaction stoichiometry can be represented as:

$$\underset{\text{glucose}}{3C_5H_{10}O_5} \xrightarrow{\text{yeast}} \underset{\text{ethanol}}{5C_2H_5OH} + \underset{\text{carbon dioxide}}{5CO_2}$$

Once again, most of the heat of combustion of the hemicellulose is preserved in the ethanol despite the significant loss of weight to carbon dioxide during fermentation; fermentation serves to concentrate the energy from the hemicellulose in a liquid energy carrier [5]. The primary challenge is to ensure that most of the xylose follows the pathway to ethanol production without a significant loss of yield to other by-products such as xylitol.

Ethanol recovery

During fermentation, a 3 to 12 percent solution of ethanol in water is produced, with the exact concentration determined by the substrate, yeast, enzyme, and process configuration. In addition, yeast, inert substances such as lignin, enzymes, and unreacted carbohydrates remain in the broth. In most commercial applications, the entire mixture is fed to a distillation (beer) column that concentrates the ethanol in the overhead product while allowing the solids and water to exit from the bottom. The enriched ethanol stream then passes to a sec-

ond distillation (rectification) column for concentration to about a 95 percent by weight ethanol-in-water product known as an azeotrope.[3] To use ethanol as a hydrated fuel, this azeotrope mixture needs no further processing.

Because water has a low miscibility in gasoline, almost all of it must be removed from the ethanol that will be blended with gasoline. Water in the azeotrope must be removed by some method other than simple distillation. A third component such as benzene or cyclohexane can be added to break the azeotrope and allow purification of ethanol by distillation. Alternatively, molecular sieves can be used to preferentially adsorb the ethanol or water on a solid material such as corn grits. Membranes can also be used that are permeable to one of the components, typically water, while retaining the other by a technology called pervaporation. At present, distillation with a third component and molecular sieves are favored commercially.

Lignin utilization

The amount of the third largest fraction of cellulosic biomass, lignin, is close to that of hemicellulose; thus it is important to derive value from the lignin if ethanol is to be produced economically. Because lignin has a high energy content, it can be used as a process fuel [47, 65, 78]. The amount of lignin in most feedstocks is more than enough to supply all the heat and electricity required for the entire ethanol production process. In addition, the excess electricity or heat can be sold for additional revenue. Alternatively, the phenolic fraction from lignin can be reacted with alcohols to form methyl or ethyl aryl ethers, which are oxygenated octane boosters [79], although high product yields must be realized at low costs to provide a net income gain for the ethanol plant. Or a number of chemicals could be produced from lignin, including phenolic compounds, aromatics, dibasic acids, and olefins [80], which could augment the revenue for the ethanol plant, but the cost must be low enough and chemical yields high enough to ensure a net gain.

METHANOL PRODUCTION

Methanol is produced thermochemically via a two-stage process. The feedstock is first converted to a synthesis gas, composed primarily of H_2 and CO, and the intermediate syngas is then catalytically converted to methanol at elevated pressures. Current global demand for methanol is approximately 23 billion liters per year [81]. Methanol is used as a precursor in the synthesis of many other chemicals. For example, approximately 8.5 billion liters are used each year to make formaldehyde, 1.8 billion liters for ethanoic (acetic) acid, and 3.6 billion liters for MTBE.

3. An azeotrope is a liquid mixture whose composition is the same as that of the vapor in equilibrium with the liquid; separation of the components of the mixture cannot be carried out by distillation or other methods that rely on differences in liquid and vapor composition.

At present, methanol is produced primarily from natural gas and to a lesser extent from other hydrocarbons including propane, naphtha, and heavy oil. These technologies have been commercially available since the 1930s and have evolved into efficient, highly selective processes [82, 83]. But methanol can be produced from almost any carbon-containing resource, including biomass, the only methanol feedstock that is renewable. Although biomass-derived methanol is not produced commercially at present, recent advances in gasification technologies offer potential for the future.

Methanol from biomass

The production of methanol from biomass requires pretreatment of the feedstock, its conversion to syngas, cleanup of the syngas, and then conversion to methanol.

Pretreatment

Biomass must be dried and sized prior to methanol synthesis. Drying to a moisture content of 5 to 15 percent is accomplished using waste process heat, which may come from various unit operations in an integrated methanol production facility. For systems using an indirectly heated gasifier, waste heat for drying typically comes from hot flue gases produced during char combustion. For partial oxidation gasifier/reformer systems, waste heat typically comes from reformer furnace flue gases. The minimum heat required to dry biomass from 50 to 10 percent moisture, about 2 gigajoules per tonne of dry biomass, represents approximately 10 percent of the lower heating value of typical woody biomass, about 19 gigajoules per tonne.

Sizing depends on the specific gasifier technology used to produce synthesis gas. Because of the equipment and energy requirements for biomass size reduction, processes capable of using biomass with the least amount of size reduction or waste have an economic advantage in pretreatment costs over those requiring either fine feeds or very uniform particle size. Some gasifiers require very fine particles; for example, the Koppers–Totzek (K–T) entrained flow gasifier uses a minus-30 mesh (about 595 microns) feed, while many fixed-bed gasifier feeds cannot contain fines. Fluid-bed gasifiers have the greatest flexibility in feed particle size, although extra fine material may be blown from the bed before being gasified.

Synthesis gas production

Synthesis gas, or syngas, is produced from biomass through a gasification process that maximizes carbon monoxide and hydrogen while minimizing unwanted products, including methane. Gasification occurs in an atmosphere of steam and/or oxygen at moderately high temperatures (> 1,000 K) and short residence times (0.5 to 20 seconds). The gasification reactors are operated at pressures of 0.1 to 2.5 megapascals.

Gasification may include both partial oxidation and thermal pyrolysis of the feedstock according to the simplified reactions:

$$\text{Biomass} + O_2 \rightarrow CO + H_2 + \text{heat (partial oxidation)}$$

$$\text{Heat} + \text{biomass} + \text{steam} \rightarrow CO + H_2 \text{ (pyrolysis)}$$

As shown, the pyrolysis step is endothermic and requires heat input, while the partial oxidation step is exothermic. In fact, both reactions occur during gasification. In oxidative systems, the reaction with oxygen provides heat to drive the pyrolytic reactions that break apart the solid biomass. In systems that are primarily pyrolytic, heat must be added from an outside source. The overall heat balance depends on the gasification system and feedstock selected.

The high reactivity of biomass allows processing options that are not available for coal. Not only is there a higher fraction of volatile material in the feedstock, but the resulting char is highly reactive, and so it is possible to use either partial oxidation or thermal pyrolysis as the primary conversion route. With coal, partial oxidation must be used to bring about the high temperatures needed to attain sufficient gasification rates.

Gasifiers using partial oxidation inject oxygen, which has been separated from air, into the reactor to provide heat for the gasification reaction. Operated at high temperature, these gasifiers can produce a syngas with low methane content but require the added cost of an oxygen separation facility. Steam is frequently added to improve char gasification. Oxygen-blown biomass gasifiers, including entrained-flow, fluidized-bed, and fixed-bed configurations, have successfully been demonstrated at scales of 5 to 100 tonnes of wood per day (tpd) [84–86]. Gasifiers designed specifically for wood feedstocks include the Institute of Gas Technology (IGT) and SynGas gasifiers in the United States, the Creusot-Loire facility in France, and the Biosyn gasifier in Canada. Work is either under way or planned for some of these gasifiers.

Even though the use of oxygen will produce a gas suitable for downstream synthesis gas operations, oxygen production is expensive and accounts for a large percentage of capital and operating costs. For example, oxygen costs $40 to $60 per tonne, and is typically used at the rate of 0.25 to 0.30 tonnes per tonne of biomass. This translates to a cost of $10 to $21 per tonne of biomass processed. There are, of course, economies-of-scale in oxygen production. The Union Carbide Company has estimated that a plant producing 2,000 tonnes per day of oxygen has a capital investment, in dollars per tonne of oxygen per day, of approximately two-thirds of that required for a 500 tonne per day facility [87]. In 1990, Chem Systems estimated the capital cost of an approximately 4,340 tpd oxygen facility to be about $23,500 per daily tonne [88].

Biomass can also be converted to syngas in indirectly heated gasifiers, which use pyrolytic reactions. These reactors use heat generated externally by combustion of part of the biomass to drive the pyrolysis and steam gasification reactions. The heat can be provided through the use of fire tubes in a fluidized bed or with multivessel concepts. Examples include the Battelle Columbus Laboratory (BCL)

or the Manufacturing and Technology Conversion International (MTCI) gasifiers in the United States and the Studsvik gasifier in Sweden [89–91]. The fire tube designs may be limited to atmospheric pressure. Other designs should be capable of higher pressures but have not yet been demonstrated above atmospheric. The main advantage of these reactors is the elimination of a separate facility to provide purified oxygen. However, higher methane yields in the product gas will require a reforming step prior to methanol synthesis. Indirectly heated gasifiers could also potentially be operated using heat from solar collectors or other sources. Such alternative methods would increase the amount of gas that would be produced from a given supply of biomass. Although not currently cost effective, they might become attractive with improvements in solar-thermal conversion technology and/or if biomass feedstock costs rise.

Typical biomass gasifiers

Three conceptual gasifiers, which are representative of oxygen-blown and indirectly heated gasifiers, have been used to develop material and energy balances and process economics [92, 93]. The conceptual processes include syngas generation using low-pressure oxygen gasification (LPO), high-pressure oxygen gasification (HPO), and indirectly heated gasification (IND), followed by syngas upgrading and methanol synthesis (see figure 4). Although not shown, all processes require syngas compression prior to methanol synthesis.

The K–T gasifier is a low-pressure oxygen-blown gasifier developed originally for coal and is considered representative of commercially available LPO technology. Table 2 presents typical operating conditions and yields for the K–T gasifier. Also given in table 2 is an estimate of the order of magnitude increase in potential synthesis gas that can be realized through steam reforming of methane and higher hydrocarbons. This estimate is simplified because the shift reaction equilibrium and gas composition after reforming are not shown; the estimate is meant only to indicate that gasifier exit gas rate and composition cannot be used to compare the final methanol production rate.

The process generates a synthesis gas with an H_2/CO molar ratio that is less than 1 and low levels of methane and other light hydrocarbons. The processing downstream of the gasifier is typical of systems proposed for methanol from coal: 1) the syngas H_2/CO ratio is adjusted to match that required for methanol synthesis ($H_2/CO > 2$) in a shift conversion reactor; 2) acid gases (primarily CO_2 for biomass) are removed; and 3) methanol is synthesized and purified. The K–T gasifier requires a small-feed particle size, less than about 600 microns. Because comminution for biomass is energy and equipment intensive, the size requirement results in substantial feed preparation costs. Also, adjustment of synthesis gas composition by rejection of carbon as carbon dioxide results in lower yields compared with the other processes.

The IGT "Renugas" is a high-pressure oxygen-blown fluid-bed gasifier developed specifically for biomass. The gasifier has been operated at a 10 tpd pilot scale, at temperatures up to about 1,255 K, and at pressures up to about 2.38

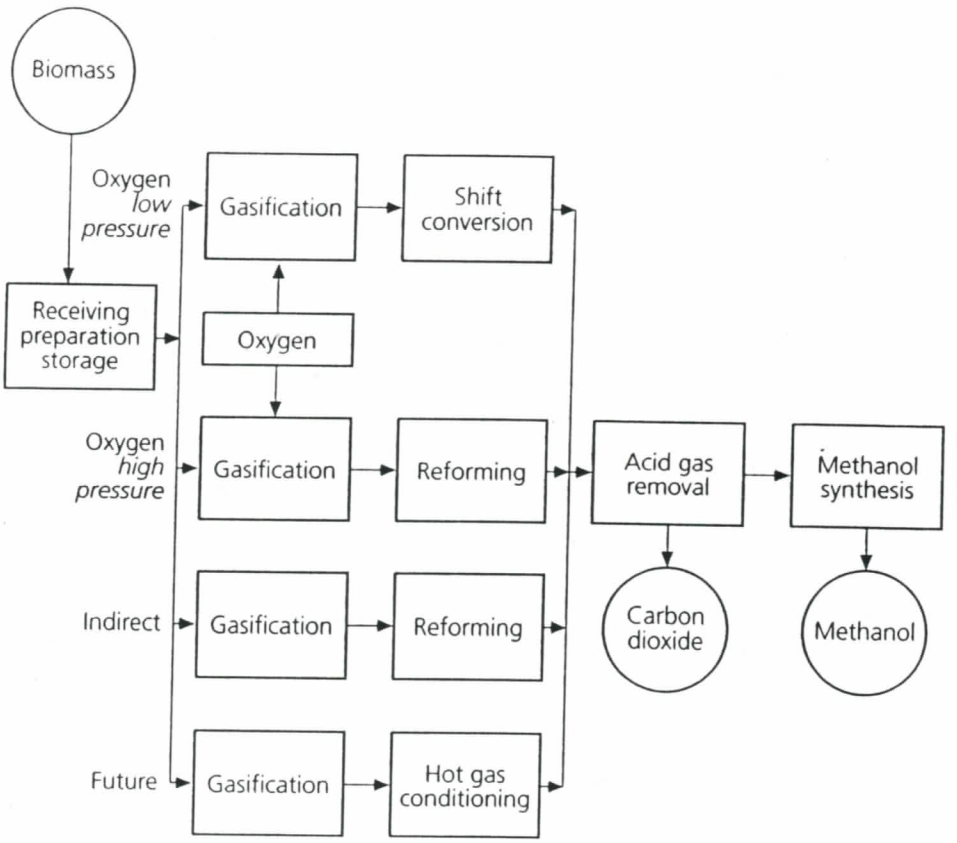

FIGURE 4: Thermochemical production of methanol from cellulosic biomass involves preparation of the feedstock, gasification through one of four primary technologies, removal of carbon dioxide, and synthesis of methanol.

megapascals [85]. Operation at high pressure produces a synthesis gas containing a high level of methane (see table 2). Methane acts as an inert diluent in methanol synthesis. Therefore, the synthesis gas must be reformed to reduce the concentration of methane before methanol is synthesized, in order to increase yields and improve economics. The Chem Systems study assumes that the IGT gasifier can be operated at pressures up to 4.44 megapascals and that no gas conditioning other than particulate removal is required before reforming. These assumptions will have to be confirmed during process scale-up. Operation of the gasifier at pressure eliminates costs and potential problems associated with the compression of syngas before reforming.

The BCL gasifier is a low-pressure, indirectly heated gasifier in which the product char is burned to heat sand, which in turn is mixed with fresh biomass to supply heat for gasification. Indirect gasification (IND) produces a synthesis gas with a low H_2/CO ratio, high levels of light hydrocarbons, and a low level of carbon dioxide. The high level of methane requires reforming prior to methanol synthesis. The synthesis gas is compressed prior to reforming in order to improve reforming economics. In the case study presented here, it is assumed that the raw synthesis gas is quenched, and that tars are recycled to extinction in the gasifier.

Alternatively, tars could be recycled to the combustor to provide process heat. A variation (IND2), in which catalytic hot-gas conditioning is used to both destroy tars and reform methane, gives the same overall conversion. Development of hot-gas conditioning in the United States is at the bench-scale stage and will need significant development; European hot-gas conditioning has not been directed toward elimination of downstream reforming. The BCL gasifier has been operated at the 12 tpd scale and at temperatures up to about 1,280 K [89].

A number of other systems have been developed at the pilot or demonstration scale (see table 3), but are not discussed in this chapter.

Syngas conditioning

Prior to methanol synthesis, the raw syngas must be cleaned and conditioned. Particulate removal is accomplished with cyclones, wet scrubbing, or high-temperature filters. For gasifiers that produce high yields of hydrocarbons, the unreacted methane and other organics must be reformed to generate additional CO and H_2. The reforming reaction is accomplished at 1,000 to 1,150 K, and catalysts, such as sulfided cobalt/molybdate, are used because of small amounts of sul-

Table 2: Gasifier comparison

	Units	K–T[a]	IGT[b]	BCL[c]
Temperature	*K*	1,255	1,255	1,255
Pressure	*megapascals*	0.1013	3.44	0.1013
Dry gas production	*Nm^3 per tonne* [d]	1,347.5	1,065.8	1,027.2
Dry gas composition	*mol percent*			
H_2		36.2	30.9	30.6
CO		44.4	19.8	41.2
CO_2		19.1	36.2	10.9
CH_4		0.3	13.1	14.0
C_2		–	–	3.3
H_2/CO		0.82	1.56	0.74
Dry gas (normalized for CH_4 + decomposition)	*Nm3 per tonne*[e]	1,360	1,485	1,510

a. Koppers - Totzek (K-T) gasifier [92].

b. Institute of Gas Technology (IGT) gasifier [85].

c. Battelle Columbus Laboratory (BCL) gasifier [89].

d. At 273.15 K and 0.10125 megapascals.

e. Example reaction: $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$ (steam reforming).

fur in the gas stream. In general, biomass is deficient in hydrogen for methanol production. The shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$

will be used if necessary to obtain an H_2/CO ratio slightly greater than 2:1. The final step is acid-gas removal, where sulfides and most of the CO_2 are removed from the gas stream. The sulfur content (< 0.1 percent) of the syngas from most biomass is considerably lower than for coal, and a nonselective adsorption system can be used. Final sulfur removal is accomplished by adsorption on zinc oxide.

Methanol synthesis

Methanol is produced from clean syngas by catalytically recombining the carbon monoxide and hydrogen according to the reaction:

$$2H_2 + CO \xrightarrow{\text{catalyst}} CH_3OH + \text{heat}$$

If excess hydrogen is present, carbon dioxide in the syngas reacts with hydrogen to form additional methanol:

$$3H_2 + CO_2 \xrightarrow{\text{catalyst}} CH_3OH + H_2O$$

Table 3: Selected gasification processes and feed materials used

Process	Feed
American Thermogen (U.S.)	Municipal solid waste
Cruesot–Loire (France)	Wood
Davy McKee (U.K., U.S.)	Wood
HTW (Germany)	Peat, lignite
MINO (Studsvik, Sweden)	Wood
MTCI (U.S.)	Wood, agricultural wastes, black liquor
Omnifuel (Canada)	Wood
Pacific Northwest Laboratory (U.S.)	Wood
Pillard (France)	Vegetable wastes
Purox (U.S.)	Municipal solid waste
SynGas, Inc. (U.S.)	Wood, municipal solid waste
Twente (Netherlands)	Wood
University of Missouri-Rolla (U.S.)	Wood
Wellman Galusha	Wood

Methanol is not currently produced from biomass, but the production of clean syngas would lead to the use of systems very similar to those now used for natural gas. Methanol catalysts are highly selective. Less than 2,000 parts per million (ppm) of other products including ethanol and higher alcohols, dimethyl ether, and ketones are produced. Overall process efficiencies are discussed in the section "Methanol from cellulosic biomass, natural gas, and coal."

Methanol synthesis is accomplished at temperatures from 500 to 570 K and at pressures from 5.2 to 10.3 megapascals. Commercial methanol reactors use fixed catalyst beds but vary in the way that heat from the exothermic synthesis reaction is removed from the system. The Imperial Chemical Industries (ICI) axial flow reactor, for example, injects cold syngas at various points to moderate temperature. The Lurgi system uses a tubular reactor system surrounded by a pressurized water boiler. Other heat control designs are available or under development.

Approximately 20 to 25 percent of the syngas is converted to methanol on each pass through the reactor. Methanol is separated by condensation and the remaining syngas is recycled for additional conversion. Purging of the system is required to prevent buildup of inert materials, such as methane or excess CO_2. Because purging also removes CO and H_2, it is important to produce a high-quality syngas prior to methanol synthesis.

Methanol purification

The initial methanol product contains water and small quantities of other organic products. For high-purity chemical applications, the methanol is distilled in a two- or three-column system where the water and higher alcohol fractions are recovered separately. For fuel applications, a single stage distillation would reduce water content to less than 1 percent, and the higher alcohols would be blended back into the fuel.

Methanol from coal

The production of methanol from coal is similar in most respects to that from biomass. Initial processing involves washing and reduces the size of coal particles. Following front-end processing, the coal is gasified to syngas, the syngas is processed, and methanol is produced from the clean product. Again, the type of gasifier chosen will determine the size reduction needed.

Coal-gasification technology is commercially available. For example, the Lurgi gasifier is a fixed-bed reactor, the Winkler gasifier is a fluidized-bed reactor, and the Koppers–Totzek gasifier is an entrained-bed reactor. All three concepts partially oxidize the coal with oxygen separated from air. The Texaco gasifier [94] is a high-pressure, oxygen-blown, entrained-flow coal gasifier based on partial oxidation technology, which was originally commercialized in the late 1950s for converting hydrocarbon liquids and gases to carbon monoxide and hydrogen. The Texaco gasifier operates as a slagging, pressurized, downflow, entrained gasifier in which a coal/water slurry is pumped into the reactor along with oxygen.

Gasification takes place at temperatures in excess of 1,500 K, producing fixed gases such as carbon dioxide, carbon monoxide, and hydrogen, but no liquid hydrocarbons. The raw product gas contains some unburned carbon and molten ash, which must be removed before the gas is used. Texaco gasifier installations include the Tennessee Eastman plant in Kingsport, Tennessee, and the Cool Water plant in Daggett, California. The Texaco gasifier is the basis for coal-to-methanol economics presented later in this chapter.

In addition, a number of indirectly heated coal gasification systems have been developed. While coal is not reactive enough to be gasified indirectly, indirect gasification is feasible with two-stage processes in which coal is first converted to an intermediate product such as coke or char, which is then gasified. The historical "blue water gas" process in which coal is heated in the presence of air to produce an incandescent coke, which is then gasified by steam, is a classic example of indirect coal gasification. In recent times the COGAS process [95] exemplifies a staged pyrolysis-char gasification process.

The syngas from coal is cleaned using technologies similar to those for biomass. The ash content of coal is high and will require special attention, particularly in fixed-bed reactors. The syngas is also reformed to convert unreacted hydrocarbons into additional CO and H_2. The updraft Lurgi reactor, for example, produces significant quantities of partially reacted organics. Coal, being even more hydrogen deficient than biomass, will also require extensive shifting to obtain an acceptable H_2/CO ratio.

Higher sulfur concentrations in most coals require the use of selective adsorbent systems followed by sulfur recovery. CO_2 is also largely removed from the product stream. The resulting syngas is converted to methanol using the technology described above.

Methanol from natural gas

As indicated previously, more than 80 percent of current methanol is produced from natural gas in an efficient, highly selective process. Natural gas is usually processed to remove condensates, propane, and similar components. Sulfur is removed in the initial stages by passing the gas over metal-impregnated activated carbon or zinc oxide. Sulfur must be reduced to less than 0.5 ppm to prevent poisoning of the catalysts downstream.

Pretreated natural gas is then steam reformed to produce primarily CO and H_2 as follows:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

Steam reforming has been practiced commercially since about 1930, and reactor units are available from several manufacturers.

The steam reformer consists of a furnace with an internal tube bundle. Part of the natural gas feedstock is burned to provide heat to the furnace. The natural gas/steam mixture is preheated to 800 to 870 K and passed through the

tubes containing the catalyst, which is generally nickel on a ceramic support. The syngas exits the reactor at 1,170 to 1,270 K and usually contains 0.5 to 3.0 percent residual methane.

Reforming is typically performed at pressures of about 0.1 to 2 megapascals, although pressures up to about 4 megapascals can be used. Pressurization to intermediate levels leads to lower overall system costs, but also suppresses the reforming reaction thermodynamically. For this reason, the percent of unreacted methane will be greatest in the pressurized systems.

Steam reforming leads to a greater ratio of H_2/CO than is required for methanol synthesis. In contrast, biomass systems are hydrogen deficient. In recent natural gas facilities, steam reforming is combined with catalytic partial oxidation by adding purified oxygen from a separation plant. In other cases, CO_2 is purposely added to the reactor. In the methanol synthesis step, the catalyst reacts CO_2 with H_2 to form additional CO and H_2O by the reverse of the second reaction above, so that no additional processing of the syngas is necessary. Methanol is produced from the syngas as described previously.

ECONOMICS

Ethanol from starch crops

The cost of corn varies with the weather, fuel and fertilizer costs, agricultural policy, and other factors. For instance, between 1981 and 1988, the lowest average cost of number 2 yellow corn was $56.80 per dry tonne in 1986, while the highest cost was $164 per tonne in 1984 (see table 4). However, coproduct revenues also vary considerably from a low of $35.90 per tonne of corn in 1985 to a high of $76.90 per tonne in 1984 for the dry milling operation. For wet milling, the low coproduct revenue was $57.80 per tonne of corn produced in 1985, and the high was $86.70 per tonne in 1983. Values for both wet and dry milling coproduct revenues are shown in table 4, assuming no coproduct market for carbon dioxide.

Perhaps more important is the difference between the cost of corn and the revenue gained from the sale of coproducts produced from the corn, a quantity defined by many as the net cost of the corn. For dry milling operations, the highest net cost between 1981 and 1988 was in 1985, when corn cost $130 per tonne and generated only $35.90 per tonne in coproduct revenue; the lowest net cost for dry milling was in 1986, when corn cost $56.80 per tonne and coproduct revenues were $48.90 [96]. Wet milling operations have greater coproduct revenues and lower net corn costs. The lowest net cost was in 1986, when the cost was $56.80 per tonne, but revenues from corn oil, corn gluten meal, and corn gluten feed sales totaled $58.20. On the other hand, only two years earlier, the highest net corn cost occurred for wet milling, with corn costing $149 per tonne, producing only $62 of revenue in coproduct sales. By comparison, remember that ethanol is worth about $0.14 per liter as a neat fuel and about $0.31 per liter

when blended with gasoline, depending on the prevailing price of gasoline. Thus, corn costs and coproduct prices for the dry and wet milling operations can quickly swing from unprofitable to profitable and back.

Table 5 presents the capital and operating costs for corn ethanol plants [9]. Capital costs and maintenance and personnel expenses vary with the size of the operation, with larger plants benefiting from economies-of-scale and more efficient use of personnel. In contrast, energy, chemical, enzyme, and yeast costs are more sensitive to the type of process and whether or not the enzymes and yeasts are purchased or produced on site. The costs in table 5 are for modern ethanol facilities built on bare ground (grassroots plants). The capital costs for wet milling

Table 4: Historical real prices of corn and coproducts for dry and wet milling processes[a]

	Year	Corn cost		Coproduct price[c]		Net cost[d]	
		$per tonne of dry corn[b]		*$per liter of ethanol produced*			
High corn cost							
Dry milling	1984	164.00	*0.358*	69.40	*0.152*	94.60	*0.206*
Wet milling	1984	164.00	*0.373*	80.20	*0.182*	83.80	*0.191*
Low corn cost							
Dry milling	1986	56.80	*0.124*	48.90	*0.107*	7.90	*0.017*
Wet milling	1986	56.80	*0.129*	58.20	*0.132*	–1.40	*–0.003*
High coproduct price							
Dry milling	1984	154.20	*0.337*	76.90	*0.168*	77.30	*0.169*
Wet milling	1983	158.00	*0.358*	86.70	*0.197*	71.30	*0.161*
Low coproduct price							
Dry milling	1985	130.00	*0.285*	35.90	*0.078*	94.10	*0.207*
Wet milling	1985	116.00	*0.265*	57.80	*0.131*	58.20	*0.134*
High net cost							
Dry milling	1985	130.00	*0.285*	35.90	*0.078*	94.10	*0.207*
Wet milling	1984	149.00	*0.338*	62.00	*0.141*	87.00	*0.197*
Low net cost							
Dry milling	1986	56.80	*0.124*	48.90	*0.107*	7.90	*0.017*
Wet milling	1986	56.80	*0.129*	58.20	*0.132*	–1.40	*–0.003*

a. Data from [96] without credit for sales of carbon dioxide for 1981 to 1988.

b. *Multiply values shown by 0.02151 to obtain price in $per bushel.*

c. Coproduct price is revenue generated by coproduct sales per tonne of corn processed.

d. Net cost is defined as the cost of the corn less the revenue generated from the sales of coproducts produced per dry tonne of corn.

operations tend to be near the high end of the range, whereas those for dry milling plants are near the low end. Capital costs are lower if the process is constructed on an existing site, perhaps tying into an existing wet milling operation that already produces other starch products.

Table 6 presents the cost of producing ethanol from corn by both wet and dry milling processes. The wet mill was assumed to be a large, efficient process with a capital cost of 1989 $0.65 per liter for a grassroots plant, and operating costs at the low end of the ranges shown in table 4. Because taxes were not included in this analysis, annual insurance costs from table 5 were taken as 0.5 percent of capital costs. In the first row of table 6, a low net corn cost corresponding to the values shown for 1986 in table 4 was used. Ethanol produced by this scenario would cost $7.76 per gigajoule for a 6 percent rate of return discounted over a 20 year operating life and would cost $9.90 per gigajoule for a 12 percent rate of return over the same period. For the highest net cost of corn values for 1984 in table 4, the cost of ethanol production rises to $17.27 per gigajoule at a 6 percent rate of return and $19.48 per gigajoule at a 12 percent rate of return (these values are presented in the second and sixth rows in table 6). Such tremendous swings in ethanol production costs, varying with corn costs and coproduct prices, show

Table 5: Ranges in production and capital costs for production of ethanol from corn[a]

	Plant size			
	10^3 liters/year		*(10^3 gallons/year)*	
	< 150	***(< 40)***	**150–950**	***(40–250)***
	$ per annual liter		*($ per annual gallon)*	
Capital investment	0.85	*(3.20)*	0.55–0.70	*(2.10–2.70)*
	$ per liter produced		*($ per gallon produced)*	
Fuel				
Coal	0.026–0.37	*(0.10–0.14)*	0.026–0.37	*(0.10–0.14)*
Gas	0.084	*(0.32)*	0.084	*(0.32)*
Electricity	0.010–0.013	*(0.04–0.05)*	0.010–0.013	*(0.04–0.05)*
Chemicals, enzymes, yeasts	0.010–0.032	*(0.04–0.12)*	0.010–0.032	*(0.04–0.12)*
Maintenance	0.042	*(0.16)*	0.029	*(0.11)*
Personnel	0.050	*(0.19)*	0.018	*(0.07)*
Taxes and insurance	2 percent of capital			

a. From [9] for a modern plant built on an undeveloped site (grass roots); transformed to 1989 dollars

how sensitive ethanol prices are to these factors, even for a low-cost, efficient operation. Furthermore, the U.S. Department of Agriculture (USDA) projects that the cost of corn will rise and coproduct prices will drop as ethanol production increases by four to five times current levels [43].

Also shown in table 6 are the costs of ethanol for a small dry milling operation for both low and high net corn cost scenarios from table 4. Capital costs were taken from the entries for smaller plants in table 5 and from the upper portion of the range of costs, as appropriate. It is apparent that the cost of ethanol is about 50 to 60 percent higher for dry milling of corn than for wet milling. All smaller plants in the United States are dry milling operations, mostly smaller in size than the example chosen in table 6.

Ethanol from cellulosic biomass

The preliminary economics of ethanol production from cellulosic biomass presented here are based on a 1990 study performed by Chem Systems for the National Renewable Energy Laboratory (NREL) [97]. Chem Systems developed cost estimates for SSF technology, for two biomass feed rates: 1,745 and 9,090 tonnes plant were comparable in size to the second Chem Systems case. Other improve-

Table 6: Pretax cost of production (COP) for ethanol from corn[a]
1989 U.S.$per gigajoule (LHV) of ethanol

Process	Capital	Feed	O&M	Coproducts	Ethanol
		COP at 6 percent discount rate			
Wet mill *265 million liters of ethanol per year*					
low net corn cost	3.139	6.086	4.771	6.236	7.760
high net corn cost	3.221	15.914	4.771	6.635	17.271
Dry mill *76 million liters of ethanol per year*					
low net corn cost	4.013	5.852	7.433	5.037	12.262
high net corn cost	4.076	13.431	7.433	3.694	21.247
		COP at 12 percent discount rate			
Wet mill *265 million liters of ethanol per year*					
low net corn cost	5.274	6.086	4.771	6.236	9.895
high net corn cost	5.434	15.914	4.771	6.635	19.484
Dry mill *76 million liters of ethanol per year*					
low net corn cost	6.741	5.852	7.433	5.037	14.990
high net corn cost	6.864	13.431	7.433	3.694	24.035

a. Ethanol yields are 440 liters per tonne of corn for a wet mill process and 458 liters per tonne of corn for a dry mill process.

Table 7: Capital and operating cost estimates for producing ethanol from cellulosic materials

	Reference case[a]	Larger scale[a]	Improved technology[b]
Plant size, feed rate *dry tonnes per day (tpd)*	1,745	9,090	2,727
Product rate *Millions of liters per year (denatured, hydrated)*	219	1,096	507
Feed price *1989 U.S. $per GJ (LHV)*	2.45	2.45	2.00
Capital cost *millions of 1989 U.S. $*			
Feed handling	6.91	27.59	10.99
Prehydrolysis	22.54	89.60	36.35
Xylose fermentation	6.02	24.05	3.80
Cellulase production	2.60	10.39	1.37
SSF fermentation	21.60	86.26	10.58
Ethanol purification	3.73	10.71	5.18
Offsite tankage	3.04	7.40	9.09
Environmental systems	3.98	11.42	3.12
Utilities/auxiliaries	57.60	165.34	49.91
Erected plant cost	128.04	432.75	130.40
Owner's costs, fees, and profit	12.81	43.29	
Start-up	6.40	21.62	6.52
Total capital investment	147.24	497.66	136.92
Working capital	9.70	37.54	7.24
Operating costs *millions of 1989 U.S. $per year*			
Variable costs			
Feedstock	26.88	134.39	34.34
Catalyst and chemicals	9.25	46.24	14.83
By-product credits	0.40	2.00	0.63
Utilities	(3.10)	(15.52)	(3.72)
Fixed costs			
Labor	1.59	3.18	1.42
Maintenance	4.40	14.87	3.93
General overhead	3.77	11.31	3.27
Direct overhead	0.72	1.43	0.64
Insurance	0.74	2.49	0.68
Total operating cost	44.65	200.39	56.02

a. [97]. Because Chem Systems estimated all costs in 1987 U.S. dollars, the values were translated to the 1989 U.S. dollar values shown by application of the Nelson–Farrar index [99].

b. [98].

per day (see table 7). Hardwood costing $46 per tonne was received as 2.5 centimeter chips with a 50 percent by weight moisture content and milled to 3 millimeter size by disc refiners. The milled wood was pretreated with dilute sulfuric acid, and a recombinant *E. coli* strain fermented the xylose removed during pretreatment into ethanol. The fungus *Trichoderma reesei* produced the cellulase enzyme in a simple batch process for the SSF process step. Continuous processing was used for cellulase conversion to ethanol. Conventional distillation removed the ethanol from the fermentation broth to produce a neat fuel containing 5 percent water. Gasoline was added as a denaturant to give a product composition of 90.3 percent ethanol, 4.7 percent water, and 5 percent gasoline by weight. Lignin recovered from the bottom of the distillation unit was burned as boiler fuel to provide the heat and electricity for the process, with excess electricity sold. Based on the best estimates of current technical performance for each of these process steps, Chem Systems derived capital and operating costs for the process and carried out sensitivity analyses to identify opportunities for improving the technology. Substantial yield losses, slow reaction rates, large power requirements, and other problems were identified. Using this information, NREL developed preliminary economics for ethanol production from cellulosic biomass based on improved technology that increases yields, speeds fermentation rates, improves energy efficiencies, and addresses other important problems [98].

The improved technology case results in cost reductions from enhanced ethanol yields, rates, and efficiencies judged to be attainable through research. These changes are not exhaustive and do not include radical departures in technology. The costs shown in the improved case were derived from Chem Systems values, vendor quotes, and application of Aspen/SP simulation software [100], where necessary. Mature technology representative of an *n*th plant was assumed throughout.

Capital costs ranged from $498 million for the 9,090 tpd feed rate to $147 million for the 1,745 tpd rate for current technology. For the improved-technology case, the capital cost drops to $137 million for a feed rate of 2,727 tpd.

A cash flow analysis for the Chem Systems reference case with a feed rate of 1,745 tpd is presented in table 8 to estimate the unit cost of ethanol production; the cash flow analysis does not include taxes or depreciation. Similar cash flows were projected for the other two cases described in table 7, and the cost of ethanol production is summarized in table 9 for all three cases. Subtotals are given for unit capital, feedstock, and operating and maintenance costs. At a 12 percent discount rate, the projected price of ethanol ranges from $15.36 per gigajoule for the Chem Systems reference case with a feed rate of 1,745 tpd to $12.59 per gigajoule for a feed rate of 9,090 tpd. At a 6 percent discount rate, costs drop to $13.12 per gigajoule and $11.06 per gigajoule, respectively. With the improved technology, ethanol costs are projected to be only $7.54 per gigajoule for a 12 percent discount rate and $6.65 per gigajoule for a 6 percent discount rate with a feed rate of 2,727 tpd. Costs with improved technology could be reduced further if the

Table 8: Cash flow (excluding taxes) for ethanol production from cellulosic feedstocks
millions of 1989 U.S. $

Year	Ethanol revenue	Electricity revenue	Capital	Working capital	Feed cost	Fixed op costs	Variable op costs	Total costs	Pretax cash flow	Cumulative pretax cash flow
1			44.172					44.172	(44.172)	(44.172)
2			73.620					73.620	(73.620)	(117.792)
3			29.448					29.448	(29.448)	(147.240)
4	35.764	1.860		9.700	16.128	6.732	5.790	38.350	(0.726)	(147.966)
5	47.686	2.480			21.504	8.976	7.720	38.200	11.966	(136.000)
6	59.607	3.100			26.880	11.220	9.650	47.750	14.957	(121.043)
7	59.607	3.100			26.880	11.220	9.650	47.750	14.957	(106.086)
8	59.607	3.100			26.880	11.220	9.650	47.750	14.957	(91.129)
9	59.607	3.100			26.880	11.220	9.650	47.750	14.957	(76.171)
10	59.607	3.100			26.880	11.220	9.650	47.750	14.957	(61.214)
11	59.607	3.100			26.880	11.220	9.650	47.750	14.957	(46.257)
12	59.607	3.100			26.880	11.220	9.650	47.750	14.957	(31.300)
13	59.607	3.100			26.880	11.220	9.650	47.750	14.957	(16.343)
14	59.607	3.100			26.880	11.220	9.650	47.750	14.957	(1.386)
15	59.607	3.100			26.880	11.220	9.650	47.750	14.957	13.571
16	59.607	3.100			26.880	11.220	9.650	47.750	14.957	28.529
17	59.607	3.100			26.880	11.220	9.650	47.750	14.957	43.486
18	59.607	3.100			26.880	11.220	9.650	47.750	14.957	58.443
19	59.607	3.100			26.880	11.220	9.650	47.750	14.957	73.400
20	59.607	3.100			26.880	11.220	9.650	47.750	14.957	88.357
21	59.607	3.100			26.880	11.220	9.650	47.750	14.957	103.314
22	59.607	3.100			26.880	11.220	9.650	47.750	14.957	118.271
23	59.607	3.100		(9,700)	26.880	11.220	9.650	38.050	24.657	142.929

Table 9: Pretax production cost of ethanol from cellulosic biomass
1989 U.S.$per gigajoule (LHV) of ethanol

Process	Capital	Feed	O&M	Electricity	Ethanol
		COP at 6 percent discount rate			
Reference *219 million liters of ethanol per year*[a]	3.292	5.915	4.593	0.682	13.117
Larger scale *1,096 million liters of ethanol per year*[a]	2.237	5.915	3.588	0.683	11.057
Improved *507 million liters of ethanol per year*[a]	1.314	3.268	2.417	0.354	6.646
		COP at 12 percent discount rate			
Reference *219 million liters of ethanol per year*[a]	5.538	5.915	4.593	0.682	15.364
Larger scale *1,096 million liters of ethanol per year*[a]	3.767	5.915	3.588	0.683	12.587
Improved *507 million liters of ethanol per year*[a]	2.208	3.268	2.417	0.354	7.540

a. Denatured hydrated ethanol.

ments in the process steps or application of other enzymatic options offer alternative routes for reducing costs.

Through these engineering studies, several technological opportunities have been identified for reducing the cost of ethanol to about $7 per gigajoule ($0.15 per liter) or lower. First, high yields of ethanol must be achieved with low enzyme costs, realized with improved enzymes, better enzyme production or more efficient pretreatment. High yields of ethanol from hemicellulose are important with high xylose yields from pretreatment, low-cost media for xylose fer-

Table 8: notes

Process: Chem Systems reference case
Capital cost: 147.24 million $
Ethanol COP: $13.44 per gigajoule
Production rate:
219.189×10^6 liters per year
(denatured hydrated product)
4.54×10^6 gigajoules per year
Feed cost: 26.88 million $per year
Discount rate: 6.00 percent

Basis: constant 1989 U.S. $
No escalation
Three-year construction, 20 year operating life
Investment schedule: year 1, 30 percent
year 2, 50 percent
year 3, 20 percent
Production schedule: year 4, 60 percent of nameplate
year 5, 80 percent of nameplate

mentations, and prolonged microbial stability. The economics of production would also benefit by increasing the ethanol concentration to 6 to 8 percent, although advanced distillation apparently can recover lower ethanol concentrations at a reasonable cost [101, 102]. Reducing the enzyme processing times from the current five to seven days to three days for complete fermentation would also achieve significant capital cost reductions through improvements in pretreatment or cellulase technology. The cost of ethanol production could also be reduced by use of low-power mixing devices. Improved fermenter designs can still improve process economics by reducing product accumulation and inhibition of yeast and enzymes and minimization of by-product formation [71, 103]. Although considerable progress has been made in this direction, full-process integration is a key step to establishing the performance of the entire SSF process when operated on actual feedstocks in the actual process sequence to establish interactions among steps.

The feedstock cost for present-day technology was $46 per dry tonne ($2.45 per gigajoule), and the improved technology was based on reducing the cost to about $37 per tonne ($2.00 per gigajoule). The former price is based on prices typical of wood-fired boilers and other operations. The future price is the goal of the Biomass Production Program of the U.S. Department of Energy for production of biomass on energy plantations. A key goal of this technology is to increase biomass productivities to about 20 tonnes per hectare per year.

The current projected selling price of $11.06 to $15.36 per gigajoule ($0.23 to $0.32 per liter) is for engineering designs based on data produced at the bench scale and information on commercial corn ethanol processes. Because significant portions of the process are similar to the production of ethanol from starch crops such as corn, there is good evidence that major sections of cellulosic conversion should perform as predicted from bench-scale experience. In addition, pilot plants for converting biomass to ethanol have been successfully operated in the past, although the level of development was inadequate to achieve economic viability. Nevertheless, before commercialization, the technology must be demonstrated at a large enough scale to gain experience with key items of equipment and gather accurate material and energy balance data. In any such scale-up, problems are to be expected with the selection of equipment, although the largest challenge is the handling of the viscous solids suspensions that must be processed. However, cellulosic biomass slurries are successfully used in the pulp and paper and other industries, so these problems should not be insurmountable. The process should be scaled-up as soon as possible to determine its performance and define areas where R&D is required to ensure that the process will operate as designed. Larger scale operation is particularly needed to verify energy requirements for such operations as size reduction and mixing, as well as to establish the effects of full material balance integration and mixing hydrodynamics.

Waiting for such a pilot plant until all the research targets are met would result in delays in final commercialization of the technology due to unanticipated operational problems and other issues measurable only at a larger scale. In addi-

tion, the pilot plant would provide an opportunity to prove the technology with low-cost feedstocks (such as cellulosic waste streams) once confidence is gained in the operation of the process. Technological improvements can then be integrated into the pilot unit as they become ready for commercial application. Currently, NREL, with funding from the Biofuels Systems Division of the U.S. Department of Energy, is undertaking operation of a pilot plant for ethanol production from cellulosic biomass.

The size and cost of scale-up units are dictated by certainty in process performance, the risk one is willing to accept, the type and cost of the feedstock, and the time frame desired to reach commercial applications. The smallest possible pilot plant [probably in the range of 1 tpd of feedstock] should be built first to provide the data needed so that larger plants can be built with confidence. Following successful operation of this unit, a large demonstration process at the scale of about 50 dry tpd might be built, followed by a commercial unit at the scale of approximately 2,000 dry tpd.

Methanol from biomass

In this section, preliminary economics for methanol production from biomass are presented. The costs of production are presented for a commercial coal gasifier that is adapted to biomass, and for gasifiers currently being developed in the United States specifically for biomass. In a Chem Systems study [92] carried out for NREL, preliminary economics were developed for two systems: one based on the Koppers–Totzek gasifier and one on the IGT "Renugas" gasifier. In addition, preliminary economics have been developed by NREL for the BCL gasifier [93].

Capital and operating cost estimates for the four systems (LPO, HPO, IND, and IND2) are shown in table 10. Costs for the indirect systems, IND and IND2, were based on gasifier costs presented separately [105], in conjunction with reformer and methanol synthesis costs based on Chem Systems estimates. Feed costs are for 2.5 centimeter chips with 50 percent moisture content delivered at the plant gate. Yields and energy balances were estimated using the Aspen/SP [100] process simulator. Plant size was for bimass input of about 1,814 dtpsd, and reported in table 10 in terms of tonnes per stream day of methanol product. An *n*th plant estimate for a 9,090 dtpsd biomass plant is presented for IND2. The cost for the large plant was estimated from the smaller 1,814 dtpsd IND2 plant using a 0.7 scaling factor and parallel trains for the gasifier and methanol synthesis. There is no "learning curve" factor used to reflect increased reliability, efficiency, or process improvements. For the 1,814 dtpsd plants, costs range from $158.19 million for the IND2 plant to $321.73 million for the LPO plant.

Table 11 presents a typical cash-flow analysis carried out to determine the cost of production (COP) of methanol (pre-tax basis) from biomass using the IND gasifier. Table 12 presents summary COP values for methanol production. Values (1989 U.S. $per gigajoule of methanol) are presented at 6 and 12 percent discount rates and are divided into capital, feed and operating and maintenance costs. At a 12 percent discount rate the COP ranges from $7.65 per gigajoule of

Table 10: Capital and operating costs for producing methanol[a]

	Biomass LPO[b]	Biomass HPO[b]	Biomass IND[c]	Biomass IND2[c]	Biomass IND2[c]	Natural gas[d,f]	Coal[d]
Plant size *tpsd*[e] *methanol*	790	920	1,110	1,110	5,550	2,500	5,000
Feed price *1989 U.S. $per GJ (LHV)*	2.45	2.45	2.45	2.45	2.00	1.90	1.42
Capital cost *millions of 1989 U.S. $*							
Feed handling, preparation	37.95	16.95	20.34	20.34	65.89		73.55
Oxygen plant	49.46	42.96					122.59
Gasification	96.69	29.10	7.93	7.93	25.69		129.95
Gas conditioning		0.75	1.67	12.79	41.42		
Compression	10.77	8.10	25.72	25.58	82.98	23.77	
Shift reaction/heat exchange	0.75						122.59
Reforming		31.66	41.32			80.44	
Acid gas removal/cooling	10.98	13.75	11.64	11.64	26.90		46.59
Sulfur recovery							39.23
Methanol synthesis/purification	21.21	23.99	32.23	32.23	109.76	55.57	57.62
Utilities/auxiliaries	56.92	41.79	35.18	27.63	107.74	68.57	226.79
Overhead, E&C, if listed separately							286.62
Erected plant cost	284.73	209.04	176.03	138.14	460.36	228.55	1,105.53
Owner's costs, fees, and profit	24.87	20.90	14.67	11.51	46.04		110.55
Catalysts and chemicals						6.40	32.00
Land	2.13	2.13	2.13	2.13	13.50	5.33	10.66
Start-up	6.40	6.40	6.40	6.40	24.85	4.26	32.00

Table 10: (cont.)

	Biomass LPO[b]	Biomass HPO[b]	Biomass IND[c]	Biomass IND2[c]	Biomass IND2[c]	Natural gas[d,f]	Coal[d]
Total capital investment	321.73	238.48	199.22	158.19	544.77	244.54	1,290.76
Working capital	15.40	13.00	15.00	12.00	60.00	12.05	53.10
Operating costs *millions of 1989 U.S. $ per year*							
Variable costs							
Feedstock	28.50	28.10	28.00	28.00	113.30	55.56	101.12
Catalyst and chemicals	0.51	1.78	2.67	2.67	12.09	2.95	11.77
By-product credits							(8.89)
Utilities	2.12	3.25	5.52	5.52	25.01	0.00	4.11
Fixed costs							
Labor	0.92	0.92	1.09	1.09	5.10	0.82	4.42
Maintenance	7.67	5.69	4.74	4.03	14.10	9.97	26.84
General overhead	5.61	4.31	3.85	3.28	9.12	7.10	20.55
Direct overhead	0.42	0.42	0.49	0.49	2.65	0.42	2.07
Insurance	1.61	1.19	0.98	0.82	2.31	1.26	6.45
Total operating cost	47.36	45.66	47.34	45.90	183.68	78.08	168.44

a. LPO = low-pressure oxygen gasifier; HPO = high-pressure oxygen gasifier; IND = low-pressure indirect gasifier; IND2 = low-pressure indirect gasifier with hot-gas conditioning.

b. Costs for the LPO and HPO systems were taken from Chem Systems [92] as 1987 U.S. dollars and updated to 1989 U.S. dollars using the Nelson–Farrar index [99]. The Nelson–Farrar index was used for methanol because most plant unit operations (for example, reforming and methanol synthesis) are considered to be refining operations.

c. [93].

d. [104].

e. Tonnes per stream day.

f. Costs for a 2,500 tpd methanol plant located on the U.S. Gulf Coast have been converted to 1989 dollars using the Nelson–Farrar index.

Table 11: Cash flow (excluding taxes) for methanol production
millions of 1989 U.S. $

Year	Methanol revenue	By-product credit	Capital	Working capital	Feed cost	Fixed op costs	Variable op costs	Total costs	Pretax cash flow	Cumulative pretax cash flow
1			59.766					59.766	(59.766)	(59.766)
2			99.610					99.610	(99.610)	(159.376)
3			39.844					39.844	(39.844)	(199.220)
4	40.949	0.000		15.000	16.800	11.150	4.914	47.864	(6.915)	(206.315)
5	54.598	0.000			22.400	11.150	6.552	40.102	14.496	(191.639)
6	68.248	0.000			28.000	11.150	8.190	47.340	20.908	(170.731)
7	68.248	0.000			28.000	11.150	8.190	47.340	20.908	(149.824)
8	68.248	0.000			28.000	11.150	8.190	47.340	20.908	(128.916)
9	68.248	0.000			28.000	11.150	8.190	47.340	20.908	(108.008)
10	68.248	0.000			28.000	11.150	8.190	47.340	20.908	(87.101)
11	68.248	0.000			28.000	11.150	8.190	47.340	20.908	(66.193)
12	68.248	0.000			28.000	11.150	8.190	47.340	20.908	(45.285)
13	68.248	0.000			28.000	11.150	8.190	47.340	20.908	(24.377)
14	68.248	0.000			28.000	11.150	8.190	47.340	20.908	(3.470)
15	68.248	0.000			28.000	11.150	8.190	47.340	20.908	17.438
16	68.248	0.000			28.000	11.150	8.190	47.340	20.908	38.346
17	68.248	0.000			28.000	11.150	8.190	47.340	20.908	59.254
18	68.248	0.000			28.000	11.150	8.190	47.340	20.908	80.161
19	68.248	0.000			28.000	11.150	8.190	47.340	20.908	101.069
20	68.248	0.000			28.000	11.150	8.190	47.340	20.908	121.977
21	68.248	0.000			28.000	11.150	8.190	47.340	20.908	142.885
22	68.248	0.000			28.000	11.150	8.190	47.340	20.908	163.792
23	68.248	0.000		(15.000)	28.000	11.150	8.190	32.340	35.908	199.700

methanol for the large IND2 system to $19.60 per gigajoule of methanol for the LPO case.

Methanol from natural gas

More than 80 percent of the methanol commercially manufactured today is produced by natural gas reforming followed by methanol synthesis. The economics of methanol production from natural gas have been estimated, based upon a Chem Systems report published in 1989 [104], for comparison with the biomass cases. Capital and operating costs are shown in table 10, and cost of production in table 12. The COP is $6.24 per gigajoule of methanol at a 6 percent discount rate and $7.27 per gigajoule of methanol at a 12 percent discount rate. These COP values are lower than COPs for the smaller-scale biomass systems, and a little higher than a conceptual *n*th plant biomass system COP. Large-scale, 4,000 to 5,000 tpd, biomass-to-methanol plants have the potential to compete with world-scale natural-gas–based plants in areas that have natural gas costs comparable to those in the United States.

The impact of plant size on COP for the processes studied is shown in figure 5. Although the natural gas COP is comparable to the COP of a biomass IND2 system at half the scale of operation, no learning curve improvements have been included in the biomass plant estimates.

Process economics includes a natural gas feed cost of $1.90 per gigajoule ($2.00 per million Btu). This feed cost is considered representative of present-day natural gas costs in the United States and is used in most U.S. evaluation studies. Process economics is greatly influenced by feed costs, since natural gas represents approximately 44 percent of the COP at the above cost. Recent projections [106] of natural gas prices in the United States show the wellhead price increasing from $1.73 per gigajoule in 1990 to $3.58 per gigajoule in 2000, and to $5.77 per gigajoule in 2010. Much of the world's future methanol production will be located in remote locations having large amounts of natural gas and small domestic markets. Areas such as the Middle East, South America, and Southeast Asia are considered significant methanol production areas [19]. Low fuel costs in these areas are partially offset by increased transportation costs for their delivery

Table 11: notes

Process: biomass-indirect		Basis:	constant 1989 U.S. $
Capital cost: 199.22 million $		No escalation	
Methanol COP: $9.25 per gigajoule		Three-year investment, 15 year operating life	
Production rate:	1,110 tpsd	Investment schedule:	year 1, 30 percent
	370,000 tonnes per year		year 2, 50 percent
	7.37×10^6 gigajoules per year		year 3, 20 percent
Feed cost: 28 million $per year Discount rate: 6.00 percent		Production schedule:	year 4, 60 percent of nameplate year 5, 80 percent of nameplate years 6–18, 100 percent of nameplate

Table 12: Pretax production cost of methanol
1989 U.S.$ per gigajoule of methanol

Process	Capital	Feed	O&M	Total
	COP at 6 percent discount rate			
Biomass: LPO[a] *790 tpsd of methanol*	6.35	5.43	3.56	15.34
Biomass: HPO[b] *920 tpsd of methanol*	4.07	4.59	2.85	11.51
Biomass: IND[c] *1,110 tpsd of methanol*	2.85	3.79	2.61	9.25
Biomass: IND2[d] *1,110 tpsd of methanol*	2.27	3.79	2.42	8.48
Biomass: IND2 *5,550 tpsd of methanol*	1.59	3.07	1.90	6.56
Natural gas *2,500 tpsd of methanol*	1.60	3.34	1.30	6.24
Coal *5,000 tpsd of methanol*	4.01	3.04	2.00	9.05
	COP at 12 percent discount rate			
Biomass: LPO *790 tpsd of methanol*	10.62	5.43	3.55	19.60
Biomass: HPO *920 tpsd of methanol*	6.81	4.59	2.84	14.24
Biomass: IND *1,110 tpsd of methanol*	4.78	3.79	2.60	11.17
Biomass:IND2 *1,110 tpsd of methanol*	3.81	3.79	2.41	10.01
Biomass: IND2 *5,550 tpsd of methanol*	2.68	3.07	1.90	7.65
Natural gas *2,500 tpsd of methanol*	2.68	3.34	1.30	7.32
Coal *5,000 tpsd of methanol*	6.70	3.04	1.99	11.73

a. LPO = low-pressure oxygen gasifier.

b. HPO = high-pressure oxygen gasifier.

c. IND = low-pressure indirect gasifier.

d. IND2 = low-pressure indirect gasifier with hot-gas conditioning.

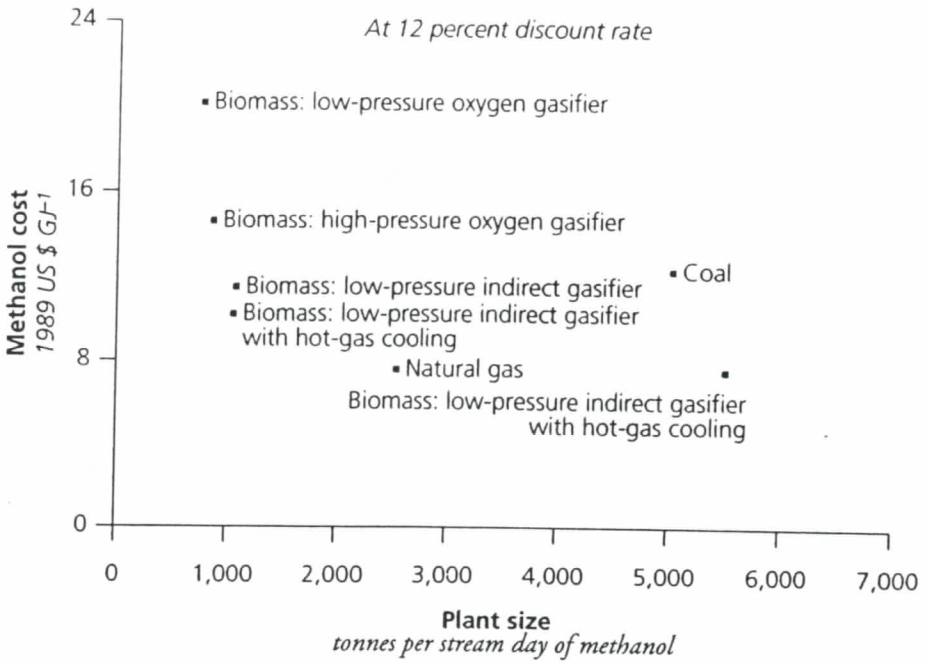

FIGURE 5: Methanol cost versus plant size.

to major markets. For example, the fuel-plus-transportation cost estimates in table 13 were projected as part of methanol costs.

Capital and operating costs also vary somewhat, about ±15 percent, depending on the location, but the major variables for methanol production from natural gas are fuel and transportation costs. Methanol produced from natural gas in remote regions can often be delivered to areas such as the U.S. Gulf Coast at very competitive prices.

Methanol from coal

Systems are also being proposed for methanol production from coal. Comparative costs for a second-generation coal gasification–based system using a commercial Texaco gasifier have been developed by Chem Systems [88]. Second-generation coal gasification assumes operation at high pressure. Capital and operating costs are shown in table 10, and the cost of production is shown in table 12. The COP for a coal-based system at 5,000 tpd of methanol is $9.53 per gigajoule of methanol at a 12 percent discount rate; this is comparable to an indirect biomass system at the 1,110 tpd methanol size, despite the assumption that biomass feedstock is 65 percent more costly than coal. Because of added costs, coal systems will have to operate at a larger scale than biomass-based systems to obtain comparable economic returns. For example, for comparable 5,000 tpd methanol plants, the coal-based system has acid gas/sulfur recovery costs of $86 million, whereas the biomass system has acid gas removal costs of $27 million.

Table 13: Fuel-plus-transportation cost estimates[a]
$per gigajoule of methanol

Location of production	Natural gas	Transportation	Natural gas plus transportation
Venezuela	0.26	1.00	1.26
Saudi Arabia	0.26	1.50	1.76
Southeast Asia	1.90	1.75	3.65

a. FOB U.S. Gulf Coast, 1991 U.S. $ [103].

ENERGY BALANCES AND CARBON DIOXIDE

Ethanol from biomass

Energy use for ethanol production can be measured by subtracting energy inputs from the energy produced, and dividing this difference by the energy content of the feedstock:

$$\text{Energy Ratio} = \frac{\text{Energy in products} - \text{External energy inputs}}{\text{Energy in feedstock}}$$

See table 14 for the energy balance information and energy ratios for ethanol produced from corn and cellulosic biomass according to this definition.

For corn-to-ethanol plants in the United States, steam is generally provided by the combustion of coal. Steam usage is reported to be from 11.1 to 16.7 megajoules per liter of ethanol produced, with the lower values typical of modern plants [9, 109]. Electrical power requirements are around 0.95 megajoules per liter (1.0 kWh per gallon) produced [109]. These values are for medium- to large-size plants, with capacities of approximately 113 million liters per year (30 million gallons per year) or more.

For corn, only the starch is considered in the feedstock energy content in table 14 because the remaining portion of the kernel is sold as animal and human food and not used as fuel. On this basis, the energy ratio for ethanol from corn is about 27 percent based on modern processing technology. If the total energy content of the corn kernel is included, efficiencies drop to about 70 percent of those shown in table 14. Adding the amount of energy required to plant, fertilize, cultivate, and harvest the corn lowers the energy ratio further to between –13 and 1 percent because about one-third to more than half as much fossil energy is required in fuel and fertilizer to produce corn as can be provided by the ethanol produced [22].

The first column in table 14 assigns all of the energy to ethanol production and does not deduct energy for drying the feed coproducts resulting from ethanol

production from corn. Several approaches have been employed in the past to account for the use of energy to produce coproducts, such as assigning energy based on the value of the coproducts [110] or on the energy required to produce the equivalent amount of protein from soybeans [107]. The latter approach is taken here because it considers the alternative to produce the same protein content an-

Table 14: Ethanol production energy ratio[a]

Process	Corn ethanol only	Corn energy to coproducts[b]	Cellulosic biomass reference case	Cellulosic biomass improved technology
Ethanol *liters per tonne*	440–458	440–458	338[c]	497[c]
Ethanol LHV *megajoules per liter*	21.2–111	21.2	21.2	21.2
Feedstock LHV *gigajoules per tonne*	16.2[d]	16.2[d]	18.87	18.87
Energy ratio for ethanol *percent*	26.5–27.5[e]	36.8–38.3[e]	38.0	55.8
Electricity *gigajoules per tonne feed*	–	–	0.658	0.365
Energy ratio for ethanol plus electricity *@ 3.6 MJ per kWh*	–	–	41.5	57.8
Energy ratio for ethanol plus electricity *@ 10.8 MJ per kWh*	–	–	48.4	61.6
Energy ratio including energy inputs for biomass production	−13.3 – +0.6	−2.5 – +11.4	41.6–43.5	54.8–56.7

a. Defined as energy produced minus fossil energy inputs divided by biomass energy content.

b. Energy assigned to coproducts based on energy required to produce soybeans and energy value of fuel oils @ 2.8 megajoules per liter ethanol [107].

c. Ethanol only after subtracting water and denaturant (gasoline) from product.

d. [78].

e. Corn energy ratios are based on the energy content of starch only. Other components of the corn kernel are sold as animal and human food. Average starch content is 73.4 percent [108].

PERSPECTIVES ON PRODUCTION OF ALCOHOLS FROM BIOMASS

With potential improvements, production costs for ethanol and methanol from biomass are projected to be lower than those for methanol from coal. Furthermore, the investments required for plants that would produce alcohols from renewable feedstocks would be only about one-third to one-tenth of those for coal–methanol plants. A reduction in capital requirements of this magnitude

Table15: Methanol production energy balances

Process	Biomass: LPO[a]	Biomass: HPO[a]	Biomass: IND[b]	Natural gas[c]	Coal[c]
Methanol *tonnes per day*	790	920	1,110	2,500	5,000
Tonnes feed per tonne of methanol	2.30	1.97	1.63	0.64	1.76
Feed LHV *gigajoules per tonne*	18.87	18.87	18.87	52.25	24.75
External power required[d] *gigajoules·per tonne feed*	0.84	1.29	1.94	e	e
Methanol LHV[f] *gigajoules per tonne*	19.92	19.92	19.92	19.92	19.92
Energy ratio *percent*	40.3	50.8	53.4	59.6	50.6
Carbon use *percent*	32.6	38.0	45.9	79.2	ND

a. [92].

b. [93].

c. [104].

d. External power reported assuming 33 percent electrical generation efficiency.

e. No external power required.

f. LHV methanol liquid.

could facilitate financing for biomass plants and allow smaller firms to commercialize the technology.

Because the costs of producing ethanol and methanol from biomass are projected to be quite similar if the technology for each can be improved to meet the goals identified, factors other than price may dictate the choice between alcohols. As mentioned before, engines with fuel-line sensors could be designed to accommodate both fuels.

One advantage offered by methanol is that much of the technology needed for biomass-derived methanol can be readily adapted from technology already developed for making methanol from natural gas and coal. Moreover, methanol production technology is much less sensitive to feedstock composition than ethanol technology and may thus be preferred in places where good ethanol feedstocks are not readily available. Methanol might also be favored because it is easier to reform than ethanol and because reforming technology is more advanced for methanol than for ethanol, making methanol a better candidate for fuel cell applications, at least in the near term. However, the fact that methanol can be produced from coal at a cost comparable to that for biomass-derived methanol poses the risk that coal might one day be the feedstock of choice for methanol production if land-use constraints should drive the cost of biomass feedstocks out of the competitive range. Such an outcome would be undesirable from the perspective of global climate change.

Ethanol may be preferred because of its low toxicity, although a denaturant would undoubtedly have to be added to prevent people from drinking it. Ethanol production also employs predominantly natural materials such as the biomass itself, proteins (enzymes), and yeast, and selectivity to target products is very high. Thus, the environmental impacts associated with its manufacture should be very low. Because wet cellulosic waste streams are well suited for conversion into ethanol, the need to dispose of such wastes could provide a near-term niche for ethanol production technology. Furthermore, ethanol production may well continue to benefit from the ongoing advances in biotechnology to realize even greater price reductions than presented herein.

CONCLUSIONS

As alternatives to petroleum-based fuels, alcohols from biomass can be blended with gasoline or used as neat fuels. The use of alcohols produces less air pollution than gasoline and helps solve local air quality problems. If alcohol-fuel cells can be successfully developed, it will be possible to achieve much lower emissions than for internal combustion engines. Moreover, the greater efficiencies of fuel cells would reduce the fuel use and associated land needed to grow biomass. When made from biomass that is subsequently regrown, alcohols contribute no net carbon dioxide to the atmosphere during their use cycle. This characteristic makes them particularly well suited to a world in which carbon dioxide emissions

are limited. With new technologies currently being developed, both ethanol and methanol from biomass have the potential to be cost-competitive with gasoline.

Both acid- and enzyme-catalyzed reactions have been evaluated for conversion of cellulosic biomass into ethanol. Research has been focused on enzymatic hydrolysis technology because of its potential to achieve high yields under mild conditions. In particular, the SSF process is favored for ethanol production from the major cellulose fraction of the feedstock because of its low cost potential. Technology has also been developed for converting the second largest fraction, hemicellulose, into ethanol; the remaining lignin can be burned as boiler fuel to power the conversion process and generate extra electricity for export. Together, developments in conversion technology have reduced the selling price of ethanol from about $45 per gigajoule ($0.95 per liter) ten years ago to only about $13 per gigajoule($0.28 per liter) (at 12 percent discount rate) today. Additional technical targets have been identified to render ethanol competitive with gasoline produced from $25 per barrel oil, if an aggressive research and development program is followed.

Methanol can be produced from cellulosic biomass in the near-term with oxygen-blown pressurized fluidized-bed gasifiers and natural gas-derived reformer and methanol synthesis technology. The cost for this option is estimated to be $14.66 per gigajoule (12 percent discount rate) at 920 tonnes per day. Technical targets, including indirect gasification to eliminate the oxygen plant investment and to increase yields of syngas, coupled with new gas-conditioning technology, have been identified. Achieving these targets would make biomass derived methanol competitive with gasoline derived from $25 per barrel crude oil.

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