OVERVIEW AND EVALUATION OF FUEL ETHANOL FROM CELLULOSIC BIOMASS: Technology, Economics, the Environment, and Policy

Lee R. Lynd

Biochemical Engineering Program, Thayer School of Engineering, Dartmouth College, Hanover, New Hampshire 03755

KEY WORDS: ethanol, biomass, fuel, environment

ABSTRACT

Ethanol is a high performance fuel in internal combustion engines. It is a liquid, which is advantageous in terms of storage, delivery, and infrastructural compatability. Ethanol burns relatively cleanly, especially as the amount of gasoline with which it is blended decreases. Evaporative and toxicity-weighted air toxics emissions are consistently lower for ethanol than for gasoline. It is likely that vehicles can be configured so that exhaust emissions of priority pollutants are very low for ethanol-burning engines, although the same can probably be said for most other fuels under consideration. Recent work suggests that ethanol may be more compatible with fuel cell—powered vehicles than has generally been assumed. Research and development-driven advances have clear potential to lower the price of cellulosic ethanol to a level competitive with bulk fuels. Process areas with particular potential for large cost reductions include biological processing (with consolidated bioprocessing particularly notable in this context), pretreatment, and incorporation of an advanced power cycle for cogeneration of electricity from process residues. The cellulosic ethanol fuel cycle has a high thermodynamic efficiency (useful energy/high heating value = from 50% to over 65% on a first law basis, depending on the configuration), and a decidedly positive net energy balance (ratio of useful energy output to energy input). Cellulosic ethanol is one of the most promising technogical options available to reduce transportation sector greenhouse gas emissions. It may well be possible to develop biomass-based energy on a very large scale in the United States with acceptable and in some cases positive environmental impacts. To do so will however require responsible management and increased understanding of relevant technological

and natural systems. The potential biomass resource is large, but so is demand for transportation fuels as well as other uses. The following hypotheses are offered as tentative hypotheses pertaining to biomass supply and demand in the United States: There will probably not be enough suitable land available to meet transportation demand if total vehicle miles traveled increase relative to current levels, and vehicle efficiency and animal protein utilization are unchanged. There probably is enough suitable land to meet transportation demand, even given some increase in vehicle miles traveled, given large but probably possible increases in vehicle efficiency, or large but probably possible decreases in reliance on animal protein, or a combination of less aggressive changes in both of these factors. The policy debate concerning fuel ethanol has tended to ignore cellulosic ethanol. It is suggested that an appropriate policy objective is to foster a transition to cellulosic feedstocks at a pace such that opportunities for ethanol producers and the farmers that supply them are expanded rather than contracted.

CONTENTS

INTRODUCTION	404
FUEL PERFORMANCE	405
Internal Combustion Engines	405 408
FEEDSTOCKS	409
Composition	409 410 414
CONVERSION TECHNOLOGY	415
Pretreatment Biological Conversion Product Recovery Utilities and Waste Treatment	417 422 428 428
CURRENT PROCESS ECONOMICS	430
MATURE CONVERSION TECHNOLOGY	433
RESEARCH PRIORITIES	434
ENERGY BALANCE	438
GREENHOUSE GAS IMPACTS	440
PRIORITY POLLUTANT EMISSIONS	442
NEAR-TERM COMMERCIALIZATION PROSPECTS	445
MARKET FACTORS AND POTENTIAL EXPANSION	448
CONCLUDING REMARKS AND POLICY COMMENTARY	452

INTRODUCTION

Ethanol produced from cellulosic biomass—cellulosic ethanol—has received attention as a potential transportation fuel of the future. Prior to the early 1990s,

projected selling prices for cellulosic ethanol were generally higher than the price of production from corn, and the number of unresolved technical issues was sufficient to make research and development (R&D) the main focus of activity. Over the past 5 years or so, commercial interest in ethanol has heightened markedly, reflecting advances in the cost competitiveness of conversion technology. In parallel with these technical developments, analyses of the efficacy and desirability of cellulose ethanol have appeared regularly, although with a perhaps surprising lack of resolution.

The two primary goals of this review are to provide a primer on cellulosic ethanol production technology and to synthesize recent information relevant to evaluation of the cellulose ethanol fuel cycle. The cycle is examined in relation to technology both as it is today and as it could be in the future. Commentary on policies impacting fuel ethanol is also offered (in Concluding Remarks and Policy Commentary section). This review focuses on the United States, as this country is among the most active worldwide in both developing cellulosic ethanol technology and using ethanol as a vehicular fuel.

FUEL PERFORMANCE

Ethanol can be used as a motor fuel in several forms: low-level blends (e.g. < 22% ethanol in gasoline), high-level blends (e.g. > 85% ethanol in gasoline), neat (containing no gasoline but usually containing water in amounts $\leq 20\%$), and as ethyl tert-butyl ether (ETBE). In addition, ethanol may be used in vehicles with nonmodified internal combustion engines (which are typically warrantied for low-level ethanol blends), "flexible-fuel" internal combustion engines (capable of using ethanol, methanol, and gasoline in any proportion), compressionignited engines, dedicated internal combustion engines (optimized to take advantage of the particular properties of alcohols), or fuel cells (1, 2). Many fuel performance metrics depend significantly on the form in which ethanol is supplied and the type of vehicle in which it is used. The situation is further complicated by the fact that available data are decidedly sparse for many fuel-vehicle combinations. Fuel performance is considered below with respect to internal combustion engines and fuel cells. The matter of emissions from fuel ethanol in various forms is addressed in the section on Priority Pollutant Emissions.

Internal Combustion Engines

Available information indicates that ethanol is in many respects superior to gasoline as a fuel for spark-ignited engines and that the utility of ethanol as a fuel per se is unlikely to limit its adoption. Information on the fuel performance of ethanol comes from three kinds of sources: ethanol test data (which are quite

Fuel property	Ethanol value relative to gasoline ^b	Qualitative impact(s)	Thermal efficiency impact (%)
Energy density	0.65-0.69	Lower miles/gallon	-0.9
		for same range	
Heat of vaporization	2.3	Greater mass of air enters the cylinder	—
		Increased power	
		Decreased cooling system duty	
Lower flame temperature	0.976	Higher efficiency in an optimized engine	—
Relative volume of combustion products	1.07	Increases the work available from gas expansion	+7
Octane number	1.15	Allows increased compression ratio and hence higher power and efficiency	+6-10

Table 1 Summary of ethanol fuel properties in relation to fuel performance^a

^aFrom Sinor & Bailey (5).

^bValues are the unit-less ratios of value for ethanol: value for gasoline. The range for energy density reflects the difference between regular gasoline and RFG. Flame temperature calculated based on degrees centigrade. Octane based on mid-range (R + M)/2 values.

limited), methanol test data (which are more extensive), and analysis of the impact of fuel properties on combustion fundamentals. The fuel properties of ethanol and methanol are rather similar; differences between the alcohols and gasoline are much greater than differences between the alcohols (1).

The physical properties of ethanol and other fuels, and discussion of the mechanistic impact of these properties on engine performance, are presented elsewhere (3, 4). The salient fuel performance advantages of ethanol, relative to gasoline, in spark-ignited internal combustion engines include lower volumetric energy density, somewhat more power and thermal efficiency (mile/Btu) in nonoptimized engines, and the potential for larger power and thermal efficiency gains in optimized engines. Table 1 summarizes Sinor & Bailey's review (5) of the impact of specific fuel features on vehicle performance.

In nonoptimized vehicles, Sinor & Bailey (5) project a 1–2% increase in thermal efficiency (miles/million Btu) for ethanol E10 compared to reformulated gasoline (RFG). Changes of this magnitude are difficult to confirm experimentally, and available test data are not sufficient to conclusively confirm or reject the hypothesis that such small efficiency gains accompany use of low-level ethanol blends. For high-level blends, Sinor & Bailey project an increase of approximately 6–7%, relative to gasoline in fuel-flexible vehicles (FFVs), due to the increased volume of combustion products. Estimates for the efficiency increase in optimized dedicated vehicles using ethanol rather than gasoline range from 15% (5) to 20% (1). These projections are consistent with available data, although the volume and consistency of data are not sufficient to definitively confirm them. Projected efficiency benefits are over and above improvements in vehicle efficiency due to engine, transmission, and aerodynamic improvements, which are generally independent of fuel type (5).

Materials compatibility issues associated with use of alcohol fuels can be significant (see 4 for discussion). Such issues also appear to be solvable (4), as indicated by the extensive use of high-level ethanol blends as vehicular fuels in Brazil over the past 15 years. All gasoline-powered light-duty vehicles sold in the United States have been warrantied for low-level ethanol blends throughout the 1990s (1). Only blends with up to 10% ethanol have been available, but McNutt et al (6) indicate that blends with up to 17% ethanol would be compatible with the vehicle stock as it develops in the next 5–10 years. FFV technology compatible with use of ethanol in high-level blends is fully developed (1). The cost of FFV technology, which is based on adjusting the air-to-fuel ratio in relation to the fuel oxygen content, is about \$100 for a new car (6). Coldstarting is more challenging for ethanol than for gasoline because of ethanol's lower volatility and higher heat of vaporization. Cold-starting is no longer a problem with ethanol in forms other than E100 (1). Prototype vehicles have been shown to be capable of satisfactory cold starts on E100 (4), suggesting that this issue may also be solvable given sufficient motivation.

Ethanol may also be used in compression-ignited engines, although performance and emission data on these engines are even more sparse than the data on spark-ignited engines. As discussed by Black (4), conventional diesel engines require that fuel auto-ignite upon compression, and the fuel must provide lubrication for the pumps used to inject the fuel into the combustion chamber. Because ethanol has neither of these properties, its use in a compression-ignited engine requires engine modification, fuel additives, or both. Engine modifications used to overcome the low cetane number of ethanol include higher compression ratios, glow plugs, and spark plugs. Organic nitrates have received particular attention for improving ethanol's ability to ignite. Recent work by the National Renewable Energy Laboratory (NREL) (7) on ethanol-powered buses found reliability (as measured by the time between road calls) to be similar for 10 buses powered by E95 and a control group of diesel-powered buses. Fuel economy on a per-Btu basis was also similar for the E95 and diesel buses during a test period of 9-23 months (for two different sites) and 400,000 miles of service. On the basis of the fuel and combustion properties of ethanol, Sinor

& Bailey project a 2% thermodynamic efficiency advantage for ethanol relative to diesel in compression-ignited engines without traps for particulate matter, and a 4–6% efficiency advantage compared to diesel engines with particulate traps.

Fuel Cells

Fuel cells are attractive because they offer high efficiency and very low emissions. Hydrogen for conversion to electricity in a fuel cell can either be carried on a vehicle as such or can be produced from an organic fuel in a reformer. Among fuels that are liquids at atmospheric pressure, methanol has most frequently been considered for use in fuel cells because it can readily be dissociated into synthesis gas (a mixture of H₂, CO) at moderate temperatures by steam reforming in the presence of appropriate catalysts. In contrast, no known catalysts are effective at promoting steam reforming of ethanol (8). However, several alternatives to steam reforming exist for reformation of organic fuels, including partial oxidation and autothermal reforming (9). Partial oxidation reforming is essentially oxygen-limited combustion, which occurs at a higher temperature than steam reforming and results in a mixture of H₂, CO, and CO₂. As with methanol, the gas-water shift reaction, which converts CO and water into CO₂ and H₂, respectively, must be carried out before ethanol is used in a proton exchange membrane (PEM) fuel cell.

Since 1991, Arthur D Little (ADL) has investigated the development of an ethanol-compatible reformer for use in fuel cell-powered vehicles (9). Using a partial oxidation reformer capable of running on ethanol in the presence of significant amounts of water (e.g. 150 proof ethanol), ADL has demonstrated reformer efficiencies (energy as CO and hydrogen/ethanol high heating value) of about 80% (9). Use of the reformer has been analyzed in the context of a system consisting of the reformer (including a section equipped with catalysts effective in facilitating the reaction of methane), a shift reactor (in which CO and water are converted to CO_2 and H_2), a PEM fuel cell, and a heat recovery unit (which exchanges heat between the exhaust gas and incoming fuel and air). The projected system efficiency (electricity/ethanol high heating value including the reformer) is about 43%, a value projected to roughly double miles per gallon (mpg) over an equivalent ethanol-powered vehicles using an internal combustion engine (J Bentley, personal communication). Priority pollutant emissions (hydrocarbons, CO, and NO_x) are undetectable in steady-state tests, and they are expected to be very low in transient operation as well. The prototype reformer yields power densities of 1.44 liters per kW and 1.74 kg per kW at an estimated cost of \$20 per kW. The potential for lower costs is thought to be considerable, particularly in the area of catalyst development (J Bentley, personal communication).

ADL's work, outlined above, suggests that the efficiency and emission benefits of using ethanol in a fuel cell may be similar to those of using methanol in a fuel cell. In particular, the system efficiency of the ethanol/partial oxidation reforming system investigated by ADL is essentially identical to the system efficiency projected for the methanol/steam reformer under development by General Motors (GM) (11). Analysis by ADL (12) also indicates that partial oxidation reformers have inherent advantages relative to steam reforming and autothermal reforming: low weight and volume, the possibility for low cost construction, multiple fuel capability, and superior response to variable loads.

The availability of reformer technology to make ethanol compatible with fuel-cell applications is a significant factor impacting the long-term desirability of ethanol as a transportation fuel (see section on Concluding Remarks and Policy Commentary). The ADL work provides reason for optimism that such a reformer can be developed. Considerable work remains to be done, however, on this reformer/fuel cell combination as well as others. For example, the ADL reformer has yet to be coupled to a fuel cell and to be subjected to variable loads, and a lower concentration of CO exiting the shift reactor is desirable (J Bentley & AD Little, personal communication).

FEEDSTOCKS

Composition

Cellulosic materials of potential use for ethanol production can originate either as waste materials arising from processes other than fuel production (e.g. agriculture, forest products industries), or as energy crops grown expressly for the purpose of fuel production. Although these two categories of raw materials, or feedstocks, may differ greatly in cost and volume of production, the composition of otherwise diverse cellulosic materials is often rather similar in general terms. The three major components of the vast majority of native cellulosic materials are cellulose, hemicellulose, and lignin. Cellulose and hemicellulose (typically comprising roughly two thirds of the dry mass of biomass materials) can be fermented to ethanol; lignin (typically a significant fraction of the balance) cannot. Detailed consideration of the composition of cellulosic materials is available elsewhere (12a, 12b, 13).

Cellulose is a polymer of glucose—a six-carbon sugar or hexose—joined by beta-linkages. Linear cellulose chains are typically arrayed in a parallel arrangement with extensive hydrogen bonding between them. The result is a highly ordered, crystalline material that is recalcitrant to rapid reaction under many conditions. Cellulose comprises about two thirds of the total carbohydrate

content for most woody plants and about half of the total carbohydrate content for herbaceous plants.

Hemicellulose is a polymer that occurs in association with cellulose and generally comprises 20–35% of the dry mass of biomass. Characterized by a branched structure, hemicellulose is essentially noncrystalline and generally more reactive than cellulose. Hemicellulose is composed primarily of several sugars, the identity and proportion of which depend on the type of plant material. Xylose—a five-carbon sugar or pentose—is the dominant constituent of hemicellulose in plants other than softwoods.

Lignin is a random polymer of phenylpropylene subunits. These subunits are joined to other subunits by ether and carbon-carbon linkages, and they are covalently bound to hemicellulose. Lignin occurs as a "net" surrounding carbohydrate-rich microfibrils in plant cell walls, and it also occurs in the interstitial space between mature plant cells. The mass fraction of lignin in plant material varies from 7% to 30%. Leafy herbaceous materials are generally at the low end of this range; agricultural residues are generally lower than hardwoods, and hardwoods are generally lower than softwoods. In the context of an ethanol production process, lignin is nonbiodegradable for practical purposes. Because the heating value of lignin is about five thirds that of carbohydrates, lignin contributes a significant fraction of the overall heating value for woody materials.

Production and Availability

The first materials used for biomass ethanol production will almost certainly not be energy crops, but rather wastes (14). This expectation is due to the costs of waste feedstocks, which are lower in many cases than dedicated energy crops.

Waste availability data from the 1970s and early 1980s have been reviewed (15). More recently, Tyson (P Bergeron, personal communication) has completed a detailed waste inventory, presented in Table 2. This study differs from most earlier efforts in that it presents prices for waste materials in addition to estimates for available tonnages. Tyson's estimates total 186.5 million tons of waste at \leq \$56 per delivered dry ton (1994 basis) and about 142.5 dry tons at \leq \$45 per delivered dry ton (linearly interpolating for the high cost agricultural waste). The corresponding alcohol production potentials, determined using yields associated with the advanced process scenario (Table 7) are 20 billion gallons and 15.3 billion gallons for material available for \leq \$56 per delivered dry ton, respectively. Only a fraction of the material costing less than \$45 per dry ton is likely to be utilized in plants exclusively processing wastes, because of scale considerations, but the assumption that most of this material could be utilized once a fuel ethanol industry were established and co-utilization of wastes and dedicated feedstocks became possible is probably

-		
Waste	Availability (million dry tons)	Cost (1994 dollars/delivered dry ton)
Mixed paper	26.0	0–19
Packaging	14	0-5.2
Urban wood	3.5	12.9–25.9
Yard waste	11	0-12.9
Agricultural residues	120	12.9–56.0
Low cost	4	12.9
Medium cost	36	38.8
High cost	50	47.4
Forest residues—logging	9	12.9–43.1
Low cost	3	12.9
Mid cost	3	25.9
High cost	3	43.1
Forest residues-mill	3	17.2

 Table 2
 Availability and cost of cellulosic wastes^a

^aModified from values developed by Tyson (see text). Tyson considered the contiguous 48 states, with values based on the year 2000. For consistency with other values in this work, Tyson's values are multiplied by 0.862 (consistent with a compounded annual Consumer Price Index (CPI) increase of 2.5%) to convert from 2000 dollars to 1994 dollars.

reasonable. Wastes costing more than \$45 per dry ton might never be used for ethanol production, because energy crops are expected to be available at lower cost.

Tyson projects smaller (on the order of threefold) amounts of available material than most previous estimates (15). This difference may be at least partly due to the fact that many of the previous studies were done in the late 1970s and early 1980s (often based on data that were even older), a period when trends such as use of forest industry wastes and paper recycling were much less established. Using Tyson's numbers with a \$45-per-ton cutoff, the potential contribution of wastes (about 1.3 quadrillion Btu) is still significant.

Although it is widely agreed that waste feedstocks will be utilized before energy crops, the fact that large-scale displacement of conventional transportation fuels with cellulose ethanol will require significant production from dedicated energy crops is equally apparent. Examples of cellulosic energy crops are short rotation woody crops (e.g. poplar, willow) and perennial herbaceous crops (e.g. switchgrass). A comprehensive volume of articles on energy crop production recently appeared (17).

The economics of energy crop production have been examined by Turhollow (18) in terms of both cost of production and break-even selling price relative to conventional crops. Because traditional crops (at least grains, corn, and

sovbeans) have negative returns without subsidies, prices are lower than costs. Prices and costs are presented for production and delivery of hybrid poplar, sorgum, switchgrass, and energy cane in the Midwest and the Southeast for 1989 and 2010. Selling prices range from \$39.1 to \$53.6 per dry ton in 1989 and from \$27.3 to \$38.2 per dry ton in 2010. Cost of production ranges from \$47.3 to \$61.8 per dry ton in 1989 and from \$30.0 to \$43.6 per dry ton in 2010. These ranges reflect variability for different energy crops, yet further variability exists in relation to site characteristics. Perlack & Wright (19) have estimated a national average cost of \$38.6 per delivered dry ton for energy crops in 2020 based on a three- to fourfold increase in research and development (R&D) effort up to that time. The largest components in the cost of producing energy crops are typically for harvesting, handling, storage, and transportation. Generally, smaller cost factors are for land, fertilizers, weed control, seeds, and stand establishment. If the biomass from chipped wood and herbaceous energy crops can be used almost immediately, thereby avoiding storage losses and costs, Turhollow (18) estimates that cost reductions in the range of \$5.5-\$17.3 per dry ton can be realized.

The United States has had a surplus of cropland for most of this century. Moreover, recent trends indicate that productivity increases are outstripping increased demand, so cropland excesses are expected to increase in the future (20). Federal programs have idled an average of 60 million acres over the past 10 years (21). The Conservation Reserve Program (CRP) removes about 36 million acres from production with the primary goal of erosion control. The vast majority of CRP land is planted in perennial grasses that could be harvested as energy crops while still meeting the goal of erosion prevention, were this not prohibited. Acreage reduction programs motivated by support of farm prices remove an average of about 25 million acres, although this amount is highly variable from year to year. The amount of land that could be used to grow energy crops without significant displacement of food crops is believed to be less than the total idled by federal programs; 35 million acres is believed to be a reasonable estimate (M Walsh, personal communication). The difference between this estimate and the 60 million acre average cited above arises primarily because not all idled land is suitable for energy crop production.

Figure 1 provides a perspective on land availability and requirements for cellulose ethanol production, while also showing the possible reduction in land area requirements available from increased vehicle efficiency. The number of assumed annual VMT (corresponding to 15 quads of fuel use or 130 billion gallons of gasoline at 30 mpg) is 3.9 trillion. Wastes are assumed to provide 15.3 billion gallons of ethanol (see discussion above) with no land requirements.



Figure 1 Land area requirements for cellulose ethanol production in relation to transportation efficiency. Note: Based on 3.6 trillion annual vehicle miles traveled—see text.

An energy crop productivity of 8.4 dry tons per acre per year is assumed, corresponding to the average research goal productivities presented by Perlack & Wright (19). The ethanol yield is taken to be 107.7 gallons per ton, consistent with the advanced technology scenario outlined below in the section on Mature Conversion Technology. Based on these assumptions, the amount of land required to displace a given quantity of conventional fuel can readily be calculated. In Figure 1 such calculations are presented in relation to a vehicle efficiency multiplier, which reflects the multiple of current vehicle efficiency. Three cases are considered: ethanol only, ethanol plus electricity (valued based on energy content) with electricity yields taken from the advanced scenario with a Rankine power cycle (Table 8), and ethanol plus electricity with yields as in the advanced scenario with a biomass gasification combined cycle gas turbine power cycle. The land area requirements presented correspond to a constant number of miles traveled, with the amount of land required decreasing as vehicle efficiency increases. At least some high-efficiency transportation options would result in priority pollutant emission reductions of equal or greater relative magnitude to that shown in Figure 1 for land requirements.

The land area benchmarks presented in Figure 1 include the CRP program, the average total amount of land idled by federal programs over the past decade, and the total amount of land devoted to production of animal feed for domestic

consumption (23). At an efficiency multiplier of 1, which is probably conservative in light of the potential of both ethanol and electricity to increase vehicle efficiency, an amount of land equal to the CRP program represents on the order of one quarter of the land required to provide for 3.9 trillion miles of mobility, depending on the accounting and scenario assumed for electricity, and subject to the assumptions of this analysis. At an efficiency multiplier of 3, which some project for "leap-forward"-type vehicles (24, 25), this same acreage would provide most or all of this land requirement. The acreage devoted to production of animal feeds, much of which would be available were the country to shift to a diet emphasizing vegetable protein, is roughly commensurate with the land required at an efficiency multiplier of 3. Consideration of land devoted to feed production emphasizes the point that society has options for making land available for energy production, and not all of these involve feeding fewer people.

Land Use Considerations and Feedstock-Related Environmental Impacts

Conversion of waste materials into ethanol in general raises fewer environmental issues than does conversion of dedicated feedstocks. This difference arises because no land is required for this conversion—land may even be saved by decreasing material flows to landfills—and little or no resource investment is typically required, except for collection. Depending on the wastes, collection may either be easier than it is for energy crops (as in the case of a waste produced at a centralized processing facility such as a paper mill) or more difficult (as in the case of agricultural residues that would not otherwise be collected). For some wastes, issues associated with soil fertility are appropriate to consider, although most studies do acknowledge and consider such issues. Some agricultural residues present disposal problems for which current methods are becoming environmentally unacceptable, for example, the open-field burning of straw or sugar cane leaves.

Most who have analyzed energy crop production (e.g. 26–28) stress that a significant number of issues related to its environmental impacts are incompletely understood, and they advise a cautious approach and further research. A second common observation is that good management practices are likely to result in environmental benefits, whereas poor management represents a significant potential liability. Finally, most land use–related impacts depend greatly on what form of land-use energy crops are replacing. These remarks may be particularly relevant to the issue of biodiversity. Christianson et al (27) indicate that bird and mammal abundance and diversity are in general as high, and in some instances higher, on energy crop plantations as they are on croplands.

Similarly, Ranney & Mann (28) project slightly improved wildlife habitat when energy crops are planted on croplands. Conversion of wildlands to energy crop production is, however, expected to have a negative effect on biodiversity (27).

Increasingly, analyses of energy crop production focus on cropland. In general, most metrics of environmental quality improve when short rotation woody crops or herbaceous perennial crops replace conventional row crops. Table 3 presents a compilation of some of the more quantifiable land use impacts associated with production of energy crops. Compared to row crop production, energy crops involve far less erosion, slightly less fertilizer application, and much reduced pesticide application. These trends are consistent with the possibility of very positive water quality benefits resulting from energy crop planting (28). Ranney & Mann (28) also project improved soil organic carbon levels when energy crops are grown on cropland, resulting in slower leaching of nutrients, more efficient use of nutrients by energy crops, and reduced NO_x emissions to the atmosphere.

Representatives of the American Council for an Energy-Efficient Economy, the Audubon Society, the National Resource Defense Council, and the Sierra Club have presented their positions on biofuel production in various recent fora (29, 30). From these and other interactions, I have the impression that an increasingly widely held belief among environmentalists and conservation-minded scientists is that conversion of cellulosic energy crops grown on cropland into transportation fuel can be a highly desirable enterprise from an environmental standpoint.

CONVERSION TECHNOLOGY

Steps in the conversion of cellulosic materials to ethanol in processes featuring enzymatic hydrolysis include pretreatment, biological conversion, product recovery, and utilities and waste treatment. An overview of conversion technology

Table 3	Comparison of agricultural intensity metrics for energy
crops and	conventional crops ^a

Metric	Reduction relative to corn-wheat-soybean average					
	Woody short rotation	Herbaceous perennial				
Erosion	12.5-fold	125-fold				
Fertilizer	2.1-fold	1.1-fold				
Herbicide	4.4-fold	6.8-fold				
Insecticide	19-fold	9.4-fold				
Fungicide	39-fold	3.9-fold				

^aFrom Ranney & Mann (28).

is provided by Wyman (31). Lynd et al (32) have recently addressed future improvements to conversion technology, and several detailed process design studies are available (33, 34).

Cellulose ethanol processes are differentiated primarily on the basis of the methods used to achieve hydrolysis and fermentation, the two steps that are the least technologically mature and the most specific to ethanol production. Hydrolysis processes can be categorized into those that use mineral acids (e.g. sulfuric acid) and those that use cellulase enzymes. Although acid-reliant processes are more technologically mature, enzymatic processes have roughly equal projected costs today, and they are expected to have an increasing cost advantage as the technology is improved (1). In addition, processes relying on acids generally have greater environmental liabilities than enzymatic processes. Because of these considerations, most if not all studies that project technology for large-scale production of ethanol from cellulosic biomass feature enzymatic hydrolysis, which is the primary focus here. Acid-reliant processes do have one significant advantage over enzymatically based processes: They are equally effective with softwoods and hardwoods. Current enzymatic processes are much more readily applied to hardwoods and herbaceous materials than to softwoods.

An entirely different approach to producing ethanol from cellulosic biomass has been proposed by James Gaddy and coworkers. This approach involves gasification of biomass to synthesis gas, followed by fermentation of synthesis gas by *Clostridium ljundahlii* or similar microorganisms to form ethanol (35). The outlook for the gasification/synthesis gas fermentation approach appears similar to that for biomass-derived methanol. The essential steps of both are gasification and synthesis, the latter carried out with inorganic catalysts (e.g. copper-zinc oxide) in the case of methanol and fermentation in the case of ethanol. The dominant factors in the economics of methanol production from biomass are costs associated with synthesis gas production via gasification (2). In contrast, the dominant economics factor for production of ethanol using enzymatic hydrolysis is biological conversion (see section on Process Economics). Order-of-magnitude reductions in the cost of biological processing for ethanol production have been projected (see section on Mature Conversion Technology), but not, to my knowledge, for gasification. Because projected costs for production of ethanol and methanol are roughly equal based on current technology (2), and because larger cost reductions are foreseeable for ethanol relative to methanol, the cost of production using mature technology can be expected to be less for ethanol produced via enzymatic hydrolysis than for methanol-and by implication ethanol-produced via gasification.

Notwithstanding the above line of reasoning, the gasification/synthesis gas fermentation approach is important in that 1. This approach represents an "end

run" with respect to pretreatment and cellulase production, both of which are significant factors constraining the advancement of biomass ethanol technology. 2. The approach may be cost competitive in the near term before biological conversion technology is fully developed. 3. This approach may be the best long-term technology for producing ethanol from forms of biomass that are less readily processed enzymatically (for example, softwoods). Because this technology is under private development and has been investigated primarily by one group, few details about it are available in the public literature.

Pretreatment

Within the context of production of fuels from biomass, pretreatment has come to denote processes by which cellulosic biomass is made amenable to the action of hydrolytic enzymes. All naturally occurring, and most refined, cellulosic materials require pretreatment to become accessible to the enzymes that mediate hydrolysis. Typically, hydrolysis yields in the absence of pretreatment are < 20% of theoretical yields, whereas yields after pretreatment often exceed 90% of theoretical. The limited effectiveness of current enzymatic processes on softwoods (see above) is thought to be due to the relative difficulty of pretreating these materials. Recent reviews of pretreatment have been done by Converse (36), McMillan (38, 39), Hsu (37), and Weil et al (40), and the older reviews by Dale (41) and Grethlein (42) are still highly relevant. Pretreatment is considered here first in terms of operative mechanisms and then in terms of performance metrics and processes.

MECHANISMS Mechanistic understanding of why pretreatments work is decidedly incomplete; the design of pretreatment processes is therefore largely empirical. Moreover, different mechanisms are important for different processes. In naturally occurring cellulosic materials, cellulose is closely associated with hemicellulose and other structural polysaccharides, and carbohydrate-rich microfibrils are surrounded by a lignin seal (11). Clearly, a primary function of pretreatment is to open up this multicomponent-matrix so that it becomes accessible. Evidence to support this view comes from the finding that pretreatment effectiveness is associated with accessible pore volume (43, 44). Although the idea that accessible pore volume is a determinant of pretreatment effectiveness is appealing and may yield beneficial insights, this approach also presents certain dilemmas. For example, the cellulase system of the bacterium Clostridium thermocellum has been reported to be many times larger than that of the aerobic fungus Trichoderma reesei (45), which might be expected to result in a correspondingly large reduction in the accessible pore volume. However, the bacterial enzyme system has significantly higher specific activity (e.g. 50-fold) (46) than the fungal system, and both enzyme systems appear to be similarly

effective at bringing about near-theoretical hydrolysis yields when acting on pretreated lignocellulosic substrates (47).

Pretreatment effectiveness has been correlated with removal of hemicellulose and lignin (see 38). Such correlations do not appear to be absolute, at least for lignin removal. For example, pretreatment of corn husks with 5% NaOH is not particularly effective, although 61% of the lignin is solubilized (48). In contrast, neither dilute acid nor steam explosion pretreatment involves appreciable lignin solubilization (36), yet both result in high hydrolysis yields. Although lignin solubilization is beneficial for enzymatic hydrolysis, its benefits must be weighed against the potential for fermentation inhibition by higher concentrations of soluble lignin derivatives and also against the increased difficulty of recovering energy from solubilized lignin as compared to insoluble lignin.

Although lignin does not have to emerge from pretreatment in soluble form (see above), it probably does have to be chemically modified. Indeed, I know of no effective pretreatment that does not involve either extensive lignin solubilization or elevated temperatures. Lignin melts at elevated temperatures $[>90^{\circ}$ wet, $> 160^{\circ}$ dry (49)], and several investigators have noted that lignin does not return to its original form when it condenses upon cooling (50–52). The reprecipitation of lignin is not a purely physical phenomenon, as it may be enhanced or inhibited by the presence of low-molecular-weight aromatic compounds from the extractives component of biomass (53, 54).

Cellulose crystallinity is known to be an important determinant of reactivity, and some pretreatments may enhance reactivity by decreasing crystallinity (55). However, decreasing crystallinity is not the key mechanism underlying pretreatment, as there are examples of effective pretreatments that result in unchanged or even increased crystallinity (40, 56). Sinitsyn et al (57) report a strong negative correlation between the enzymatic hydrolysis rate and the crystallinity index for cellulosic, but not lignocellulosic, substrates. In addition to crystallinity, the concentration of cellulose chain ends, particle size, and degree of polymerization have also been proposed as determinants of reactivity for pretreated materials (36).

Notwithstanding the considerable volume of information on substrate factors that are correlated with, and perhaps influence, pretreatment effectiveness, design of pretreatment processes is entirely empirical, and much of the process optimization has tended to be largely Edisonian as well. The dominant link between input parameters of a pretreatment process (temperature, residence time, acid or solvent concentration, etc) and effectiveness with respect to enzymatic hydrolysis is the chemistry operative within the pretreatment reactor. The literature on such operative chemistry is largely separate from that on the substrate features determining the effectiveness of pretreatment. Abatzoglou et al and Belkacemi et al (58, 59) have proposed a quasi-mechanistic phenomenological "severity parameter," which they have used to represent the interrelationship of time, temperature, and acid concentration. This parameter has also been used to correlate pretreatment effectiveness with reaction conditions (60).

The proton concentration is an important player in the reaction chemistry involved in pretreatment processes. Even in the absence of exogenously added acid, an acidic environment is favored by the endogenous formation of organics acids, principally acetic and formic, and by the increased dissociation of water at high temperatures (see below). Low pH accelerates degradation of soluble sugars (55, 61), and Kohlmann et al (55) have suggested that maintaining neutral pH during pretreatment may improve performance. Caustic addition was much more beneficial for Avicel than for native biomass substrates, and it may have been necessary because of the rather long (~ 1 h) reaction time used. In processes that involve exogenously added acids, protons must diffuse into the particle. Consistent with this mechanism, a rather small (e.g. 1–3 mm) particle size is usually used and is probably required for dilute acid pretreatment, whereas steam explosion and liquid hot water pretreatment are effective with much larger particle sizes (e.g. as-delivered wood chips or bagasse).

The role of water itself should not be underestimated. The presence of water lowers the softening point of lignin (62), allowing easier separation of the fibers (63). Internal bonds in lignin and glycosidic linkages in both hemicellulose and cellulose are cleaved by hydrolytic reactions. Hemicellulose, the most readily hydrolyzed constituent, is partially deacetylated, as well as depolymerized (64). Similarly, lignin can be depolymerized with only water in the absence of other biomass constituents (65, 66). The cleavage of chemical bonds may be enhanced by the increased disproportionation of water at elevated temperatures. At 220°C, for example, the ion product of liquid water is 10^{-11} (67), resulting in a pH of 5.6, compared to 7.0 at 25°C. Because of this effect, water may be a more significant acid under conditions typical of pretreatment than acetic or formic acid (M Antal, personal communication).

PERFORMANCE METRICS Important performance metrics for pretreatment are listed and discussed below. Dilute acid hydrolysis is used as a reference point for these metrics because it may be regarded as something of a benchmark. More detailed commentary on process alternatives follows this discussion. The important performance metrics for pretreatment are:

 Fiber reactivity. Effective pretreatments in general approach or exceed 80% of theoretical cellulose conversion upon subsequent hydrolysis of a representative hardwood feedstock (e.g. poplar) using moderate (e.g. 10–15 IU/g

cellulose) cellulase loadings. Such conversions are achieved in a period on the order of five days, although this is highly feedstock dependent.

- 2. Pentosan recovery. In light of the pervasive impact of process yield (15, 69), and the increasing availability of organisms capable of converting pentoses to ethanol (see section on Conversion Technology), high recovery of pentoses is a key feature of leading pretreatment technologies. Dilute acid hydrolysis generally produces 80% of the theoretical yield (33).
- 3. Extent of hydrolyzate inhibition. Inhibitory compounds are present in hydrolyzates from most pretreatment processes, with some form of postpretreatment detoxification such as overliming or steam stripping required in order for fermentation to proceed effectively (39).
- 4. Extent of size reduction required. Pretreatment processes differ widely in the extent of size reduction required. Costs and energy requirements for particle size reduction can be very significant, and they increase geometrically with decreasing particle size (38). The dilute acid pretreatment process used in the NREL design involves grinding to 1–3 mm, which accounts for one third of the power requirements of the entire process (33).
- 5. Low-cost materials of construction. Reactor size is determined by residence time and solids concentration. Materials requirements are a function primarily of the corrosivity of the process feed and secondarily of the pressure at which the process operates.
- 6. Production of process residues. Process residues arise principally from neutralization of acids, e.g. formation of gypsum when limestone is used to neutralize sulfuric acid. Such residues are largely if not entirely inert, and they are usually assumed to pass harmlessly through fermentation and distillation. They do however require disposal, most likely via landfill.
- 7. Potential for process simplicity. Process simplicity, which generally fosters process operability and low cost, is favored by the absence of postprocessing neutralization and/or reagent recovery.
- 8. Effectiveness at low moisture contents. Operation at high moisture levels generally increases energy requirements. This effect is likely to become increasingly significant at moisture contents ≥ 80 wt%. Much of the pretreatment literature is, however, based on studies using 10 wt% or less solids.

Evident from the above discussion is the fact that many of the largest cost impacts of the choice of pretreatment technology are manifested in other process

steps. In particular, pretreatment cost and performance are intimately linked with cost and performance in subsequent hydrolysis and fermentation steps.

PROCESSES Generalizing about pretreatment processes is challenging because so many different approaches have been shown to positively impact biomass reactivity. Most processes involve some degree of size reduction, e.g. at least to the size of chips for woody materials and often much smaller. Heat, often introduced by direct steam injection, is also commonly used. The most thoroughly characterized pretreatment process options include dilute-acid pretreatment (e.g. 50, 52, 56, 71, 72), steam explosion (e.g. 60, 73–76) including acid-catalyzed steam explosion (77, 78), ammonia fiber explosion (e.g. 34, 79, 80), and treatment with organic solvents (e.g. 81, 82). Additional processes that have been proposed but have received less attention to date include the use of milling (see 41), supercritical fluids (see 37), irradiation (83), biological delignification (55), oxidizing agents (84), alkali (48), lime (85), and liquid hot water (86).

Both steam-explosion and dilute-acid pretreatment have been the object of over a decade of R&D, much of which has been specifically targeted at fuel production from biomass. Both processes have been studied on a pilot scale (87), and are the subject of many dozens of papers. Dilute acid hydrolysis is preferred by NREL (38). The chief advantage of dilute acid hydrolysis relative to steam explosion appears to be higher recoveries of hemicellulose sugars. Specifically, hemicellulose sugar recoveries of 80% following hardwood pre-treatment are representative of dilute acid pretreatment (33), whereas I know of no steam explosion study reporting recoveries higher than the 65% observed by Heitz et al (60). In general, high recovery of hemicellulose sugars can be expected to have the dual advantages of higher ethanol yield and lower production of fermentation inhibitors.

Pretreatment is one of the most costly steps in cellulosic ethanol production, accounting for 33% of total processing costs (exclusive of feedstock) in the base-case NREL design presented below (see section on Current Process Economics). This value very likely underestimates the real importance of pretreatment, because pretreatment greatly affects the performance of fermentation and enzyme production. Of particular note is the tendency for pretreatment processes to produce biological inhibitors.

Inhibitor production has been documented for pretreatment with dilute acid pretreatment (39), steam explosion pretreatment (88, 89), and acid hydrolysis (90, 91). McMillan (39) and Olsson & Hahn-Hagerdal (92) provide excellent reviews of inhibitor production. Inhibitory compounds originate from 1. hydrolysis of extractive components, organic and sugar acids esterified to hemicellulose (e.g. acetic, formic, glucuronic, galacturonic), and solubilized phenolic

	Process						
Feature	Dilute acid	Steam explosion	AFEX	Liquid hot water			
Reactive fiber	Yes	Yes	Yes	Yes			
Particle size reduction required	Yes	No	No ^b	No			
Hydrolyzate inhibitory	Yes	Yes	No	Slightly			
Pentose recovery	Moderate	Low	High	High			
Low cost materials of construction	No	Yes	Yes	Yes			
Production of process residues	Yes	No	No	No			
Potential for process simplicity	Moderate	High	Moderate	High			
Effectiveness at low moisture contents	Moderate	High	Very high	Not known			

Table 4 Comparison of pretreatment processes^a

^a Modified from (86); AFEX ratings from Bruce Dale (personal communication).

^bFor grasses, data for wood not available.

lignin derivatives; 2. degradation products of solubilized sugars (e.g. furfural, hydroxymethylfurfural); 3. degradation products of lignin (e.g. cinnamaldehyde, p-hydroxybenzaldehyde, syringaldehyde); and 4. corrosion products (e.g. metal ions). Largely because of inhibition, reports of fermentation of as-received pretreated slurries (including both fiber and liquid hydrolyzate as they emerge from pretreatment) are exceedingly rare.

In terms of the performance metrics presented above, the ideal pretreatment process would produce reactive fiber; yield pentoses in nondegraded form; exhibit no significant inhibition of fermentation; require little or no size reduction; entail reactors of reasonable size, built of materials with a moderate cost; not produce solid residues; have a high degree of simplicity; and be effective at sufficiently low moisture contents to avoid significant economic penalty. As indicated in Table 4, the most thoroughly-studied pretreatment processes (dilute acid hydrolysis and steam explosion) do not meet these criteria. AFEX and liquid hot water pretreatment appear promising, but will require additional study before a more definitive evaluation can be made (86).

Biological Conversion

MICROORGANISMS AND FERMENTATION An element common to essentially all proposed processes for producing ethanol from cellulosic biomass is microbial fermentation. A variety of microorganisms, generally either bacteria, yeast, or fungi, ferment carbohydrates to ethanol under oxygen-free conditions. Cells carrying out such fermentations do so to obtain energy (in the form of adenosine triphosphate) and are thus dependent upon ethanol production for growth and long-term survival. The net result of fermentation is:

Carbohydrate + Cell mass \rightarrow Ethanol + CO₂ + More cell mass.

In the absence of cell production, the maximum possible yield of ethanol is 0.51 (mass ethanol/mass carbohydrate, corresponding to 51% of the carbohydrate converted to ethanol on a mass basis), the balance being carbon dioxide. Typically, about 5-12% of the carbohydrate is converted to cells, which results in most proposed ethanol production processes converting not more than 47% of the fermented carbohydrate to ethanol.

The ideal organism or system of organisms for producing ethanol from cellulosic biomass in a process featuring enzymatically mediated hydrolysis would simultaneously exhibit the following properties: (*a*) synthesis of an active cellulase enzyme system at high levels, (*b*) fermentation and growth on sugars arising from both cellulose and hemicellulose, and (*c*) production of ethanol at high selectivity and high concentration.

As illustrated in Table 5, all described microorganisms and compatible combinations of microorganisms fall short of this ideal. Most commonly, this shortfall is due to one of two limitations: (a) an inability to utilize the range of carbohydrates present in biomass (e.g. cellulose, xylan) while also producing ethanol at high yield or (b) differing requirements for oxygen for various functions essential to the process. Examples of microorganisms with the first limitation include Clostridium papyrosolvens C7 (92a) and a coculture of C. thermocellum and Clostridium thermosaccharolyticum (93). Examples of microorganisms with the second limitation are fungi that are unable to grow and ferment under oxygen-free conditions, with the result that carbohydrate is respired to CO₂ to support production of cells and often cellulase that could otherwise have been converted to ethanol. Thus, oxygen-requiring cellulase production by T. reesei is incompatible with ethanol production in the sense that cellulase production using this organism cannot occur in the same vessel as ethanol fermentation. For the pentose-fermenting yeasts (94) and the cellulaseproducing Fusarium oxysporum (95) and Neospora crassa (96), robust growth occurs when oxygen is plentiful, ethanol production occurs when oxygen is limiting (and hence at very low concentrations), and it is difficult to obtain both growth and high ethanol yields at the same time.

Addressing the above limitations is a key focus for R&D involving improvement and development of microorganisms. For example, a concerted effort has been made to develop improved pentose fermenters using recombinant DNA technology. Using xylose-fermenting organisms, *Escherichia coli* (97) and later *Klebsiella oxytoca* (98), Ingram and coworkers improved ethanol yields by introducing genes from *Zymomonas mobilis*. Ho and coworkers introduced

		Capability					
Functional description	Examples	Utilize hexoses	Utilize pentoses	Produce cellulase	Produce ethanol	High yields ^b	Anaerobic growth and fermentation
Nonmodified hexose fermenters	Saccharomyces sp. Zymomonas mobilis	Yes Yes	No No	No No	Yes Yes	Yes Yes	Yes Yes
Nonmodified xylose fermenters	Pichia stipitis/ Candida shehatae Xylose-fermenting thermophiles ^c	Yes Yes	Yes Yes	No No	Yes Yes	No No	No Yes
Modified xylose fermenters	Escherichia coli Saccharomyces Zymomonas mobilis	Yes Yes Yes	Yes Yes Yes	No No No	Yes Yes Yes	Yes ^d Yes ^d Yes ^d	Yes Yes Yes
Cellulase producers (non ethanol- producing)	Trichoderma reesei	Yes	Yes	Yes	No	—	No
Cellulase/ethanol coproducers	Clostridium thermocellum	Yes	No	Yes	Yes	No	Yes
	Clostridium papyrosolvens C7	Yes	Yes	Yes	Yes	No	Yes
	Neospora crassa, Fusarium oxysporum	Yes	Yes	Yes	Yes	No	No

Table 5 Properties of selected microorganisms considered for production of ethanol from cellulosic biomass^a

^aSee text for references.

^bDenotes essentially no formation of by-products with near-theoretical yields (allowing for carbon diverted to cell production and considering process steps involving both cell production and fermentation if these are envisioned to be separate).

^cFor example, *Clostridium thermohydrosulfuricum, Clostridium thermosaccharolyticum, Thermoanerobacter ethanolicus.* ^dUnder at least some conditions.

genes for xylose utilization into the yeast *Saccharomyces cerevisiae* (99, 100), and Picatagio and coworkers have introduced genes for xylose utilization into *Z. mobilis* (101). A focus of work on the pentose-fermenting yeasts (94, 102, 103) and *F. oxysporum* (104) is optimization of the oxygenation to achieve the optimal balance between growth and fermentation. Organism development efforts involving both *Z. mobilis* (S Picatagio, personal communication) and pentose-fermenting yeasts (T Jeffries, personal communication) are directed toward developing strains capable of fermenting arabinose, a key component of the fibrous component of corn kernels. The author's group is working to characterize and improve thermophilic ethanol-producing bacteria via both fermentation studies and molecular techniques (105–107). Organism development to address the issue of inhibition by pretreatment by-products is difficult to undertake systematically at present because understanding of the identity of

inhibitory compounds and mechanisms is so incomplete. As such understanding becomes available, development of inhibitor-resistant strains could well become important.

Development of pentose-fermenting ethanol-producing microorganisms is equally important for processes based on acid hydrolysis as it is for processes based on enzymatic hydrolysis. The matter of fermentation inhibitors is equally or more important for acid hydrolysis with respect to corrosion products. In comparison to enzymatically based processes, inhibition by sugar and lignin degradation products is less important for processes using concentrated acid and of roughly equal importance for processes using dilute acid. Cellulase production is irrelevant for a process reliant on acid hydrolysis.

CELLULASES AND ENZYMATIC HYDROLYSIS Hydrolysis of cellulose is generally rate limiting in enzymatically based biomass ethanol processes (108), and it occupies a similarly central position in process economics. A voluminous literature exists on biochemical and genetic features of enzymes responsible for the hydrolysis of insoluble biomass polymers. No attempt is made to review this literature herein; only general comments are offered. A detailed treatment of the subject is provided in the recent, comprehensive reviews of Beguin & Aubert (109) and Wong & Saddler (110).

Microorganisms accomplish enzymatic hydrolysis of cellulose and hemicellulose by systems of multiple functionally and structurally distinct enzymes collectively referred to as cellulases (which catalyze the hydrolysis of cellulose) and xylanases (which catalyze the hydrolysis of xylan). Some such systems consist of discrete enzymes whereas others involve multi-enzyme complexes. In either case, components of cellulase and xylanase systems act synergistically with each other to accomplish hydrolysis.

The interaction between hydrolytic enzymes and cellulosic substrates is exceedingly complex, in part because of the significant number of interactions possible in a system involving a multicomponent biocatalyst that adheres to and acts catalytically upon a multicomponent (e.g. cellulose, hemicellulose, and lignin) insoluble biomass substrate. Further complexity is introduced by the substantial variation of physical properties among biomass particles, the effects of soluble compounds (sugars resulting from hydrolysis, fermentation products, and compounds produced in pretreatment) on enzymatic activity, profound changes in substrate properties as the hydrolysis reaction proceeds, and equally profound changes in substrate properties as a result of pretreatment. Finally, the production of hydrolytic enzymes is subject to metabolic control mechanisms about which current understanding is quite incomplete.

As a result of the above complexity, a mechanistically valid quantitatively accurate model of the action of cellulase enzymes does not exist and may

well not be forthcoming soon. Most research on cellulases involves either elucidation of particular features and mechanisms or efforts to describe the action of cellulases based on largely descriptive models that incorporate less than full mechanistic detail. As an example of the latter, South et al (110a) have suggested the following as essential phenomenological features of models for the enzymatic hydrolysis of cellulose: 1. adsorption that allows for either enzyme or substrate to be in relative excess; 2. a conversion-dependent rate equation that reflects the declining ratio of rate per enzyme adsorbed to cellulose as the reaction proceeds; and 3. for continuous reactors, a particle-population that accounts for variation in rate over the time individual particles spend in the reactor. Each of the above features represents a deviation from widely accepted paradigms for the kinetics of enzymes acting on soluble substrates.

Dedicated cellulase production has been investigated most extensively for the aerobic fungus *T. reesei*. Esterbauer et al (111) and Kadam (112) provide detailed discussions of this subject. In the context of considering strain development for high cellulase production, Esterbauer et al make the statement that "We and others feel that cellulase production by *Trichoderma* has its limitations and a significant further improvement cannot be expected" (111, p. 53). However, further reductions in the cost of cellulase can likely be achieved via improved production and utilization technology, and/or consideration of cellulase-producing organisms other than those belonging to the *Trichoderma* genus.

The influence of the cost of cellulase production on overall economics is somewhat subtle because the primary impact of the high cost of cellulase production is associated with the cost of hydrolysis rather than from the cost of cellulase production per se. When cellulase production is carried out separately from hydrolysis and fermentation, as in simultaneous saccharification and fermentation (SSF), there is a tradeoff between the cost of cellulase production and the cost of hydrolysis/fermentation.¹ As illustrated in Figure 2, short hydrolysis reaction times involve higher cellulase and lower hydrolysis/fermentation costs than longer reaction times. The optimum, corresponding to the point at which the combined cost is minimized, is constrained by the cost of cellulase. Overall cost reductions can be achieved by technologies that shift the cellulase cost curve to the left and/or shift the hydrolysis/fermentation curve to the right. As the cost of cellulase production approaches zero, which it does with a consolidated bioprocessing strategy (113), the total cost curve becomes coincident with the hydrolysis/fermentation cost curve and large reductions can be achieved in both reaction time and cost.

¹An analogous tradeoff exists for single organisms that both produce cellulase and ferment the resulting hydrolysis products, a topic under consideration by my research group.



Figure 2 Tradeoff between cellulase and fermenter costs for cellulosic ethanol production via SSF. Modified from (113).

PROCESS CONFIGURATIONS Four biologically mediated events occur in the course of producing ethanol from cellulosic biomass using enzymatic hydrolysis: cellulase production, cellulose hydrolysis, hexose fermentation, and pentose fermentation. Process configurations proposed for the biological steps differ in the degree to which these events are integrated. As shown in Figure 3, separate hydrolysis and fermentation (SHF) involves four bioreactors. SSF consolidates hydrolysis and C6 fermentation with cellulase production that is carried out in a separate step by different organisms; either two or three bioreactors are involved, depending on how C5 sugars are processed. Consolidated bioprocessing (CBP) accomplishes cellulase production, hydrolysis, and fermentation simultaneously in a single bioreactor. The state of the art currently involves SSF, with cofermentation of hexoses and pentose sugars a focus for near-term development (114). Organisms and process configurations for cellulosic ethanol production have been reviewed by Wyman (31).²

²The term "consolidated bioprocessing" (abbreviated CBP) is synonymous with the term "direct microbial conversion" (abbreviated DMC). However, the current process nomenclature may benefit from revision, as indicated by the observations that SSF is often confused with DMC although they are quite distinct. DMC (as well as SSF) involves simultaneous saccharification and fermentation, and SSF might also be considered to be "direct" in that nonhydrolyzed pretreated substrate is fed to the vessel in which fermentation occurs (just as in DMC). Since SSF and what has hitherto been termed DMC are differentiated by the extent of consolidation, the term "consolidated bioprocessing" is proposed and used herein.

The difference between SHF and SSF is one of arrangement of the same components. In both of these alternatives, one microorganism is used to produce cellulase, and a second is used to carry out fermentation. Based on extensive study by the Solar Energy Research Institute (now NREL) (69, 115), the SSF approach appears to enjoy a substantial economic advantage over SHF. As depicted in Figure 2, CBP is the logical endpoint in the evolution of biomass conversion technology. CBP is less well developed than SSF, but it is expected to offer the lowest costs if limitations of current systems can be overcome. The key difference between CBP and other biomass processing strategies is that a single microbial community is employed for both cellulase production and fermentation. This difference has several significant ramifications, including no capital or operating costs for dedicated enzyme production, greatly reduced diversion of substrate for enzyme production, and compatible enzyme and fermentation systems. Dedicated cellulase production, e.g. by an aerobic fungus such as T. reesei, is relatively slow and expensive-some would say prohibitively expensive for biocommodity applications (116). As a result, there is a strong economic incentive to operate with low cellulase loadings and hence large and expensive SSF reactors (1, 113; see Figure 2). CBP is in principle not subject to this constraint. The large cost impact of these features is discussed in the section on Mature Conversion Technology.

Product Recovery

Purification of ethanol from the concentration produced by fermentation to concentrations useful as fuels is normally accomplished via distillation. As



¹SHF: SEPARATE HYDROLYSIS AND FERMENTATION.

SSF: SIMUTANEOUS SACCHARIFICATION AND FERMENTATION, SEPARATE PENTOSE FERMENTATION.

SSCF: SIMULTANEOUS SACCHARIFICATION AND CO-FERMENTATION.

CBP: CONSOLIDATED BIOPROCESSING.

Figure 3 Consolidation of biologically mediated events in cellulosic ethanol production.

discussed by King (117), distillation involves the counter-current contacting of an ascending vapor stream and a descending liquid stream. These streams are arranged so that at any given point in the column the vapor contains less than the equilibrium amount of one or more volatile components than does the liquid with which it is in contact. As a result, the vapor is enriched in the more volatile component(s) as it moves up the column. Distillation is a standard unit operation of chemical engineering, and thus the product recovery section of an ethanol plant can be designed with a high degree of certainty and little or no development work. In contrast, for pretreatment and biological conversion, design is largely empirical, and technology has generally not been proven on a commercial scale for cellulosic materials.

Ethanol recovery has been reviewed by Busche (118) and Katzen et al (119). Essentially all of the ethanol resulting from fermentation is recovered from the fermentation broth in a stripping or beer column. Thereafter, ethanol is concentrated in a rectifying column up to a concentration \leq that of the ethanol-water azeotrope (about 95% ethanol by weight). If essentially water-free ethanol is desired, purification beyond the azeotrope can be achieved by further distillation in the presence of an entrainer (e.g. benzene, cyclohexane) that is subsequently recovered, adsorption using corn grits or some other solid material, or pervaporation or other membrane-based operations.

Regardless of the fermentative organism used, ethanol production from cellulosic biomass is likely to involve operation at lower product concentrations (e.g. < 5 wt%) than are typical of ethanol production from corn. This situation arises as the result of both biological and processing constraints. Although the maximum concentration of ethanol tolerated by industrial yeasts and Z. mobilis is on the order of 10 wt% at 30° C (120–123), the tolerance of microorganisms to ethanol generally decreases with increasing temperature (124). All SSF designs I know of call for operation at near the maximum temperature tolerated by the fermentative organism in order to maximize cellulase activity, an approach consistent with the dominant cost impact of cellulase production relative to distillation. For example, the current NREL SSF design is operated at 37°C, at which the maximum ethanol concentration tolerated by both yeast and Z. mobilis is reduced by half to 5 wt% (125, 126). On the processing side, cellulosic slurries become progressively more paste-like and difficult to handle at solids concentrations exceeding 15 wt% (the NREL design uses 16 wt%). At a representative carbohydrate content for cellulosic feedstocks-approximately two thirds on a dry weight basis-a 15 wt% feed corresponds to a potential ethanol concentration of 5 wt%.

Distillation is examined below in terms of both cost (in the sections on Current Process Economics and Mature Conversion Technology) and process energy

balance (in the section on Energy Balance). These considerations support the general conclusion that distillation is often overrated as a constraint on the practicality and desirability of ethanol production.

Utilities and Waste Treatment

In addition to production and recovery of ethanol per se, the functional components of a stand-alone cellulosic ethanol plant provide steam and other process utilities as well as treatment of process effluent streams.

The unfermentable lignin remaining after ethanol production can in principle be converted to chemicals (127, 128), but it is likely to be burned as a process fuel in a large-scale industry because markets for most lignin-derived byproducts are much smaller than the markets for fuels. Although lignin seldom comprises more than 25% of the mass of dry hardwood, it can easily represent a third or more of the heating value for woody materials. The dewatered lignin-rich solid residue resulting from fermentation is a good boiler fuel with some resemblance to low-sulfur soft coal or peat. Designs for larger plants very often involve cogeneration of electricity. For woody feedstocks, combustion of process residues is sufficient to provide all of the steam and power required by the plant, with some electricity usually exported for sale. Rankine cycle-based biomass combustion and power generation is used commercially today. At the same time, significant advances in biomass power generation are expected to result from use of gasification and combined cycle gas turbines (129). Electricity export represents about 4.2% of the high heating value of the biomass in the base-case NREL design for a poplar feedstock (Table 8). As cellulose ethanol technology matures, the energy required by the various process steps is likely to decrease, making coproduction of electricity more significant (130).

Process effluents envisioned for cellulosic ethanol production facilities have been reviewed in detail (131–133). Although the effluent composition depends on the conversion technology used, some generalizations may be made. It is anticipated that air pollution control will be applied to flue gas components (NO_x, SO₂, CO) as well as to lesser amounts of volatile organics released in various process steps. Water pollution control will be applied to reduce biological oxygen demand and particulates. Available information suggests that air and water emissions can be maintained below applicable standards with available control technology. Solid waste disposal will be required, primarily for boiler ash and flue gas desulfurization solids. The amount of ash generated will depend strongly on whether acid is used in pretreatment/hydrolysis with generation of precipitates upon neutralization. None of the solid wastes generated is considered to be hazardous.

CURRENT PROCESS ECONOMICS

No commercial facility currently produces ethanol from cellulosic biomass via enzymatic hydrolysis. Thus, understanding of the cost of such processes is necessarily based on projections developed from laboratory and, in some cases, pilot data. Because the NREL is coordinating the largest and most comprehensive effort in the world dedicated to developing cellulosic ethanol conversion technology, their publicly available and well-documented designs are used as a benchmark in this review and elsewhere.

The most recent publicly available NREL designs are based on a poplar energy crop assumed to cost \$42 per delivered dry ton and on an SSF-based process involving fermentation via yeast and cellulase production by *T. reesei*. Table 6 presents a cost and selling price summary, developed by Lynd et al (32), based on an NREL design that was reviewed and validated by Chem Systems (33). For the purpose of this analysis, the process steps are as follows: pretreatment (including feedstock handling and milling), biological conversion (accomplishing,

	Selling price breakdown						
	С	ents/gallon					
	Capital, labor and			% of Total			
	related	Energy	Total	Processing	Overall		
Raw Materials							
Feedstock			45.97	_	39.0		
Other			9.78	_	8.3		
Subtotal			55.75		47.3		
Processing							
Pretreatment	13.75	6.55	20.3	32.7	17.2		
Biological	18.60	6.00	24.6	39.6	20.9		
Cellulase production	1.55	1.67	3.22	5.2	2.7		
SSF	13.83	3.34	17.17	27.7	14.6		
Pentose conversion	3.22	0.99	4.21	6.8	3.6		
Distillation	2.74	5.10	7.84	12.6	6.7		
Power cycle	28.61	-26.96	1.65	2.7	1.4		
Other	7.34	0.36	7.70	12.4	6.5		
Subtotal	71.04	- 8.95	62.09	100.0	52.7		
Grand total			117.84		100.0		

 Table 6
 Biomass ethanol cost summary—base-case technology^{a,b}

^aFrom (32).

^bFeedstock: 658,000 dry tons/year. Plant capacity: 60.1 million gallons/year. Installed capital cost: \$150.3 million (first quarter, 1994).

in various configurations, cellulase production, cellulose hydrolysis, hexose fermentation, and xylose fermentation, and including associated seed fermentors, compressed air, and chilled water), distillation, the power cycle (including the boiler, turbine, and related equipment), and other (including environmental, tankage, and miscellaneous). Costs for these steps are broken down into two categories: energy and nonenergy. Nonenergy costs include direct capital and labor costs, as well as items proportional to one or both of these (maintenance at 3.0% of total fixed investment, general plant overhead at 65% of labor and maintenance, direct overhead at 45% of labor, taxes and insurance at 1.5% of total fixed investment). Results are reported on a per-gallon pure ethanol basis, although the actual distillate is 90% ethanol suitable for use as a neat fuel. The feedstock is assumed to be poplar, a leading candidate for a hardwood energy crop. Additional information on procedures underlying the analysis is presented in (32).

The projected base-case selling price is 117.8 cents per gallon, based on the sum of operating costs and allowance for capital recovery. Dominant cost elements include raw materials, biological conversion (most notably SSF), pretreatment, and the capital cost for the power cycle. Process energy requirements—steam at two pressures and electricity—are represented in terms of lost electricity revenue (electricity valued at 4 cents per KWh).

Of the overall projected selling price of 117.8 cents per gallon in the NREL design, capital recovery accounts for 50 cents per gallon. Thus the cost of capital, as indicated by the effective investment return for funds used to build a facility, has a strong impact on economic viability. The data presented in Table 6 are consistent with a return on investment of 14.2% based on construction time and capacity build-up assumptions anticipated for mature technology, and of 10% based on assumptions likely to be more representative of a first-of-kind process (32). Although a \$1.18 per gallon selling price is entirely competitive with current prices for corn-based ethanol, the risk associated with a cellulose-based plant is higher than the risk for a corn-based plant, and this added risk is not adequately rewarded by a 10% investment return. Thus, production of ethanol from cellulosic energy crops is thought to be roughly cost competitive with production from corn at comparable cost of capital, but not when the higher cost of capital for a cellulose-based plant is considered.

Although the largest body of publicly available information on the costs of ethanol production has been developed for energy crops, production from waste feedstocks is very likely to become more economically attractive in the near term. "Niche" opportunities involving waste feedstocks and other costreducing factors are discussed in the section on Near-Term Commercialization Prospects.

MATURE CONVERSION TECHNOLOGY

The vast majority of analyses of selling price for cellulose ethanol have had a near-term focus and have thus incorporated few, if any, future research-driven improvements. The disparity in the conclusions of studies comparing the costs of cellulosic ethanol and other energy technologies often results from a failure to compensate for the fact that the technologies are not at the same level of maturity.

Lynd et al (32) have undertaken an analysis motivated by the following question: What are the likely features and cost of a facility producing ethanol from cellulosic biomass at a level of maturity comparable to a refinery? We developed an "advanced" technology scenario representing our best estimate of the most likely features of mature biomass ethanol technology. We also developed a "best parameter" scenario, which is intended to be indicative of the potential for R&D-driven cost reductions, based on the best values for individual process parameters in the literature. Cost reductions due to increased scale, reduced feedstock costs, and improved conversion technology are considered. The plant scale assumed in the analysis corresponds to the largest existing corn ethanol facility (330 million gallons per year). Although this capacity is probably sufficient to realize most economy of scale benefits, it is far below the capacity at which feedstock delivery becomes a constraint for a plant processing energy crops (32). A feedstock cost of \$38.6 per delivered dry ton is assumed for the advanced case and of \$34.00 per delivered dry ton for the best parameter case. The former corresponds to the average cost projected by Perlack & Wright (19) for 2020, although it is by no means a limiting value. The latter amount corresponds to the goal of the Biofuels Feedstock Development Program at the Oak Ridge National Laboratory. Finally, the impact of conversion technology improvements was considered for pretreatment and biological conversion but not for other process steps.

Selling prices projected by Lynd et al are 50.3 cents per gallon for the advanced technology scenario and 34.3 cents per gallon for the best parameter scenario. Improved conversion technology is by far the largest contributor to reducing the cost of ethanol production; conversion-related cost reduction for the advanced scenario is 3 times larger than that associated with scale and 10 times larger than that associated with less expensive feedstock. Table 7 presents a cost and selling price summary for the advanced case.

The largest conversion-related cost reductions are due to a more than eightfold reduction in the cost of biological conversion, the most expensive step in the base case (Table 6). More efficient biological processing is the major factor behind increasing electricity exports in the advanced case, and it is a significant factor in reducing the cost of raw materials and increasing process yields.

		Selli	ng price bre	eakdown	
		Cents/gallor	1		
	Capital,				
	labor and			% of To	otal
	related	Energy	Total	Processing	Overall
Raw Materials					
Feedstock			35.84	_	71.3
Other			0.95	_	1.9
Subtotal			36.79		73.2
Processing					
Pretreatment	3.22	5.63	8.85	65.5	17.6
Biological	1.95	1.00	2.95	21.8	5.9
Distillation	1.79	2.83	4.62	34.2	9.2
Power cycle	14.06	-22.03	-7.97	-59.0	- 15.8
Other	4.74	0.32	5.06	37.5	10.1
Subtotal	25.76	-12.25	13.51	100.0	27.0
Grand total			50.30		100.2

 $\label{eq:table_$

^aFrom (32).

^bFeedstock: 2,738,000 dry tons/year. Plant capacity: 294.9 million gallons/year. Installed capital cost: \$268.4 million (first quarter, 1994).

RESEARCH PRIORITIES

Information presented in the above sections is consistent with the existence of a substantial gap between conversion technology believed to be deployable today and mature technology, as exemplified by the base-case and advanced scenarios, respectively. R&D is the key to closing this gap. Logical priorities for R&D are process steps or functionalities that are both costly and have significant potential for improvement through R&D. For an enzymatic-hydrolysis based process such as the base-case considered above, process steps that meet this high-cost, high-impact criterion include biological conversion, pretreatment, and the power cycle. At the most general level, the greatest cost reduction impacts come from reductions in the cost of making biomass fermentable. As discussed below, several strategies to achieve such reductions can be pursued.

Figure 4 provides a more detailed perspective on the cost impacts of various R&D targets and documents the relative contribution of factors responsible for the difference between the base-case and advanced scenarios (see figure legend for details). Of the improvements considered, process improvements contribute most by far to the lower cost of the advanced scenario. Figure 4 shows that consolidated bioprocessing, improved pretreatment, and elimination of seed



Figure 4 Cost sensitivity of cellulosic ethanol process improvements. Based on (32).

reactors (discussed below) have the largest cost impacts among the individual improvements in the advanced design. Of the potential process improvements not incorporated into the advanced design, use of an advanced power cycle is thought likely to have the greatest potential for further cost reductions (32), although this remains to be investigated in detail. Relatively incremental improvements in various process steps (product recovery, wastewater treatment, solids receiving and handling) may also be possible as the technology matures.

The almost 10-fold reduction in the cost of biological conversion is the largest contributor to the lower projected selling price for the advanced technology scenario relative to the base-case. The improvements in biological processing in turn result largely from the assumption of consolidated processing (CBP). There are no apparent bioenergetic or metabolic barriers to coproducing ethanol and hydrolytic enzymes under anaerobic conditions, which are required for consolidated bioprocessing; I am currently working on a study to document this

point more thoroughly. Attaining the benefits of CBP as embodied in the advanced technology scenario does not appear to require better hydrolytic enzyme systems or a more ethanol-tolerant microorganism than those documented to date. Instead, attaining these benefits requires only that the properties of separate existing microorganisms be combined into a single organism (or system of organisms). Because combining properties of separate organisms is the salient feature of genetic engineering, I suggest that few experts would doubt that with sufficient effort organisms compatible with CBP can be created.

In principle, CBP organisms can be created via two paths (113). Path 1 involves modifying good ethanol producers (e.g. Z. mobilis, yeast) so that they also become good cellulase producers. Path 2 involves modifying good cellulase producers so that they also become good ethanol producers. Each path has potential advantages, and both merit much more intensive investigation than they have received. More is known about the genetic engineering of suitable host organisms for path 1 than for path 2. A second advantage of path 1 is that the ethanol tolerance of path 2 organisms may be difficult to improve using molecular genetics in the perhaps likely event that such tolerance is under the control of multiple genes. On the other hand, coordinated, high-level expression of hydrolytic enzymes (required for path 1) is a more challenging job for genetic engineering than inactivating genes associated with undesirable fermentation products (required for path 2). In addition, the economic importance of high performance hydrolytic enzymes (an intrinsic feature of path 2 organisms that may be difficult to entirely confer to path 1 organisms) is in general much greater than that of high ethanol tolerance (an intrinsic feature of path 1 organisms that may be difficult to entirely confer to path 2 organisms). Underlying both paths is a basic understanding of production of hydrolytic enzymes (in particular in conjunction with fermentative metabolism), the action and kinetics of hydrolytic enzymes, and reactor design for systems in which enzymatic cellulose hydrolysis is rate limiting. Further elucidation of such topics will support development of CBP organisms as well as other objectives.

Processes expressly designed to make biomass accessible to enzymatic hydrolysis are not a part of any established industry. Thus there is room for further development and improvement of all pretreatment processes, including those such as acid hydrolysis and steam explosion that are relatively well established. The case in support of R&D is particularly strong for less-studied processes (e.g. liquid hot water and AFEX pretreatments), because such processes may address the limitations of more established processes. Exploratory investigation of new pretreatment processes is also an important avenue for research activity. Increased fundamental understanding of pretreatment processes is needed, with respect to both the chemistry operative in the pretreatment reactor (which will depend on the process) and the interaction between pretreatment-determined substrate properties and the action of hydrolytic enzymes. Desired features of pretreatment R&D include optimization based on diverse performance metrics as well as on fiber reactivity (e.g. hydrolyzate inhibition and pentosan recovery), fermentation of as-produced pretreated fiber and hydrolyzates (as opposed to washed fiber and/or studies that only encompass enzymatic hydrolysis), and data reporting so that yields can be related to nonpretreated biomass.

"Seed reactors," as the term is used here and in the context of the base-case NREL design, are bioreactors that produce microbial biomass (cells) before this biomass is used to catalyze transformations essential to the process. Thus, in the NREL base-case, yeast is produced in an aerated seed reactor (purchased glucose is used as the substrate) before it is used to perform anaerobic fermentation in SSF. Xylose-fermenting recombinant E. coli is produced in an aerated seed reactor prior to its use in anaerobic xylose fermentation. Finally, T. reesei is produced in a seed fermentor prior to its use for production of cellulase that is eventually fed to the SSF process. These seed fermentors are not only for preparation of a small innoculum, they are also responsible for a significant fraction of overall microbial cell production. The substantial cost of such operation (12.2 cents/gallon, or 21% of total processing costs in the base case) can be attributed to a combination of capital equipment, operating costs (for aeration, cooling, and agitation, as well as general maintenance), decreased ethanol yield (because the aerobic metabolism characteristic of seed production completely oxidizes carbohydrate to water and CO₂), and substrate (in the case of glucose, which is purchased for seed production using yeast). Continuous bioreactors, including those processing cellulose (134), are well known to be capable of autogenous production of microbial biomass. Such autogenous production requires the introduction of a relatively small innoculum at the beginning of a run potentially of several months duration, with associated costs likely to be only a few percent of those associated with seed fermentors as defined above. The research priority most directly associated with reducing the cost of seed fermentors has already been alluded to: reduction of the inhibitory character of pretreatment. It may be noted that the cost of seed reactors is lower in more recent NREL process designs than in the base-case considered here.

Research priorities for power production from lignin-rich residues resulting from ethanol production appear to overlap almost completely with those for advanced power generation from biomass in general. A promising focus for power-cycle research is biomass gasification (see 8) performed in conjunction with combined cycle gas turbines (see 129) and perhaps fuel cells as well. Lobachyov & Richter (135) and Harvey & Richter (136, 137) have proposed integrating combined cycle gas turbines and fuel cells for high-efficiency

electricity production. Electrical generating efficiencies on the order of 60% are projected for coal, and this group is beginning to actively consider the application of this approach to biomass.

The above discussion has been largely framed by the particular technology path embodied in the advanced technology scenario of Lynd et al (32). However, other low-cost process concepts are also possible and provide partially or entirely separate paths by which the goal of very low-cost production of ethanol from cellulosic biomass may be approached. For example, a pretreatment process that rendered cellulose as reactive as starch would make the cost of hydrolytic enzymes much less important than it is currently. A very low-cost method of recycling cellulase would have the same effect even in the absence of pretreatment improvements. A very low-cost method of recycling mineral acids could obviate the need for pretreatment and cellulase production altogether. The need for aqueous phase cellulose hydrolysis itself is not necessarily required for low-cost biomass processing, as indicated by the work of Gaddy et al (see section on Conversion Technology). These examples illustrate the point that a breakthrough in one process area has the potential to lessen or eliminate the need for breakthroughs in other areas.

In summary, identifying process improvements that have the potential for large reductions in the cost of producing ethanol from cellulosic biomass is both possible and useful. Although such an exercise significantly narrows the list of high-priority research topics, the number of research topics and process concepts that satisfy this high-impact criterion is still substantial. Such diversity increases the overall probability of developing low-cost biomass ethanol technology. However, this diversity also exacerbates the challenge of allocating limited dollars for support of research. The majority of foreseeable processing advances that have a large economic impact involve reducing the cost of making biomass fermentable. An array of approaches can be used to pursue this goal, including consolidated bioprocessing, advanced pretreatment processes, cellulase recycling, acid recycling, and gasification followed by fermentation of synthesis gas to ethanol. I believe consolidated bioprocessing in conjunction with advanced pretreatment represents a particularly attractive strategy because it offers the potential for a highly streamlined process that takes full advantage of the power of biotechnology for efficient and low-cost catalysis.

ENERGY BALANCE

The relative magnitude of energy outputs and inputs associated with ethanol production is a key metric for evaluating the efficacy of large-scale implementation. Hwang & Jefferiss (RJ Hwang & P Jefferiss, manuscript in preparation) present a range of 4–7 for reported values of the energy-output:energy-input

ratio (unadjusted basis, see below). Shapouri et al (139) provide an overview of recent estimates for corn ethanol.

Relevant measures of energy output include the energy yielded as ethanol and electricity on either an unadjusted (e.g. Kjoule) or a displaced fossil fuel basis. These measures differ because more than one unit of fossil energy is required to produce a unit of electrical energy; a representative efficiency of 35% is used here. In addition, if ethanol is used in neat form in optimized engines, then more than one unit of fossil fuel is displaced per unit of ethanol used (see section on Fuel Performance); a ratio of 1.175 units of displaced fossil fuel per unit of ethanol is used here, indicative of the long-term potential of this fuel, assuming optimized engines become available (see section on Fuel Performance). Relevant measures of energy input include the energy content of the biomass (e.g. high heating value) and the energy inputs for feedstock production, feedstock transportation, chemical inputs, product distribution, and plant amortization.

Table 8 shows a comparison of energy-output:energy-input ratios based on the above measures for the base-case, advanced, and best-parameter scenarios defined above. An additional scenario is also defined, based on the combining of the ethanol production technology in the advanced case with electricity coproduction via a first-generation biomass gasification/combined cycle gas turbine (BGCCGT), rather than a conventional Rankine cycle, as in the other three cases. This fourth case is included to illustrate the possible impact of combining advanced ethanol production technology with advanced technology

	Energ	y output HHV) ^a	EtOH + electricity	Displaced fossil fuel ^b	EtOH + Electricity Feedstock	Displaced fossil fuel Feedstock
Scenario	Ethanol	Electricity	Biomass (HHF)	Biomass (HHV)	and process ^c	and process
Base case	46.1	4.2	0.503	0.662	4.36	5.74
Advanced	54.4	6.8	0.612	0.834	6.58	8.96
Best parameter	61.4	7.9	0.693	0.947	7.40	10.1
Advanced/ BGCCGT ^d	54.4	11.4	0.658	0.965	7.10	10.4

 Table 8
 Output:input energy ratios for current and projected cellulosic ethanol technology

^aHHV: high heating value of the biomass. All values are from (32) except the electricity value for BGCCGT (see footnote d). ^b2.86 × electricity + 1.175 × ethanol, see text.

^cEnergy values for energy crop production, raw material transport, chemical inputs, fuel distribution, and plant amortization are from (1). Fuel distribution inputs are assumed constant per unit ethanol produced, with other inputs assumed constant per unit feedstock.

 d BGCCGT: biomass gasifier combined cycle gas turbine. Values based on electricity output increasing to 11.4% of the biomass heating value. The calculation is as follows: Gross power output = (3.77 kWh/gallon produced)_{Rankine} × [(40% efficiency)_{combined cycle}/(25.8% efficiency)_{Rankine}] = 5.84. Net power output = 5.84 gross - 0.71 required for the process = 5.13 kWh/gallon exported. Electricity output goes up by 67.6% to 11.4% of output.

for biomass power generation. No cost analyses have been done for the advanced/BGCCGT case.

Ratios of energy output, relative to the biomass energy content, show an efficiency between 0.5 and 0.97, depending on the level of maturity of the technology and whether energy outputs are valued on an unadjusted or displaced fossil fuel basis. Although a detailed comparison of these metrics to other possible biomass conversion processes is not undertaken here, the range of biomass-based efficiency values presented is relatively high, suggesting that conversion of biomass to ethanol with coproduction of electricity is a thermodynamically attractive option for production of useful energy from biomass.

Ratios of energy output relative to energy input for feedstock production and processing range from 4.4 to 10.4, again depending on the level of maturity assumed and the way in which the energy outputs are valued. By way of comparison, the unadjusted energy-output:energy-input ratio for gasoline production is about 5 (M Delucchi, personal communication). These energy output:input ratios assume a woody energy crop. Much higher ouput:input values are possible if waste feedstocks are considered, because energy crop production accounts for nearly three quarters of the total energy input for feedstock production and processing (1).

Electricity is expected to be an increasingly significant coproduct of ethanol manufacture from woody materials as the technology matures. For example, the amount of energy exported as electricity in the advanced/BGCCGT turbine scenario is one fifth the amount exported as ethanol. Because the country uses over twice as much transportation fuel as electricity, every 1% of current transportation sector energy demand displaced by ethanol would displace over 0.4% of electricity demand (for electricity at 3412 Btu/kWh) in the advanced/BGCCGT scenario. Cogeneration of ethanol and electricity from biomass may be preferable, in terms of economics and resource utilization, to production of either ethanol or electricity alone. This possibility has not been examined in the published literature in the context of mature technology.

GREENHOUSE GAS IMPACTS

Of all the attributes of cellulosic ethanol, its potential to provide very large greenhouse benefits is perhaps the least controversial. The fundamental reasons for this potential are 1. The photosynthetic production of biomass removes from the atmosphere the same amount of CO_2 that is returned upon combustion of ethanol and process residues. 2. The fossil fuel inputs required for production of cellulosic energy crops are modest (e.g. relative to conventional row crops).

3. The energy content of lignin-rich process residues is sufficient to provide all process energy requirements, thereby obviating the need for direct fossil fuels inputs. The most detailed analyses I know of are those of Tyson et al (140) and (141), which are described below.

Tyson et al (140) consider CO₂ emissions associated with a fuel cycle involving feedstock production and transportation, and with fuel production, distribution, and utilization. E95 production is assumed at five different locations in the United States, each with a mixture of energy crops appropriate to that site gathered from an area with an average travel distance of 100 miles. The five-site average CO₂ production for an E95 ethanol fuel cycle is 27.9 g per mile, 9.6% that of the RFG base case. This value includes the contribution of the RFG component of E95, and it does not include deductions for CO₂ savings from displaced fossil-based electricity generation or from transient carbon sequestration upon energy crop establishment. Based on the ethanol component of E95 only, net CO₂ emissions are 4.9% of the RFG base case. If displaced electricity generation is considered, net CO₂ emissions on an ethanol-only basis are reduced to -2.5% of the base case. Although the feedstock mix varied from entirely woody to entirely herbaceous, the site-to-site variation in net CO₂ emissions was <3% of the totals reported.

The analysis of Delucchi (141) differs from that of Tyson et al primarily in that full-cycle emissions of not only CO₂ but also the other greenhouse gases—methane, carbon monoxide, nitrous oxide, nitrogen oxides, and nonmethane organic compounds—are considered. In addition, Delucchi considers a very broad range of transportation sector options, thus facilitating comparative analysis. Although the most recent comprehensive presentation of Delucchi's analysis was published in 1991, Delucchi's model has been continually updated since that time to reflect new information (e.g. the global warming potential of greenhouse gases other than CO₂). Table 9 presents full-cycle greenhouse gas emissions calculated according to the Delucchi model as of March 1996 for the four biomass ethanol scenarios defined in this paper. Values are reported on an ethanol-only basis; they include a coproduct credit for electricity production and do not reflect any consideration of vehicle manufacture.

There is a growing realization that cellulosic ethanol is one of the leading alternatives for reducing greenhouse gas emissions in the transportation sector. One reflection of this is the finding by "Car Talk" (Policy Dialogue Advisory Committee to Recommend Options for Reducing Greenhouse Gas Emissions from Personal Motor Vehicles convened by President Clinton in 1994 and 1995) that liquid biofuels and cellulosic ethanol in particular represent one of two "technological homeruns" capable of offering very large emission reductions

Scenario/	GHG emissions			
cycle	(g/mile)	% RFG base-case		
Current, Rankine	16.0	4.0		
Advanced, Rankine	-37.8	- 9.5		
Advanced, BGCCGT	-140.7	- 35.5		
Best parameter	-32.9	- 8.3		

Table 9 Full-cycle greenhouse gas emissions for cellu-lose ethanol technology scenarios^a

^ag/mile values are without vehicle manufacture and are also numerically equal to values based on fuel utilization + the difference between vehicle manufacture-related emissions for ethanol and gasoline. Values are calculated by Mark Delucchi (personal communication), based on process inputs supplied by the author and as in Table 8.

(30, 142).³ Over the 30-year time frame considered by the Committee, projected greenhouse gas benefits from these two complementary technological paths are of comparable magnitude. The Committee also presented results from a survey indicating that cellulosic ethanol was distinctive among transportation sector alternatives in having a particularly high ratio of greenhouse gas emission benefit relative to the infrastructural change/development required for implementation. Estimated cost effectiveness (cumulative cost/cumulative tonne CO₂ carbon equivalent) for a policy developed by the Committee involving increased R&D for cellulosic ethanol and price supports (see section on Policy Commentary) is \$180 in 2005, \$30 in 2015, and \$11 in 2025 (159).

PRIORITY POLLUTANT EMISSIONS

As with fuel performance, priority pollutant emissions resulting from ethanol use depend on the form of the ethanol. Car manufacturers are likely to design vehicles to meet, but not greatly exceed, emissions specifications. To the extent that ethanol makes it easier to meet emissions specifications, this benefit will probably be realized in the form of reduced vehicle costs rather than lower emissions, unless specific regulatory incentives are enacted.

In general, emissions result either from exhaust or fuel evaporation. The relative magnitudes of exhaust and evaporative emissions depend on the driving

³This assessment is consistent with both the report signed by a majority of Committee members (30) and the letter to the administration from the five auto industry representatives on the Committee (142). The liquid biofuels policy was one of the policies more thoroughly reviewed by the Committee and appeared to have widespread support among Committee members. Ultimately, though, the Committee declared its inability to reach consensus and disbanded. Thus, no policy formulated by the Committee can be said to represent all Committee members. The working version of the policy at the time the Committee disbanded is presented in (159).

cycle analyzed as well as the form in which ethanol is used. Whitten (144) presents an example involving summertime gasoline use in Minnesota, for which evaporative emissions are 34% of total (evaporative and exhaust) emissions for gasoline and 42% of total emissions for E10. Evaporative emissions are a direct function of fuel vapor pressure. Neat ethanol has a lower vapor pressure than any foreseeable gasoline, and thus high-level ethanol blends generally have significantly lower vapor pressures than gasoline. However, ethanol mixed with gasoline at low levels has a higher vapor pressure than ethanol-free gasoline, unless a low vapor pressure gasoline is used, resulting in correspondingly higher evaporative emissions. Use of ethanol as ETBE provides a means to use low-level blends while decreasing fuel vapor pressure. Definitive evaluation of exhaust emissions is made from vehicle test results. Especially while such data are rather sparse, the matter of exhaust emissions can also be approached in relation to the physical properties of ethanol. For example, the lower flame temperature of ethanol provides a basis to expect lower NO_x emissions (3). Also, with ethanol, an engine can be optimized around a single set of physical properties, which can be expected to yield more complete combustion than the gasoline engine, which must be designed around an average of the properties of fuel components (JD Wright, personal communication).

Local air quality metrics of greatest concern include ozone, carbon monoxide, and air toxics. Ozone is not actually emitted but rather is formed as a result of photochemical reactions in the atmosphere. Formation of ozone is thus a function of NO_x , volatile organic compounds (VOCs), and CO emissions, as well as temperature and other meteorological conditions. Evaluation of ozone-forming potential is complex, and much remains to be understood. Mass-based hydrocarbon emissions may be weighted according to photochemical reactivity, although this is not yet the basis for emissions regulation, and agreement on methodologies and weighting factors has not yet been reached. Estimates of the specific reactivity (generally g ozone/g organics) of ethanol exhaust emissions relative to gasoline emissions are on the order of 0.7 for E85 and near 1 for E10 (Table 10).

Table 11 presents estimates for priority pollutant emissions resulting from ethanol used in various forms. Such estimates are dependent upon vehicle type, the condition and tuning of the vehicle, and the emissions test cycle used. Relative emissions for ethanol-containing fuel and ethanol-free fuel also depend on the type of gasoline used for comparison, as shown by data sets 1–3, 4–6, 8 and 9, and 14 and 15.

For exhaust emissions from low-level blends, the most evident trends are that ETBE results in significant ozone reductions relative to regular unleaded gasoline and that RFGs are a more challenging basis of comparison than conventional gasolines. Exhaust emissions of air toxics originating from gasoline (benzene, 1,3-butadiene) are generally but not always reduced for low-level ethanol blends; results for formaldehyde are mixed, and acetaldehyde emissions are higher for ethanol-containing fuels. Evaporative emissions on ethanol blends are somewhat variable for diurnal and hot soak, but are always higher for running emissions. Whitten et al (155) concluded that the increase in evaporative emissions accompanying use of E10 without vapor pressure compensation is balanced by the decreased exhaust emissions resulting from ethanol blending. Thus, the use of splash-blended E10 for summer driving in Minnesota creates essentially no change in ozone formation.

The two studies cited for mid-level blends indicate a reduction in hydrocarbon emissions, reductions of varying magnitude for CO, and opposite trends with respect to NO_x . A point to note is that the data of Guerrieri et al (151) on E42 are based on conventional vehicles rather than FFVs.

All of the E85 exhaust data cited suggest a reduction in NO_x emissions. Results are mixed with respect to organics and ozone. Notwithstanding large increases in acetaldehyde emissions and consistent additional increases in formaldehyde emissions, all studies cited also show a decrease in toxicity-weighted air toxics. Evaporative emission data are particularly scarce for high-level blends. A reduction in evaporative emissions is expected because of the low vapor pressure of E85, and the one cited study reporting evaporative emissions data is consistent with this expectation. Because summertime evaporative emissions are on the order of one third of total emissions for gasoline (depending on vapor pressure and temperature), the omission of evaporative emissions from most considerations of E85 emissions would appear to be significant. By far the largest E85 study (Table 11, data sets 12 and 13) shows pollution benefits for E85 even when compared to a very clean-burning Phase 2 RFG. However, a second recent study (data set 15) using the same RFG for comparison, suggests

Fuel	Reference fuel	Value ^a	References
E10	Minnesota summer	0.98	144
E10	Base gasoline	0.91	146
E10	RFG	1.03	146
E85	Base gasoline	0.60	146
E85	RFG	0.68	146
E85	RFG2	0.70	147

 Table 10
 Relative specific reactivities (g ozone/g organics) for ethanol and gasoline exhaust emissions

^aOrganics measured as nonmethanol hydrocarbons in all cases except (144), in which they are measured as volatile organic compounds. the opposite conclusion. An explanation of this discrepancy and others awaits further test results and research.

There is every reason to expect E95 to have lower emissions than E85, and E100 to have lower emissions still. Gary Whitten (personal communication) has suggested that there is little reason to use E85 rather than E95, although use of 15% alcohol in M85 can be justified, and that emissions originating from gasoline make up a disproportionately large fraction of overall emissions in at least some E85 studies.

Particulate emissions are not addressed in most studies of the air pollution effects of ethanol utilization and have not been considered in detail. Wang (156) indicates that utilization-related PM_{10} emissions are expected to be lower for ethanol than for RFG, but Wang and Tyson et al (140) suggest higher full-cycle particulate emissions for ethanol. The issue of particulate emissions associated with ethanol-based fuel cycles merits further study.

The available data show that emissions standards that could be met with regular gasoline could likely be met at least as easily with low-level blends of ethanol and/or ETBE. They also show that emissions standards that could be met with RFG could likely be met at least as easily with E85 (especially when evaporative emissions are considered) and probably more easily with E95 or neat ethanol. These conclusions are necessarily tentative because of the large variation in data from available studies; they might be either strengthened or weakened by further emissions and reactivity data, engine design, or pollution control technology optimized to use ethanol in its various forms.

NEAR-TERM COMMERCIALIZATION PROSPECTS

A straightforward analysis of a cost breakdown such as that shown in Table 6 indicates that the following items are key determinants of the price of cellulosic ethanol: feedstock, power cycle and other infrastructural components, biological conversion, pretreatment, and capital. If the cost of any one of these is unusually low because of advantageous local circumstances, the overall cost may be significantly lower than for a stand-alone plant with a dedicated energy crop such as that assumed in Table 6. Many waste feedstocks cost less than dedicated feedstocks (Table 2), and waste feedstocks that require active disposal (e.g. MSW, paper sludge, certain agricultural residues) may have negative costs. Large costs savings may be realized by locating at a site that provides various infrastructural functions required at an ethanol plant. Examples of such sites include existing ethanol plants, paper mills, refineries, and power plants. Certain feedstocks are particularly susceptible to enzymatic attack, e.g. many paper sludges and corn fiber, which can result in substantial savings in biological conversion and/or pretreatment. Finally, advantageous project financing (e.g.

ID, fuel	Reference	# vehicles		% cł	nange fror	n referei	nce exha	ust emissic	suo		% change	evapora	ative en	iissions
	fuel		Org	$NO_{\rm X}$ CO	Ozone ^b	Benz.	Butad.	Formald.	Acetaid.	Toxics ^c	Diurnal	Soak R	tun.	Total ^d
Low-level blends						یں ۱		,	J G					
1. E5.7(SB)	Cal. Sum. ^e	7	1	5 0	8	-10^{1}	- 1	-	52		-16	4	22	
2. E5.7	Cal. Sum. ^e	7	-	-1 -2	ົ້	4	ິ 	ຕິ 	29'		17	6-	28	
3. ETBE	Cal. Sum. ^e	7	-7^{I}	-5 -3	-20^{I}	-28^{1}	-14^{I}	29^{I}	21^{I}		L	ŝ	48	
4. E5.5SB	$Base^g$	4	8	1 -11		-34^{f}	-18	4	63^{f}					
5. E5.5SB	Phase 1 RFG ^g	4	ŝ	-2 -10		-25^{f}	-11	7	و <i>ل</i>					
6. E5.5SB	Phase 2 RFG ^g	4	18^{f}	9 35		40	13	-25	85^{1}					
7. E10	Minnesota Sum.	- -			-11.9									+24
8. E10	Base gasoline ⁱ	1	-19	18 - 17										
9. E10	RFG	1	11	54 4										
Mid-level blends														
10. E42	Sum. unleaded ^j	9	-30	60 - 50										
11. E50	Phase 2 RFG ^k	21	-17	-26 -0.0	7 -13	- 4	-51	21	1321	-37				
High-level blends														
12. E85	Phase 2 RFG ^k	21	-24	-27 - 18	-27	-79	-81	20	2049	-65				
13. E85	Phase 2 RFG ¹	24	9-	-16_{0} 13		-57	-74	100	2500_{f}	-61				
14. E85 19	988 National Avera	ge 3 ^m	-5	-49^{1}_{t} 7	-13	-87 ^r	-85 ¹	93^{I}_{t}	2620^{1}	-66				
15. E85	Phase 2 RFG ^m	б	25	-37^{I} 56	19	-72	-79	97'	3225	-38				
16. E85	RFG ⁿ	1	69	-37 46	26									
17. E85	Indolene ^o	33	-75	-25 -44							-50	I	-13	-33

 Table 11
 Summary of ethanolemissions data^a

formaldehyde; Acetald-, acetaldehyde; Soak, Hot soak; Run, running; S.B. splash blending, that is blending ethanol with gasoline without compensation for the vapor pressure increase; RFG, All results are for the Federal Test Procedure. Abbreviations: Org. organics (basis varies, see footnotes for individual data sets); Benz., benzene; Butad, 1-3-Butadiene; Formald. reformulated gasoline; Cal., California; Sum., Summer.

^bOzone refers to composite measures of ozone formation based on the emissions of ozone precursors and the maximum incremental reactivity (MIR) factor for each pollutant.

^cToxics refers to composite measures of air toxics based on the emissions of various toxic species. The values shown are calculated by the author and represent the sum of the product of gallons/mile emissions and toxicity potency factors (unit risk per microgram per cubic meter, for each of the four compounds tabulated). Values used are benzene = 2.9 × 10⁻⁵, butadiene = 1.7×10^{-4} , formaldehyde = 6.0×10^{-6} , acetaldehyde = 2.7×10^{-6} .

^dTotal evaporative emissions refers to composite measures of evaporative emissions. These measures are in terms of ozone-forming potential for data set 7, and total hydrocarbon equivalent for data set 17.

^eFrom (149); results for fuel-injected vehicles with three-way catalysts, model years 1987–1990, 5,000–76,000 miles. Organics reported as total hydrocarbons. Evaporative emissions in erms of ozone-forming potential.

findicates statistically significant with p = .05. Significance was reported only for data sets 1–6, 13, and 14; significance was not reported for the entries under the toxics column for data sets 13 and 14.

⁸ From (150); results for fuel-injected vehicles with three-way catalysts, model years 1986–1990, 13,000–79,000 miles. Organics reported as total hydrocarbons. ^hFrom (144); not a test, but rather an emission estimate based on the EPA emission model MOBIL5a.

From (146); results for a 1993 Chevrolet Lumina with 24,000 miles tested on the fuels indicated. Organics reported in terms of nonmethane organic gases.

From (151); results for six fuel injection conventional in-use vehicles, model years 1990–1992. Organics reported as total hydrocarbons.

^kFrom (147); results for Chevrolet Luminas, model years 1992 and 1993, with average mileage < 20,000 miles. 21 FFVs were tested against a control group of 21 conventional vehicles. Organics reported as organic material nonmethane hydrocarbon equivalent.

From (152); results for Ford Taurus FFVs run alternately on both E85 and RFG. Organics reported as nonmethane hydrocarbons.

^mFrom (153); results for three fuel injection FFVs with three-way catalysts, model years 1992–1994. Catalytic converters were subjected to simulated 50,000 mile aging prior to emission esting. Organics reported as organic material hydrocarbon equivalent.

ⁿFrom (146); results for a 1993 Chevrolet Lumina with 5,000 miles tested on the fuels indicated. Organics reported as nonmethane organic gases.

^oFrom (154); results for 1992 Chevrolet Luminas. Organics reported as nonmethane hydrocarbons.



Figure 5 Impact of scale and feedstock on cellulosic ethanol selling price. Modified from (157).

through some form of governmental support) can have a large impact on economic viability. As a result of site-specific advantageous features such as these, immediate opportunities for commercial application of cellulosic ethanol technology are available. Such "niche" opportunities, recently reviewed by Wyman & Goodman (14), are expected to be the point-of-entry and proving ground for cellulosic ethanol technology and are the active focus of several companies.

For niche applications of cellulosic ethanol technology, the interplay between the cost of feedstock and the scale of feedstock availability is important. As illustrated in Figure 5, low-cost or negative-cost feedstocks provide a great deal of cost leverage, but some or all of this advantage is lost if the feedstock is only available on a small scale and per-unit capital costs are therefore increased.

MARKET FACTORS AND POTENTIAL EXPANSION

The roughly 1.3 billion gallons of ethanol sold in the United States are used almost entirely in low-level (5–10%) blends with gasoline. As discussed by McNutt et al (6), such blends are used today in three distinct markets: RFG, oxygenated gasoline, and gasohol. About 10% of currently produced ethanol is used in RFG, with the primary goal of decreasing emissions of ozone precursors. Use of ethanol in oxygenated gasoline, designed to decrease CO production,

accounts for about another 20% of production. The remaining two thirds of total production is used as a gasoline extender in gasohol. Both the RFG and oxygenated gasoline markets are results of provisions of the Clean Air Act Amendments of 1990, although ethanol faces competition in both these markets from other gasoline additives. A major factor responsible for the existence of the fuel ethanol industry in the United States is the 54 cent per gallon federal tax incentive as well as additional incentives available in some states. This incentive, which may be realized by either producers or blenders of ethanol, is currently authorized through the year 2000.

Primary factors influencing the rate of ethanol production in the future are 1. the rate of R&D investment and R&D success; 2. the extent to which policies such as price supports, tax incentives, or fuel composition standards are in place; and 3. the price of alternatives to ethanol [e.g. oil, nonethanol gasoline additives such as methyl *tert*-butyl ether (MTBE)]. Depending on the assumed interplay between these three highly uncertain factors, a wide variety of future ethanol demand scenarios may be anticipated. This point is illustrated in Figure 6, which presents ethanol demand scenarios as developed by Stork of Argonne National Lab (158) and by the author in conjunction with the Car Talk Committee.

Stork's analysis involves three demand scenarios: a low-demand scenario featuring elimination of federal ethanol incentives at the end of 2000, among other factors; a middle-demand scenario in which the current tax credit and exemptions are extended beyond 2000 and a new policy to encourage renewable oxygenates is adopted; and a high-demand scenario in which the tax credit and exemptions are renewed indefinitely and low-cost cellulosic ethanol is assumed to be produced on a large scale. The Car-Talk projection is based on a favorable policy environment consisting of accelerated R&D and price supports (configured differently from the current incentive; see section on Policy Commentary), as well as successful R&D on lowering the cost of cellulosic ethanol.

In the context of accelerated R&D investment, significant R&D success, rapid lowering of ethanol price, and increased oil prices and/or price supports, a very rapid expansion of ethanol production can be imagined. A variety of factors could potentially limit the rate of such expansion, including feedstock supply, production facilities, production and distribution infrastructure, availability of suitable vehicles, and capital. Systematic analysis of such limitations has been reported in the public literature to a very limited extent. In an analysis of making the transition to large-scale ethanol use in the US transportation sector, McNutt et al (6) conclude that transitional issues associated with cellulosic feedstocks and ethanol production are more significant than those related to end-use. All



Figure 6 Ethanol demand scenarios. "ANL" refers to the Argonne National Lab, as reported by Stork (158); values include both corn ethanol and cellulosic ethanol. "Car Talk" as developed by the author in conjunction with the Car Talk Committee (29); values are for cellulosic ethanol only.

such studies (e.g. 6, 158, 159) foresee a progression of end-use modes from the low-level blends (either as ethanol or ETBE) used in conventional vehicles, to the high-level blends (e.g. E85 or E95) used in FFVs, to the high-level blends or neat ethanol used in dedicated vehicles. There is also general agreement that low-cost technology for production of ethanol from cellulosic feedstocks is required in order for large-scale utilization to occur. The largest obstacle to expanded fuel ethanol use in the United States is the price of this fuel.

Table 12 presents a comparative perspective on alternative fuels. For fuels derived from predominantly fossil sources (LPG, natural gas, and marginal electricity), the primary barriers to large-scale commercialization are infrastructure and vehicles. By contrast, source development and conversion are the primary barriers for alcohols (ethanol, methanol) derived from cellulosic biomass. For electricity with low greenhouse gas emissions, and/or for hydrogen, the barriers are source development/conversion, infrastructure, and vehicles. The nonfossil fuels offer much greater reductions in greenhouse gas emissions than the fossil

		Key con	nmercialization b	arriers/			
			R&D priorities				DOE
	Greenhouse	Source			Required		R&D
Fuel	gas reduction (%)	development/ conversion	Infrastructure	Vehicle	research intensity	Priority pollutant benefits (criteria and/or toxics)	funding (million dollars. 1994)
Fossil fuels	~						
LPG	26	None	Distribution	Dedicated	Low	Bi-fuel ICE: small	Not
			Delivery	optimized ICE		Dedicated ICE: moderate to large Hvhrid: moderate to large	available
Natural gas	24	None	Deliverv	Storage	Moderate	Bi-fuel ICE: small ^b	116
0	i			0		Dedicated ICE: moderate to large ^b Hvbrid: moderate to large ^b	
Ĩ	Ċ		:-	č			poo
Electricity (marginal) ^c	7	None	Delivery	Storage Engine	Hıgh	Moderate to large	894
Nonfossil fuels							
Alcohols	75–98	Conversion	None	Dedicated	High	ICE/blends: small	35
(cellulosic		Biomass		optimized		ICE/M85 or E85: moderate	
biomass)		production		ICE ^e	Ī	CE/M100 or E100: moderate to large	
				Fuel cells ^e		Hybrid: moderate to large Fuel cell: large to very large	
Low GHG	> 90	PV/biomass/	Delivery	Storage	High	Large to very large	182^{f}
electricity(solar,		expansion of		Engine			
biomass, nuclear		nuclear					
		capacity					
Solar, H_2	94-100	PV	Distribution	Storage	Very	ICE: large	10
			Delivery		high	Fuel cell: very large	
^a Table developed b priority pollutant ben of meanhouse gas ben	y the author in co efits primarily fre	njunction with mem om Barry Wallerste finding for alcohol	bers of the Car Talk in (Southeast Air C from cellulosic bi	t Committee. Green Quality Managemer	thouse gas emi at District); D	ssions as per DeLucchi (MDeLucchi, person OE funding compiled by Carmen Difiglio	aal communication); o (DOE). The range

 Table 12
 Comparative features of selected alternative fuels^a

'n ^bLarge if ignore methane. ir jo I

^cMarginal electricity is grouped under fossil fuels although a minor share is provided by nonfossil sources. ^dThe indicated amount is for electric vehicle research only. ^eDevelopment of advanced vehicles is not necessary in order to use alcohols or to realize associated greenhouse gas benefits. However, such development is desirable because of efficiency and criteria pollutant benefits.

^fThe indicated amount is for electricity production only.

451

fuels. All fuel options listed are compatible with large priority pollutant benefits. The extent of priority pollutant emissions reductions depends on how the fuel is used for several options, and this is especially true for alcohols. Comparison of the R&D funding levels cited in Table 12 suggests that the effort of the United States DOE is weighted toward the short term as well as toward technologies for which an established industry already exists.

CONCLUDING REMARKS AND POLICY COMMENTARY

The above sections support the following merits of cellulosic ethanol:

- Cellulosic biomass is one of the primary renewable resources on earth. Moreover, the potential production capacity of cellulosic biomass is distributed very differently from oil; significant amounts of cellulosic ethanol can be produced indigenously in the United States and many other countries.
- Available data support the conclusion that environmental impacts associated with dedicated production of cellulosic biomass appear to be generally acceptable and can be positive.
- 3. Ethanol is a high performance fuel in internal combustion engines.
- 4. Ethanol is a liquid, which is a state of matter that can easily deliver and store energy for transportation. Its liquid state is also one of the main factors that makes ethanol more compatible with the existing transportation sector infrastructure than most other alternative fuels.
- 5. Ethanol is a relatively clean-burning liquid hydrocarbon, particularly as the amount of gasoline blended with ethanol decreases. Ethanol is compatible with at least some fuel cell configurations, offering the potential for dramatic reductions in air pollution as well as high efficiency and proportionately reduced land demand over the long term.
- 6. Provided that high process yields are achieved, the cost of most cellulosic feedstocks is lower than the unsubsidized price of the ethanol that can be produced from these feedstocks, even when ethanol is valued as a bulk fuel (1).
- 7. R&D-driven advances have clear potential to lower ethanol prices to a level competitive with bulk fuels.

- 8. The ratio of energy output to energy input is decidedly favorable for cellulosic ethanol production, especially when coproduction of electricity is considered.
- 9. Cellulosic ethanol is one of the most promising technological options available to reduce emissions of greenhouse gases from the transportation sector.

Like all current and potential energy sources, cellulosic ethanol has limitations and constraining factors, of which the following may be particularly important:

- The land required for cellulosic biomass constrains the ultimate contribution of this resource to meeting energy needs. Moreover, biomass requires more land to produce a given energy output than is anticipated for most other solar technologies, and the land most suited for production of biomass energy crops also tends to be well suited for other uses.
- Responsible management is essential to avoid abuse of soil, water, and wildlife resources in the course of producing cellulosic biomass. In order to support such management, further experience and understanding of land-use issues are needed.
- 3. Ethanol is compatible with fewer reformer technologies than methanol, which can also be produced from biomass. Thus, if steam-reforming proves to be the preferred reformer technology, ethanol will be at a disadvantage relative to methanol for fuel cell applications. Independent of reformer technology, ethanol (as well as methanol) is always likely to be at an efficiency disadvantage relative to hydrogen for use in fuel cells.
- 4. Compared to most other alternative fuels under consideration today, use of ethanol in internal combustion vehicles offers comparatively modest benefits in terms of priority pollutant emissions (e.g. see 156).
- 5. The price of ethanol (e.g. dollars/Btu) is currently higher than most other alternative fuels under consideration.

The challenge is to develop cellulosic ethanol technology so as to maximize realization of benefits while minimizing or eliminating the effects of limiting factors. Consistent with this, R&D can reasonably be expected to convert price from a limitation (based on current technology) to a merit (anticipated for future technology). R&D is also likely to allow ethanol-powered vehicles to have very low emissions, although the same is probably true of gasoline-powered vehicles.

Near-neat ethanol and/or fuel cells are particularly promising in the context of emission reductions.

Like other other sustainable energy sources, cellulosic biomass cannot satisfy the transportation demands of a world with arbitrarily high population, per mile fuel consumption, animal protein utilization, and per capita mobility. In general, sustainable energy supply needs to be approached in terms of a mix of environmentally sensitive development of new supply technologies, efficient energy utilization, and control of demand. Figure 1 and the accompanying discussion support the following statements about the size of the potential cellulosic biomass resource in the United States relative to transportation demand:

- 1. There will probably not be enough suitable land available to meet transportation demand if total VMT increase relative to current levels, and vehicle efficiency and animal protein utilization remain unchanged.
- There probably is enough suitable land available to meet transportation demand, even with some increase in VMT, given large but probably possible increases in vehicle efficiency, large but probably possible decreases in reliance on animal protein, or a combination of less aggressive changes in both of these factors.

Consideration of land availability is complicated by competing demands for cellulosic energy crops for uses other than transportation. In particular, this resource could be used for power generation and/or for production of feedstocks for a biomass-based chemical industry. It is possible that a mix of energy sources will power the transportation sector through the twenty-first century as has been the case for the utility sector during the twentieth century. It is possible that photovoltaics will eventually satisfy most electrical energy needs while cellulosic biomass meets most transportation demand (probably with cogeneration of electricity). It is possible that photovoltaics will be used to meet both eletrical and transportation needs (with energy stored using either batteries or hydrogen), with biomass used primarily for chemical feedstocks (159a); in this case cellulosic ethanol production facilities originally constructed for fuel production could readily make a transition to chemical feedstock production. It is possible that hydrogen produced from biomass will be used in transportation and/or other sectors (159b). It is probably not possible to foresee which of these possibilities will actually occur.

Because of the immature state of most sustainable energy technologies, the uncertainty associated with the success of future R&D, and the need for sustainable energy supply, a good case can be made for an R&D effort aggressively targeting multiple, somewhat parallel, technology paths (e.g. biomass ethanol,

biomass methanol, solar hydrogen, photovoltaic electricity, electric vehicles). This is not, however, possible in the context of current funding levels. As a result, technologies that are in many respects complementary are viewed as competing, and allocation of R&D support is based on decidely incomplete information regarding the features and merits of various technology options at the point of technological maturity.

In light of recent work on ethanol reformers (see section on Fuel Performance), it appears too soon to judge whether there will be a significant difference between the utility of ethanol and methanol for fuel cell–powered vehicles. The issue of fuel-cell compatability is a significant factor impacting the desirability of cellulosic ethanol as a transportation fuel over the long term, and it is an important research priority in addition to the conversion technology–related topics discussed above. If methanol proves to have an advantage in fuel cells, this advantage will have to be weighed against the likely lower cost of ethanol produced by mature technology (see section on Conversion Technology).

A definitive comparison of the merits of ethanol and hydrogen as sustainable fuels of the future is not possible today. The efficiency and simplicity of hydrogen in fuel cells are attractive. These features must ultimately be weighed against the convenience, low cost, and efficiency of a liquid fuel; the relative future prices of hydrogen and ethanol (which cannot not be accurately foreseen); and a consideration of efficiency encompassing factors other than end use. As presented herein, the anticipated efficiency of ethanol production with cogeneration of electricity is rather high on a per unit biomass basis. On the other hand, efficiency on a per unit land basis tends to be low for biomass options. The low energy output/land area of biomass-based options must in turn be balanced against attractive features of plant biomass relative to other means of harvesting solar energy: capacity for self-maintenance and regeneration, ready integration into natural elemental cycles (one does not for example have to extract or dispose of exotic elements), and the potential for beauty and wildlife habitat.

Available information suggests that cellulosic ethanol belongs among a select group of most promising routes for sustainable energy supply. This evaluation is heavily influenced by anticipated improvements in technology expected to make a cellulosic ethanol fuel cycle with a much lower production cost, somewhat higher production efficiency, substantially higher end-use efficiency, and substantially lower emissions of important air pollutants than is possible with current technology. Such improvements receive notably little attention in public debate over public policy, which is influenced almost exclusively by what the fuel ethanol industry is rather than what it is likely to become.

The current debate is over the merits and drawbacks of producing ethanol from corn. Corn ethanol production is generally agreed to increase farm income, decrease federal agricultural program outlays, reduce soybean prices, and decrease highway trust fund revenues. Improved air quality and reduced dependence on oil imports are additional factors frequently cited as advantages of ethanol. The question is whether the net effect is positive. A 1986 US Department of Agriculture (USDA) report (104) concluded that the net effect was not positive; a 1988 USDA report (105) concluded that the net effect would likely be positive in the near term but not in the longer term; and a 1990 General Accounting Office (GAO) report (106) concluded that the benefit of reduced farm program outlays outweighed lost motor fuel tax revenues. In general, these studies do not take into consideration the cost of incentives for petroleum production. Corn-based ethanol production is thought unlikely to expand beyond a roughly threefold or at most fivefold increase over current capacity because of a combination of higher prices for corn and lower prices for feed byproducts of corn ethanol manufacture (1, 158, 161).

An important, but usually neglected, factor in this debate is that the corn ethanol industry provides a crucial platform from which to launch a much larger cellulosic ethanol industry. A cellulosic ethanol industry can be expected to offer expanded opportunities to farmers and benefits to the agricultural economy and rural communities of the type offered by the corn ethanol industry. At the same time, the cellulosic ethanol fuel cycle is not subject to many of the criticisms that have been leveled at the corn ethanol industry. In comparison to corn ethanol, cellulosic ethanol has clear potential to offer lower costs for feedstocks and production overall, both of which foster the use of ethanol in forms with greater priority pollutant benefits; a much larger potential resource base; more environmentally benign feedstock production; a much more favorable process energy balance; and much larger greenhouse gas benefits.

The focal point of the public policy debate has been the 54-cent-per-gallon federal tax credit. An abrupt cancellation of the tax incentive, proposed on several occasions by members of the 1995 and 1996 Congress, poses a significant threat to the emergent cellulosic ethanol industry as well as the corn ethanol industry. Such a cancellation would likely lead to the collapse of the existing fuel ethanol industry and would delay substantially, if not indefinitely, the establishment of a significant cellulose ethanol industry and the realization of associated benefits. In addition, cancellation would impose a hardship on those who have made investments in response to the incentive, most notably farmers. What is needed instead is an orderly transition toward an industry that can deliver clear benefits on a significant scale relative to conventional fuel use and that features government incentives that diminish over time and ultimately disappear. Cellulosic feedstocks appear to be the key to such a transition.

The policy developed by the Car Talk Committee (24, 143) provides a model that is intended to be responsive to the constraints and opportunities outlined above. This policy was devised solely in response to the goal of reducing greenhouse gas reductions, and a more comprehensive policy formulation process might well lead to a different and perhaps improved result. The essential elements of the Car Talk policy are 1. ramp-up R&D funding to \$100 million through 2005 targeting low-cost conversion technology and 2. the establishment of a price support pool available to producers of alternative fuels in proportion to full-cycle greenhouse gas emissions. This pool would include the current ethanol tax incentive, which would be linearly phased out in years 5-15 of the policy. The policy articulated by the Committee was crafted so as to maximize political viability. In particular, the incentive is fuel neutral, performance based, and its overall impact on the treasury is capped. In addition, the incentive is structured so that low-emitting fuels receive the maximum advantage at low production volumes when technology is the least mature, with expanded production only proceeding as the fuels become more cost competitive. With this type of fuel-neutral approach that rewards alternative fuels based on greenhouse gas emission reductions, cellulosic ethanol is anticipated to be by far the chief beneficiary.

Commercially attractive opportunities for application of cellulosic ethanol technology exist today because of the availability of niche opportunities and because of the federal tax incentive. Moving such commercial applications forward is vital if the nascent cellulosic ethanol industry is to begin to become established. While acknowledging this need, the author also offers the perspective that the US effort dedicated to advancing cellulosic ethanol technology has overemphasized near-term commercialization at the expense of R&D. In particular, "leap forward" R&D, characteristic of efforts such as the Partnership for New Generation Vehicles, has been a small component of our overall effort in spite of the clear benefits it offers. The current, strong emphasis on commercialization is consistent with the world of the early 1980s, in which immature technologies could be expected to become cost effective in the near term as oil prices rise. This emphasis is not, however, consistent with today's world, in which lowering the cost of alternatives to oil is more promising than waiting for the price of oil to rise.

The existence of commercial applications should not be confused with the idea that available conversion technology is technologically mature; it is not. In addition, the signs that a cellulosic ethanol industry is emerging should not be confused with the notion that the private sector is likely to shoulder the

investment burden required to result in mature conversion technology. The Car Talk Committee estimated that an investment of \$850 million over 9 years (an increase of \$600 million over the same period relative to current expenditures) would be necessary to start commercial production of cellulosic ethanol using mature technology (e.g. the advanced scenario in the section on Mature Conversion Technology) in 2005. This funding level is rather small in relation to expenditures for agricultural subsidies, defense spending to protect imported oil supply, the foreign trade deficit, and possible future expenditures to reduce greenhouse gas emissions, all of which would be alleviated by advanced cellulosic ethanol technology. In particular, the cumulative R&D investment estimated by the Car Talk Committee is equivalent to approximately one year of the current ethanol tax incentive. R&D investment by an expanding fuel ethanol industry is unlikely to reach this total in the next quarter century.

Although a significantly expanded R&D investment by the federal government would be contrary to the current trend of downsizing government, it is quite possible given the relatively small amount of funds involved. The philosophical rationale for such an investment has much in common with that put forward in the Majority Report of the Car Talk Committee (29, p. 28):

We believe that the appropriate role for government is to be responsive to the public interest by taking actions that would not be undertaken by the private sector because time-to-market is too long, the risks are too high, or because environmental and other benefits to society are not reflected by market forces. In particular, the time horizon for development of new fuels and vehicles is often long relative to that for private-sector decision making, thus the need for such fuels and vehicles must be anticipated long before it becomes acute. Finally, governmental action is the only option we have to incorporate environmental goals such as reducing GHG [greenhouse gas] emissions into market-based decision-making since the market does not by itself value these goals.

ACKNOWLEDGMENTS

The author gratefully acknowledges information and perspectives provided by the following persons: Michael Antal, Stephen Allen, Jeff Bentley, Bruce Dale, Mark Delucchi, Joan Denton, Rick Elander, Jose Gomez, Tom Jeffries, Paul Jefferis, Ken Kelly, Phil Lampert, Bill Mitchell, Barry McNutt, Horst Richter, Gary Whitten, Charles Wyman, and members of the Car Talk Committee. L Lynd is partially supported by Grant No. BCS9215130 from the National Science Foundation and the Department of Energy, and Subcontract No. RCV-5-15345 from the National Renewable Energy Laboratory.

Any Annual Review chapter, as well as any article cited in an Annual Review chapter, may be purchased from the Annual Reviews Preprints and Reprints service. 1-800-347-8007; 415-259-5017; email: arpr@class.org. Visit the Annual Reviews home page at http://www.annurev.org. Literature Cited

- Lynd LR, Cushman JH, Nichols RJ, Wyman CE. 1991. Fuel ethanol from cellulosic biomass. *Science* 251:1318–23
- Wyman CE, Hinman ND, Bain RL, Stevens DJ. 1992. Ethanol and methanol from cellulosic biomass. In *Fuels and Electricity from Renewable Resources*, ed. RH Williams, TB Johansson, H Kelly, AKN Reddy, pp. 865–924. Washington, DC: Island
- Bailey BK. 1996. Performance of ethanol as a transportation fuel. See Ref. 163, pp. 37–58
- Black F. 1991. An Overview of the Technical Implications of Methanol and Ethanol as Highway Motor Vehicle Fuels. SAE Tech. Ser. 912413. Warrendale, PA: Soc. Automot. Eng.
- Sinor J, Bailey BK. 1993. Current and Potential Future Performance of Ethanol Fuels. SAE Tech. Ser. 930376. Warrendale, PA: Soc. Automot. Eng.
- McNutt B, Bergeron P, Singh M, Štork K. 1996. Making the transition to large scale ethanol use in the U.S. transportation sector. *Proc. 11th Int. Symp. Alcohol Fuels, Sun City, S. Afr.* Natl. Symp. Organ. Comm., R Datkiewicz, chair, Univ. Capetown, S. Afr.
- Motta R, Chandler K, Norton P, Kelly KJ. 1995. Alternative Fuel Transit Buses—Interim Results from the NREL Vehicle Evaluation Program. NREL/TP-425-7619. Golden, CO: Natl. Renew. Energy Lab.
- Williams RH, Larson ED, Katofsky RE, Chen J. 1995. Methanol and hydrogen from biomass for transportation. J. Int. Energy Initiat. 1(5):19–34
- Mitchell WL, Thijssen JHJ, Bentley JM, Marek NJ. 1995. Development of a Catalytic Partial Oxidation Ethanol Reformer for Fuel Cell Applications. SAE Tech. Pap. Ser. 952761. Warrendale, PA: Soc. Automot. Eng.
- 10. Deleted in proof
- General Motors Corporation. 1996. Research and Development of Proton-Exchange-Membrane (Pem) Fuel Cell System for Transportation Applications, Phase I Final Report. DOE/CH/10435-02. Washington, DC: Dep. Energy
- Arthur D. Little, Inc. Multi-Fuel Reformers For Fuel Cells Used In Transportation, Phase I Final Report. DOE/CE/5034302. Washington, DC: Dep. Energy
- 12a. Holtzapple MT. 1993. Cellulose. In Encyclopedia of Food Science, Food Tech-

nology, and Nutrition, ed. R Macrae, RK Robinson, MJ Sadler, pp. 758–67. London: Academic

- Holtzapple MT. 1993. Hemicelluloses. In Encyclopedia of Food Science, Food Technology, and Nutrition, ed. R Macrae, RK Robinson, MJ Sadler, pp. 2324–34. London: Academic
 - Holtzapple MT. 1993. Lignin. In Encyclopedia of Food Science, Food Technology, and Nutrition, ed. R Macrae, RK Robinson, MJ Sadler, pp. 2731–38. London: Academic
 - Wyman CE, Goodman BJ. 1993. Near term applications of biotechnology for fuel ethanol production from cellulosic biomass. In *Opportunities for Innovation: Biotechnology*, ed. RM Busche, pp. 151–90. Gaithersburg, MD: Natl. Inst. Stand. Technol.
 - Lynd LR. 1989. Production of ethanol from lignocellulosic material using thermophilic bacteria: critical evaluation of potential and review. In Advances in Biochemical Engineering Biotechnology, ed. A Fiechter, 38:1–52
 - 16. Deleted in proof
 - LL Wright, WH Hohenstein, eds. 1994. Dedicated feedstock supply systems: their current status in the USA. *Biomass Bioenergy* 6(3)
 - Turhollow A. 1994. The economics of energy crop production. *Biomass Bioen*ergy 6(3):229–41
 - Perlack RD, Wright LL. 1995. Technical and economic status of wood energy feedstock production. *Energy* 20(4):279
- Graham RL. 1994. Analysis of the potential land base for energy crops in the continuous United States. *Biomass Bioenergy* 6(3):175–98
- US Department of Agriculture. 1994. Agricultural Resources and Environmental Indicators. Agric. Handb. No. 705. Washington, DC: US Dep. Agric., Econ. Res. Serv., Nat. Resour. Environ. Div.
- 22. Deleted in proof
- US Department of Agriculture. 1995. *Agricultural Outlook*. USDA Econ. Res. Serv. AO-217. Washington, DC: US Dep. Agric.
- Clinton WJ, Gore A. 1993. *Global Climate Change Action Plan*. Washington, DC: The White House
- Lovins AB, Lovins LH. 1995. Reinventing the wheels. *The Atlantic Monthly*, Jan.:75–86
- 26. Beyea J, Keeler H. 1991. Biotech-

nological advances in biomass energy and chemical production: impacts on wildlife and habitat. *CRC Crit. Rev. Biotechnol.* 10(4):305

- Christianson DP, Niemi GJ, Hanowski JM, Collins P. 1994. Perspectives on biomass energy tree plantations and changes in habitat for biological organisms. *Biomass Bioenergy* 6(1/2):31
- Ranney JW, Mann LK. 1994. Environmental considerations in energy crop production. *Biomass Bioenergy* 6(3):211
- 29. US Environmental Protection Agency. 1995. Majority Report to the President by the Policy Dialogue Advisory Committee to Recommend Options for Reducing Greenhouse Gas Emissions from Personal Motor Vehicles. Washington, DC: US Environ. Prot. Agency
- Detchon R, ed. 1995. Ethanol and the environment: reopening the dialogue. Rep. Roundtable Discuss. Gov. Ethanol Coalit, Podesta Assoc., Washington, DC
- Wyman CE. 1994. Ethanol from cellulosic biomass: technology, economics, and opportunities. *Bioresour. Technol.* 50:3–16
- Lynd LR, Elander RT, Wyman CE. 1996. Likely features and costs of mature biomass ethanol technology. *Appl. Biochem. Biotechnol.* 57/58:741–61
- 33. US Department of Energy. 1993. Assessment of costs and benefits of flexible and alternative fuel use in the U.S. transportation sector. Tech. rep. 11: evaluation of a wood-to-ethanol process, DOE/EP-0004, US Dep. Energy, Washington, DC
- Grethlein HE, Dill T. 1993. The cost of ethanol production from lignocellulosic biomass—a comparison of selected alternative processes. Final rep. coop. agreem. no. 58-1935-2-050, US Dep. Agric., Washington, DC
- Klasson KT, Ackerson MD, Clausen EC, Gaddy JL. 1992. Bioconversion of synthesis gas into liquid or gaseous fuels. *Enzym. Microb. Technol.* 4:602–8
- Converse AO. 1993. Substrate factors limiting enzymatic hydrolysis. In *Bioconversion of Forest and Agricultural Residues*, ed. JN Saddler. Wallingford, CT: CAB Int.
- Hsu T-A. Pretreatment of biomass. See Ref. 163, pp. 179-95
- McMillan JD. 1994. Pretreatment of lignocellulosic biomass. See Ref. 164, pp. 292–324
- 39. McMillan JD. 1994. Conversion of

hemicellulose hydrolyzates to ethanol. See Ref. 164, pp. 411–37

- Weil J, Westgate PJ, Kohlmann K, Ladisch MR. 1994. Cellulose pretreatments of lignocellulose. *Enzym. Microb. Technol.* 16:1002–4
- Dale BE. 1985. Cellulose pretreatments: technology and techniques. Annu. Rep. Ferment. Process. 8:299–323
- Grethlein HE. 1984. Pretreatment for enhanced hydrolysis of cellulosic biomass. Biotech. Adv. 2:43–62
- Grethlein HE. 1985. The effect of pore size distribution on the rate of enzymatic hydrolysis of cellulosic substrates. *Bio/Technology* 3:155–60
- 44. Weimer PJ, Weston WM. 1985. Relationship between the fine structure of native cellulose and cellulose degradability by the cellulase complexes of *Trichoderma reesei* and *Clostridium thermocellum. Biotechnol. Bioeng.* 27:1540–47
- Coughlan MP, Hon-Nami K, Hon-Nami H, Ljungdahl LG, Paulin JJ, Rigsby WE. 1985. The cellulolytic enzyme complex of *Clostridium thermocellum* is very large. *Biochem. Biophys. Res. Comm.* 130(2):904–9
- Johnson EA, Sakajoh M, Halliwell M, Madia A, Demain AL. 1982. Saccharification of complex cellulosic substrates by the cellulase system from *Clostridium thermocellum. Appl. Environ. Microbiol.* 43(5):1125
- Lynd LR, Grethlein HE. 1987. Hydrolysis of dilute acid pretreated mixed hardood and purified microcrystalline cellulose by cell-free broth from *Clostridium thermocellum. Biotechnol. Bioeng.* 24:92–100
- Koullas DP, Christakopolous P, Kekos D, Macris BJ, Koukios EG. 1992. Correlating the effect of pretreatment on the enzymatic hydrolysis of straw. *Biotechnol. Bioeng.* 38:113–16
- Goring DAI. 1989. The Lignin Paradigm. ACS Symp. Ser. 397, pp. 2–10. Washington, DC: Am. Chem. Soc.
- Ooshima H, Burns DS, Converse AO. 1990. Adsorption of cellulase from *Trichoderma reesei* on cellulose and lignacious residue in wood pretreated by dilute sulfuric acid with explosive decompression. *Biotechnol. Bioeng.* 36:466
- Tanahashi M, Takada S, Aoki T, Goto T, Higuichi T, Hanai S. 1990. Characterization of steam exploded wood. 1. Structure and physical properties. *Wood Res.* 69:36–51

- Torget R, Walter P, Himmel M, Grohmann K. 1991. Dilute sulfuric acid pretreatment of corn residues and short rotation woody crops. *Appl. Biochem. Biotechnol.* 28/29:75–86
- Aronovsky SI, Gortner RA. 1930. The cooling process. I. The role of water in the cooking of wood. *Ind. Eng. Chem.* 22:264–74
- Lora JH, Wayman M. 1978. Delignification of hardwoods by autohydrolysis and extraction. *Tappi J*. 61:47–50
- Kohlmann K, Westgate PJ, Weil J, Ladisch MR. 1993. *Biologically-Based Systems for Waste Processing*. SAE Tech. Pap. Ser. 932251. Warrendale, PA: Soc. Automot. Eng.
- Thompson DN, Chen HC, Grethlein HE. 1991. Common aspects of acid prehydrolysis and stem explosion for pretreating wood. *Bioresour. Technol.* 36:155– 63
- Sinitsyn AP, Gusakov AV, Vlasenko EY. 1991. Effect of structural and physicochemical features of cellulosic substrates on the efficiency of enzymatic hydrolysis. *Appl. Biochem. Biotechnol.* 30:43–59
- Abatzoglou N, Chornet E, Belkacemi K, Overend R. 1992. Phenomenological kinetics of complex systems: the development of a generalized severity parameter and its application to lignocellulosics fractionation. *Chem. Eng. Sci.* 47(5):1109–22
- Belkacemi K, Abatzoglou N, Overend R, Chornet E. 1991. Phenomenological kinetics of complex systems: mechanistic considerations in the solubilization of hemicellulose following aqueous/steam treatments.*Ind. Eng. Chem. Res.* 30:2416–25
- Heitz M, Capek-Menard E, Koeberle PG, Gagne J, Chornet E, et al. 1991. Fractionation of *Populus tremuloides* at the pilot plant scale and optimization of steam pretreatment conditions using STAKE II technology. *Bioresour. Technol.* 35:23–32
- Kwarteng IK. 1983. Kinetics of acid hydrolysis of hardwood in a continuous plug flow reactor. PhD thesis. Dartmouth Coll., Hanover, NH
- Goring DAI. 1963. Thermal softening of lignin, hemicellulose, and cellulose. *Pulp Pap. Mag. Can.* 64:T517–27
- Back EL, Salmen NL. 1982. Glass transitions of wood components: implications for molding and pulping processes. *Tappi J.* 65:187–210

- Bouchard J, Nguyen TS, Chornet E, Overend RP. 1991. Analytical methodology for biomass pretreatment. Part 2: Characterization of the filtrates and cumulative distribution as a function of treatment severity. *Bioresour. Technol.* 36:121–23
- Bobleter O, Concin R. 1979. Degradation of poplar lignin by hydrothermal treatment. *Cell Chem. Technol.* 13:583– 93
- 66. Chua MGS, Wayman M. 1979. Characterization of autohydrolysis aspen (*P. tremuloides*) lignins. 1. Composition and molecular weight distribution of extracted autohydrolysis lignin. *Can. J. Chem.* 57:2603–11
- Marshall WL, Franck EU. 1981. Ion product of water substance, 0–1,000°C, 1–10,000 bars—new international formulation and its background. J. Phys. Chem. Ref. Data 10:295–304
- 68. Deleted in proof
- Wright JD. 1988. Ethanol from biomass by enzymatic hydrolysis. *Chem. Eng. Prog.* 84(8):62–74
- 70. Deleted in proof
- Torget R, Himmel ME, Grohmann K. 1991. Dilute sulfuric acid pretreatment of hardwood bark. *Bioresour. Technol.* 35:239–46
- Chen R, Lee YY, Torget R. 1996. Kinetic and modeling investigation on twostage reverse-flow reactor as applied to dilute-acid pretreatment of agricultural residues. *Appl. Biochem. Biotechnol.* 57/58:133–46
- Beltrame PL, Carniti P, Visciglio A, Focher B, Marzetti A. 1991. Fractionation and biconversion of steamexploded wheat straw. *Bioresour. Tech*nol. 39:165–71
- Brownell HH, Saddler JN. 1987. Steam pretreatment of lignocellulosic material for enhanced enzymatic hydrolysis. *Biotechnol. Bioeng*. 29:228–35
- Montane D, Salvado J, Farriol X, Chornet E. 1993. The fractionation of almond shells by thermomechanical aqueousphase (TM-AP) pretreatment. *Biomass Bioenergy* 4:427
- Ramos LP, Breuil C, Saddler JN. 1992. Comparison of steam pretreatment of eucalyptus, aspen, and spruce wood chips and their enzymatic hydrolysis. *Appl. Biotechnol. Bioeng.* 34/35:37–48
- Clark TA, Mackie KL, Wood J. 1987. Steam explosion of softwood *Pinus radiata* with sulfur-dioxide addition. *Chem. Technol.* 7:373

- Schell D, Torget R, Power A, Walter PJ, Grohmann K, Hinman ND. 1991. A technical and economic analysis of acidcatalyzed steam explosion and dilute acid pretreatments using wheat straw or aspen wood chips. *Appl. Biochem. Biotechnol.* 28/29:87–97
- Dale BE, Henk LL, Shiang M. 1985. Fermentation of lignocellulosic materials treated by ammonia freeze-explosion. *Devel. Ind. Microbiol.* 26(13):223
- Holtzapple MT, Lundeen JE, Sturgis R, Lewis JE, Dale BE. 1992. Pretreatment of lignocellulosic municipal solid waste by ammonia fiber explosion. *Appl. Biochem. Biotechnol.* 5:34–35
- Holtzapple MT, Humphrey AE. 1984. The effect of organosolv pretreatment on the enzymatic hydrolysis of poplar. *Biotechnol. Bioeng.* 26:670–76
- Kitsos HM, Roberts RS, Muzzy J. 1992. Propylamine pretreatment of buffered solvent pulp to enhance enzymatic hydrolysis. *Bioresour. Technol.* 39:241–47
- Azuma J-I, Tanaka F, Koshijima T. 1984. Enhancement of enzymatic susceptibility of lignocellulosic wastes by microwave irradiation. J. Ferment. Technol. 62(4):377
- Thompson DN, Chen H-C, Grethlein HE. 1991. Comparison of pretreatment methods on the basis of available surface area. *Bioresour. Technol.* 39:155–63
- Chang V, Burr R, Holtzapple MT. 1996. Enhancing biomass digestibility using lime pretreatment. Presented at 18th Symp. Biotechnol. Fuels Chem., Gatlinburg, Tenn.
- van Walsum P, Allen SG, Spencer MJ, Laser M, Antal M. 1996. Conversion of lignocellulosics pretreated with hot compressed liquid water to ethanol. Adv. Biochem. Biotechnol. 57/58:157–70
- Schell DJ, Duff B. 1996. Review of pilot plant programs for bioethanol conversion. See Ref. 163, pp. 381–91
- Forsberg CW, Schellhorn HE, Gibbons LN, Maine F, Mason E. 1988. The release of fermentable carbohydrate from peat by steam explosion and its use in the microbial production of solvents. *Biotechnol. Bioeng.* 28:176–84
- Mes-Hartree M, Saddler JN. 1983. The nature of inhibitory materials present in pretreated lignocellulosic substrates which inhibit enzymatic hydrolysis of cellulose. *Biotechnol. Lett.* 5(8):531–36
- Fraser FR, McKaskey TA. 1991. Effect of components of acid-hydrolyzed hardwood on conversion of D-xylose to 2-

3 butanediol by *Klebsiella pneumoniae*. *Enzym. Microb. Technol.* 13:110

- Tran AV, Chambers RP. 1986. Ethanol fermentation of red oak acid prehydrolyzate by the yeast *Pichia stipitis* CBS 5776. *Enzym. Microb. Technol.* 8:439–44
- Olsson L, Hahn-Hagerdal B. 1996. Fermentation of lignocellulosic hydrolyzates for ethanol production. *Enzym. Microb. Technol.* 18:312–31
- 92a. Leschine SB, Canale-Parola E. 1983. Mesophilic cellulolytic clostridia from freshwater environments. *Appl. Env. Microbiol.* 46:728–37
- Venkateswaran S, Demain AL. 1986. The Clostridium thermoscellum-Clostridium thermosaccharolyticum ethanol production process: nutritional studies and scale-down. Chem. Eng. Commun. 45:53–60
- Hahn-Hagerdal B, Jeppson H, Skoog K, Prior BA. 1994. Biochemistry and physiology of xylose fermentation by yeasts. *Enzym. Microb. Technol.* 16:933–43
- Christakopoulos P, Macris BJ, Kekos D. 1989. Direct fermentation of cellulose to ethanol by *Fusarium oxysporum. Enzym. Microb. Technol.* 11:236–39
- Deshpande V, Keskar S, Mishra C, Rao M. 1986. Direct conversion of cellulose/hemicellulose to ethanol by *Neurospora crassa. Enzym. Microb. Technol.* 8:149–52
- Alterthum F, Ingram LO. 1989. Efficient ethanol production from glucose, lactose, and xylose by recombinant *Escherichia coli*. Appl. Environ. Microbiol. 55:1943–48
- Ohta K, Beall DS, Mejia JP, Shanmugam KT, Ingram LO. 1991. Metabolic engineering of *Klebsiella oxytoca* M5A1 for ethanol production from xylose and glucose. *Appl. Environ. Microbiol.* 57:2810–15
- Ho NWY, Tsao GT. 1993. Recombinant Yeasts for Effective Fermentation of Glucose and Xylose. US Patent No. 08/148, 581
- 100. Ho NWY, Chen ZD, Brainard A. 1995. The design and construction of recombinant Saccharomyces yeasts for simultaneous fermentation of glucose and xylose. Presented at Annu. Meet. Soc. Indus. Microbiol., San Jose, Calif.
- Zhang MC, Eddy C, Deand K, Finkelstein M, Picatagio S. 1995. Metabolic engineering of a pentose metabolism pathway in ethanologenic Zymomonas mobilis. Science 267:240

- Jeffries TW, Kurtzman CP. 1994. Strain selection, taxonomy, and genetics of xylose-fermenting yeasts. *Enzym. Microb. Technol.* 16:922–30
- 103. du Preez JC. 1994. Process parameters and environmental factors affecting Dxylose fermentation by yeasts. *Enzym. Microb. Technol.* 16:94–106
- Lezinou V, Christakopolous Li L-W, Kekos D, Macris BJ. 1995. Study of a single mixed culture for the direct bioconversion of sorghum carbohydrates to ethanol. *Appl. Microbiol. Biotechnol.* 43:412–15
- Baskaran S, Ahn H-J, Lynd LR. 1995. Investigation of the ethanol tolerance of *Clostridium thermosaccharolyticum* in continuous culture. *Biotechnol. Prog.* 11:276–81
- 106. Klapatch TR, Demain AL, Lynd LR. 1996. Restriction endonuclease activity in Clostridium thermoscellum and Clostridium thermosaccharolyticum. Appl. Microbiol. Biotechnol. 45:127–31
- Klapatch TR, Guerinot ML, Lynd LR. 1996. Electrotransformation of *Clostridium thermosaccharolyticum. J. Indus. Microbiol.* In press
- South CR, Lynd LR. 1994. Analysis of conversion of particulate biomass to ethanol in continuous solids—retaining cascade rectors. *Appl. Biochem. Biotech*nol. 45/46:467–81
- Beguin P, Aubert JP. 1994. The biological degradation of cellulose. *FEMS Microbiol. Rev.* 13:25–58
- Wong KKY, Saddler JN. 1992. Trichoderma xylanases, their properties and application. Crit. Rev. Biotechnol. 12(5/6):413–35
- 110a. South CR, Hogsett DA, Lynd LR. 1995. Modeling simultaneous saccharification and fermentation of lignocellulose to ethanol in batch and continuous reactors. *Enzym. Microb. Technol.* 17:797–803
- Esterbauer H, Steiner W, Labudova I, Hermann A, Hayn M. 1991. Production of *Trichoderma* cellulases in laboratory and pilot scale. *Bioresourc. Biotechnol.* 36:51–65
- Kadam KL. 1996. Cellulase production. See Ref. 163, pp. 213–52
- Hogsett DA, Ahn H-J, Bernardez TD, South CR, Lynd LR. 1992. Direct microbial conversion: prospects, progress, and obstacles. *Appl. Biochem. Biotech*nol. 34/35:527–41
- Picatagio SK, Eddy C, Deand K, Franden MA, Finkelstein M, Zhang M. 1995. Metabolic engineering of a xylose-

fermenting Zymomonas mobilis for efficient conversion of cellulosic feedstocks to ethanol. Presented at 17th Symp. Biotechnol. Fuels Chem., Vail, Colo.

- Wright JD. 1988. Ethanol from lignocellulose: an overview. *Energy Prog.* 8(2):71
- Kitchar JL, leader. 1995. Trends in commercial cellulases—production, specifications, and cost. Special topics discuss. grp., 17th Symp. Biotechnol. Fuels Chem., Vail, Colo.
- 117. King CJ. 1980. Separation Processes. New York: McGraw-Hill. 2nd ed.
- Busche RM. 1984. Recovering chemical products from dilute fermentation broths. *Biotechnol. Bioeng. Symp. Ser.* 13:597
- 119. Katzen R, Ackley WR, Moon GD, Messick JR, Brush BF, Kaupisch KF. 1981. Low energy distillation systems. In *Energy from Biomass and Wastes*, ed. DL Klass, GH Emert, pp. 393–402. Ann Arbor, MI: Ann Arbor Sci.
- 120. Bazua CD, Wilke CR. 1977. Ethanol effects on the kinetics of a continuous fermentation with Saccharomyces cerevisiae. Biotechnol. Bioeng. Symp. Ser. 7:105–18
- 121. Ghose TK, Tyagi RD. 1979. Rapid ethanol fermentation of cellulose hydrolyzate. II. Product and substrate inhibition and optimization of fermentor design. *Biotechnol. Bioeng.* 21:1401–20
- 122. Jobses IML, Roels JA. 1986. The inhibition of the maximum specific growth and fermentation rate of *Zymomonas mobilis* by ethanol. *Biotechnol. Bioeng.* 28:554– 63
- Lee KJ, Rogers PL. 1983. The fermentation kinetics of ethanol production by Zymomonas mobilis. Chem. Eng. J. 27:B31–38
- Jones RP. 1989. Biological principles for the effects of ethanol. *Enzym. Microb. Technol.* 11:130–51
- Huang SY, Chen JC. 1988. Ethanol production in simultaneous saccharification and fermentation of cellulose with temperature cycling. *J. Ferment. Technol.* 66(5):509–16
- Van Uden N. 1985. Ethanol toxicity and ethanol tolerance in yeasts. Annu. Rep. Ferment. Process. 8:11–58
- 127. Huibers DTA, Jones MW. 1980. Fuels and chemical feedstocks from lignocellulosic biomass. *Can. J. Chem. Eng.* 58:718–22
- 128. Graff G. 1982. High-grade lignin schemes edge closer to reality. *Chem.*

Eng. 27:25–27

- Larson ED. 1993. Technology for electricity and fuel production from biomass. *Annu. Rev. Energy Environ.* 18:567–630
- Stone K, Lynd LR. 1995. Analysis of internal and external energy flows associated with projected process improvements in biomass ethanol production. *Appl. Biochem. Biotechnol.* 51/52:569– 84
- Waits ED, Elmore JD. 1983. Environmental consequences of industrial-scale fuel ethanol production. *Environ. Int.* 9:325–34
- Loerh RC, Sengupta M. 1985. Management of ethanol production wastes: a review of available information. *Environ. Sanit. Rev.* 16:1–48
- Corbus D, Putsche V. 1995. Environmental Analysis of Biomass to Ethanol. Golden, CO: Natl. Renew. Energy Lab.
- South CR, Hogsett DA, Lynd LR. 1993. Continuous fermentation of cellulosic biomass to ethanol. *Appl. Biochem. Biotechnol.* 39/40:587–600
- Lobachyov K, Richter HJ. 1996. Combined cycle gas turbine power plant with coal gasification and solid oxide fuel cell. J. Energy Resour. Technol. In press
- 136. Harvey SP, Richter HJ. 1994. Gas turbine cycles with solid oxide fuel cells. Part I: Improved gas turbine power plant efficiency by use of recycled exhaust gases and fuel cell technology. J. Energy Resour. Technol. 116:305–11
- 137. Harvey SP, Richter HJ. 1994. Gas turbine cycles with solid oxide fuel cells. Part II: A detailed study of a gas turbine cycle with an integrated internal reforming solid oxide fuel cell. J. Energy Resour. Technol. 116:312–18
- 138. Deleted in proof
- 139. Shapouri H, Duffield JA, Graboski MS. 1995. Estimating the net energy balance of corn ethanol. Econ. Res. Serv. Rep. No. 721, US Dep. Agric., Washington, DC
- 140. Tyson KS, Riley CJ, Humphreys KK. 1993. Fuel Cycle Evaluations of Biomass-Ethanol and Reformulated Gasoline, Vol. 1. NREL/TP-463-4950. Washington, DC: Off. Transp. Technol., Dep. Energy
- 141. DeLuchi MA. 1991. Emissions of Greenhouse Gases from the Use of Transportation Fuels and Electricity, Vol. 1. Argonne, IL: Cent. Transp. Res., Argonne Natl. Lab.
- 142. 1995. Letter to B Cutter, J Gibbons, K McGintyfrom Auto Industry Representa-

tives to Policy Dialogue Advisory Committee to Recommend Reducing Greenhouse Gas Emissions from Personal Motor Vehicles. Washington, DC: Environ. Prot. Agency

- 143. Lynd LR. 1996. Cellulosic ethanol: technology status and potential in relation to environmental goals and policy formulation. In Is Technology Enough? Sustainable Energy— Transportation Strategies, ed. J. DeCicco, MA Delucchi. Washington, DC: Am. Counc. Energy Efficient Econ. (ACEEE) In press
- 144. Whitten GZ, Austin BS, O'Connor K. 1994. Ozone Impact of Year-Round Oxy-Fuel Program in Minnesota. SYS-APP94–93/246r2. San Rafael, CA: Syst. Appl. Int.
- 145. Deleted in proof
- 146. Gabele P. 1994. Ozone Precursor Emissions for Alternatively Fueled Vehicles. SAE Tech. Pap. Ser. Pap. No. 941905. Warrendale, PA: Soc. Automot. Eng.
- 147. Kelly KJ, Bailey BK, Coburn T, Clark W, Lissiuk P. 1996. Federal Test Procedure Emissions Test Results from Ethanol Variable—Fuel Vehicle Chevrolet Lumina. SAE Tech. Pap. Ser. In press
- 148. California Air Resources Board/Office of Environmental Health Hazard Assessment. 1994. Benzo[A]Pyrene as a Toxic Air Contaminant. Sacramento, CA: Calif. Air Resourc. Board/Off. Environ. Health Hazard Assess.
- 149. Born GL, Lucas SV, Scott RD, De-Fries TH, Kishan S. 1994. Effect of use of low oxygenate gasoline blends upon emissions from California vehicles. Final Rep., Contract no. A932-15, Calif. Air Resourc. Board, Sacramento, Calif.
- 150. Dudek WD, Clark W, Lucas SV. 1995. Effect of phase 1 and phase 2 gasolines on evaporative and exhaust emissions from light duty vehicles. Final Rep., Contract no. 132-183, Calif. Air Resourc. Board, Sacramento, Calif.
- 151. Guerrieri DA, Caffrey PJ, Rao V. 1995. Investigation into the Vehicle Exhaust Emissions of High Percentage Ethanol Blends. SAE Tech. Pap. Ser. No. 950777. Warrendale, PA: Soc. Automot. Eng.
- 152. Alternative Fuels Data Center. 1996. Web page: www.afdc.doe.gov
- 153. 1995. Exhaust emissions of E85 ethanol fuel and gasoline in flexible/variable fuel vehicles. *Tech. Bull. 16, Auto/Oil Air Qual. Improv. Res. Prog.*
- 154. Baudino JH, Voelz FL, Marek NJ. 1993. Emissions testing of three illinois E85

demonstration fleet vehicles. Presented at 10th Int. Symp. Alcohol Fuels, V1, Colorado Springs, Colo.

- 155. Whitten GZ, Greenfield SM, Causle MC, Guthrie PD, Myers TC, et al. 1993. Comparison of the air quality effects of ethanol and MTBE in reformulated gasoline in the Lake Michigan region. Final Rep. A SYSAPP-93/083, Syst. Appl. Int., San Rafael, Calif.
- 156. Wang MQ. 1996. Development and use of the GREET model to estimate fuelcycle energy use and emissions of various transportation technologies and fuels. Rep. ANL/ESD-31, Argonne Natl. Lab., Argonne, IL
- 157. Donovan CT, Fehrs JE, Lynd LR. 1994. The Potential for Producing Ethanol from Biomass in the Northeast. Washington, DC: Northeast Reg. Biomass Prog.
- Stork KC. 1996. Ethanol Demand Scenarios and Base-Case Eethanol and MTBE Production Capacity Estimates. DOE OTT/DOE Policy. Argonne, IL: Argonne Natl. Lab.
- DeCicco J, Lynd LR. 1996. Combining vehicle efficiency and renewable biofuels to reduce light vehicle oil use and

CO₂ emissions. Washington, DC: Am. Counc. Energy Efficient Econ. (ACEEE)

- 159a. Morris D, Ahmed J. 1992. *The Carbohydrate Economy*. Washington, DC: Inst. Local Self-Reliance
- 159b. Yu D, Aihara M, Antal MJ. 1993. Hydrogen production by a steam-reforming glucose in supercritical water. *Energy Fuels* 7:574–77
- 160. US Department of Agriculture. 1986. Fuel ethanol and agriculture: an economic assessment. Agric. Econ. Rep. No. 562, US Dep. Agric., Washington, DC
- US Department of Agriculture. 1988. Ethanol: economic and policy tradeoffs. Agric. Econ. Rep. No. 585, US Dep. Agric., Washington, DC
- 162. UŠ General Accounting Office. 1990. Alcohol fuels: impacts from increased use of ethanol blended in fuels. Rep. No. T-RCED-90-23, US Gen. Account. Off., Washington, DC
- Wyman CE, ed. 1996. Ethanol Handbook. Washington, DC: Taylor & Francis. In press
- Himmel ME, Baker JO, Overend RP, eds. 1994. Enzymatic Conversion of Biomass for Fuels Production. ACS Symp. Ser. 566. Washington, DC: Am. Chem. Soc.

Copyright of Annual Review of Energy & the Environment is the property of Annual Reviews Inc. and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.