

BIOMASS ETHANOL: Technical Progress, Opportunities, and Commercial Challenges

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■ **Abstract** Ethanol made from lignocellulosic biomass sources, such as agricultural and forestry residues and herbaceous and woody crops, provides unique environmental, economic, and strategic benefits. Through sustained research funding, primarily by the U.S. Department of Energy, the estimated cost of biomass ethanol production has dropped from ~\$4.63/gallon in 1980 to ~\$1.22/gallon today, and it is now potentially competitive for blending with gasoline. Advances in pretreatment by acid-catalyzed hemicellulose hydrolysis and enzymes for cellulose breakdown coupled with recent development of genetically engineered bacteria that ferment all five sugars in biomass to ethanol at high yields have been the key to reducing costs. However, through continued advances in accessing the cellulose and hemicellulose fractions, the cost of biomass ethanol can be reduced to the point at which it is competitive as a pure fuel without subsidies. A major challenge to realizing the great benefits of biomass ethanol remains to substantially reduce the risk of commercializing first-of-a-kind technology, and greater emphasis on developing a fundamental understanding of the technology for biomass conversion to ethanol would reduce application costs and accelerate commercialization. Teaming of experts to cooperatively research key processing steps would be a particularly powerful and effective approach to meeting these needs.

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INTRODUCTION

No other sustainable option for production of transportation fuels can match ethanol made from lignocellulosic biomass with respect to its dramatic environmental, economic, strategic, and infrastructure advantages (1–7). Substantial progress has been made in advancing biomass ethanol (bioethanol) production technology to the point that it now has commercial potential, and several firms are engaged in the demanding task of introducing first-of-a-kind technology into the marketplace to make bioethanol a reality in existing fuel-blending markets (8). Opportunities have also been defined to further reduce the cost of bioethanol production so it is competitive without tax incentives (9).

This chapter provides a brief review of the key factors that drive interest in producing ethanol from biomass sources such as agricultural (e.g. sugar cane bagasse) and forestry (e.g. wood trimmings) residues, significant fractions of municipal solid waste (e.g. waste paper and yard waste), and herbaceous (e.g. switchgrass) and woody (e.g. poplar) crops. Next, a state-of-the-art bioethanol process is outlined, followed by an economic pro forma analysis to provide a sense of the important cost

drivers. Against this backdrop, progress made in advancing bioethanol technology is reviewed to define the key accomplishments made possible through sustained research and development. Then two important areas meriting much greater emphasis are outlined. The first is in developing a solid technical foundation built on fundamental principles to help overcome the barriers that impede introduction of first-of-a-kind technology into the marketplace. The second is in aggressively funding research to advance bioethanol technology to the point at which it can be competitive as a pure fuel in the open marketplace. Hopefully, this chapter will provide a better appreciation of how bioethanol production technology has been improved and the vast potential it has for continued advancements and large-scale benefits.

REVIEW OF FACTORS MOTIVATING DEVELOPMENT OF BIOMASS ETHANOL TECHNOLOGY

In this section, a brief review is provided of the factors motivating the development of biomass ethanol technology to provide a context for the rest of the chapter, but the reader is referred to other papers if more in-depth information is sought (1–7, 10, 11).

Greenhouse Gas Reductions

Perhaps the most unique attribute of bioethanol is very low greenhouse gas emissions, particularly when compared with the emissions from other liquid transportation fuel options. Because nonfermentable and unconverted solids left after making ethanol can be burned or gasified to provide all of the heat and power to run the process, no fossil fuel is projected to be required to operate the conversion plant for mature technology (12, 13). In addition, many lignocellulosic crops require low levels of fertilizer and cultivation, thereby minimizing energy inputs for biomass production. The result is that most of the carbon dioxide released for ethanol production and use in a cradle-to-grave (often called a full-fuel-cycle) analysis is recaptured to grow new biomass to replace that harvested, and the net release of carbon dioxide is low (4, 5, 7, 12–20). If credit is taken for export of excess electricity produced by the bioethanol plant and that electricity is assumed to displace generation by fossil fuels such as coal, it can be shown that more carbon dioxide can be taken up than is produced (15, 16).

The impact of bioethanol on greenhouse gas emissions can be particularly significant because the transportation sector is a major contributor to greenhouse gas emissions, accounting for about one-third of the total (21, 22). As part of a Presidential Advisory Committee on reducing greenhouse gas emissions from personal vehicles, a survey of experts in the field clearly showed that most alternatives to petroleum (e.g. hydrogen production from solar energy) required significant changes in the transportation infrastructure to be implemented, whereas others

that could be more readily used (e.g. methanol production from coal or natural gas) would have little impact on reduction of greenhouse gas emissions (23). On the other hand, ethanol is a versatile liquid fuel, currently produced from corn and other starch crops, that is blended with ~10% of the gasoline in the United States and is widely accepted by vehicle manufacturers and users. Vehicles that use high-level ethanol blends (e.g. in E85, a blend of 85% ethanol in gasoline) are now being introduced throughout the United States. In addition, bioethanol production technology could be commercialized in a few years and would not require extended time frames to be applied. Overall, the evidence suggests that the best choice from the coupled perspectives of greenhouse gas reduction, integration into the existing infrastructure, and rapid implementation is the production of ethanol from lignocellulosic biomass.

Although surveys show that Americans are concerned about the prospects of global climate change (24), the issue has not received broad political support, perhaps owing to the influence of special-interest groups. On the other hand, much of Europe, Canada, and other countries are actively seeking to reduce greenhouse gas emissions (22, 25). Ironically, much more attention has been focused on developing bioethanol technology in the United States, whereas other countries have only recently shown interest in the area. Thus, there is tremendous potential for application of U.S. technology in many other regions of the world, benefiting all concerned.

Growing International Fuels Market

An aspect of renewable-fuel applications that has received relatively little attention is the growing demand for energy in the developing world (26, 27). As these countries improve their living standard, energy demand per capita will increase, and an important element will likely include increased mobility through use of more public transportation and personal vehicles. Thus, the challenge will not be how to reduce petroleum use but instead how to meet a growing demand for transportation fuels that support improvements in the lives of more and more people around the world. In other words, the perspective should not be simply a myopic viewpoint to insulate the United States from petroleum shortages and resulting economic and strategic disruptions that are inconvenient to our high living standard, but should be on how to provide sufficient fuel to raise the standard of living for the much larger population of the rest of the world. An added benefit is that bioethanol could be made in many countries, including the United States, that have limited petroleum resources, helping them to reduce their trade deficit and grow their economies.

Energy Security and Trade Deficit

In the United States and throughout much of the world, governments initiated major programs to fund the development of new energy sources in response to tightening petroleum supplies and skyrocketing energy costs during the "Energy Crises" of the mid- to late-1970s. In reality, these events were actually "Petroleum Crises," because a number of oil-rich countries, particularly in the Middle East, teamed

together to form the oil cartel OPEC and control the quantity and therefore price of petroleum. Moreover, the crisis was one of regulated production rather than supply. As energy prices dropped, interest in developing new energy sources waned, and government-sponsored research and development on new energy sources declined. Thus, petroleum remains the largest single source of energy in the United States, providing ~40% of the total energy use of >80 quads (1 quad is 1 quadrillion Btus or 10^{15} Btu) (21).

Interestingly, throughout this period, far more funding and programs were devoted to developing new sources of electricity than new sources of transportation fuels. Yet, about two-thirds of the petroleum used in the United States supports the transportation sector, which consumes over one-fourth of all energy used in this country. Additionally, petroleum imports continue to rise to over half the total used. Furthermore, the transportation sector is almost totally dependent (~97%) on petroleum, whereas other energy sectors are well diversified (21). Thus, an interruption in oil supplies or prices would cripple transportation, as witnessed by the long gasoline lines characteristic of the oil crises of the 1970s.

It is important that the supply of lignocellulosic biomass from which to make ethanol is substantial. This is not meant to downplay that some uncertainty and even controversy surrounds the magnitude of the resource and the possible conflict its use would create with the demand for food. Nonetheless, most studies estimate that enough biomass could be available from wastes and dedicated energy crops to make a significant dent in the huge amount of gasoline consumed in the United States (5, 7, 10). Furthermore, it should be possible to coproduce protein that could be used as animal feed from many sources of biomass, thereby achieving dual use of productive land, but consideration of this matter is reserved for a future paper.

Solid Waste Disposal

Disposal of many waste materials is becoming more and more important. For example, farmers are being asked to reduce the amount of rice straw that they burn after a harvest in northern California to cut back on smoke pollution. In British Columbia, phase-in of similar restrictions is raising concerns about what to do with wood wastes that have been historically burned. In other areas, runoff from sawdust piles is polluting groundwater, and lumber mill owners are searching for alternative disposal options. Suppression of natural forest fires has resulted in dense forests that cause more damage to the soil and mature trees because hotter fires result when they finally rage beyond control, and many are seeking to thin the forests to restore them to their natural plant density. Processing biomass wastes from these and many other situations into valuable products such as ethanol would provide a unique solution to these growing dilemmas (28). This aspect of ethanol production has been underappreciated and deserves far more attention.

Sustainable Production of Liquid Fuels and Organic Chemicals

As mentioned previously, essentially all (~97%) transportation fuels are derived from petroleum, and most organic chemicals come from petroleum and other fossil

resources (21). This lack of diversity is a signal of the difficulty in finding technically and economically attractive substitutes to petroleum for these applications. As further testament to the difficulty of developing alternatives to petroleum, only biomass of the sustainable resources can be readily converted into liquid fuels and a wide range of chemicals in addition to food and animal feed (LR Lynd, personal communication). Such a unique match underscores the importance of developing biomass to meet the need for fuels and chemicals. On the other hand, although biomass can also be converted into electricity, many other sustainable technologies (e.g. photovoltaics, wind, solar thermal, and nuclear technologies) could meet this need without competing demands for other uses. The key to biomass use is likely to be development of a compatible set of products, such as alcohols, organic acids, and natural polymers, that integrate with one another in the same way that the complex infrastructure of fuels, solvents, plastics, and so on has evolved based on petroleum from its early roots primarily in the manufacture of kerosene for lighting homes (29). Furthermore, the compatibility of water with many biomass-derived products should improve the environmental friendliness of these materials, a particularly powerful demonstration of green chemistry.

Air and Water Pollution

In addition to augmenting the fuel supply, ethanol increases octane and provides oxygen to promote more complete combustion, particularly in older vehicles, when blended with gasoline (1, 5, 7, 10, 30, 31). The former property reduces the need for additives such as benzene or tetraethyl lead, which are toxic and often carcinogenic. The latter attribute reduces tailpipe emissions of carbon monoxide and unburned hydrocarbons. Carbon monoxide is considered a serious problem in many urban areas (particularly high-altitude cities in winter months), and use of ethanol, an ethanol derivative—ethyl tertiary butyl ether (ETBE), or a related compound, methyl tertiary butyl ether (MTBE) made from methanol—reduces carbon monoxide tailpipe emissions. These oxygenates are also said to reduce tailpipe emissions of unburned hydrocarbons that form ground level ozone, resulting in serious health effects. On the other hand, although ethanol has a much lower vapor pressure than gasoline, blending the two initially increases the vapor pressure, promoting evaporation of gasoline components that increase ozone formation and resulting in considerable controversy about the efficacy of ethanol for ozone mitigation. It is worth noting that substitution of lower-vapor-pressure base gasoline would compensate for the higher-blend vapor pressure, but this change is often claimed to be costly to the consumer, similar to the threats that never materialized when lead was phased out and reformulated gasoline was introduced. On the other hand, because MTBE is vapor pressure neutral, it is widely used for blending to reduce the release of ozone-forming compounds as well as carbon monoxide. ETBE actually reduces the vapor pressure of blends, having even greater benefit as regulators continue to mandate lower and lower vapor pressure gasoline to combat air pollution.

MTBE is not readily biodegradable and persists in the environment, raising concerns about health effects. Various states are now in the process of discontinuing use of MTBE owing to concerns about penetration of MTBE into groundwater from underground storage tanks. The issue is not a factor in direct ethanol use because ethanol is readily metabolized as evidenced by its widespread consumption as a beverage. However, ETBE could suffer from the same concerns as MTBE.

Neat ethanol provides the greatest benefits with respect to both air and water pollution (30, 31). The low vapor pressure of ethanol (about one-quarter that of gasoline) coupled with its low photochemical reactivity reduces its ozone-forming potential. Furthermore, ethanol is totally soluble and therefore readily dispersed in water, limiting the damage associated with spills compared with immiscible and much more toxic hydrocarbon-based fuels. Although ethanol has about two-thirds of the volumetric energy density of gasoline, engines tuned to take advantage of its superior fuel properties (e.g. high octane and high heat of vaporization) can actually achieve ~80% of the range on the same volume of fuel (30, 31). Until such engines are widely available, flexible fueled vehicles now offered by Ford and Chrysler at lower prices than conventional vehicles use any mixture of ethanol and gasoline that is > 15% gasoline and will facilitate transition to high-performance ethanol engines. Ultimately, use of ethanol in fuel cells promises to achieve very high efficiencies with very low emissions, with one fuel cell developer indicating that ethanol is the fuel of choice.¹ On balance, ethanol provides a versatile fuel and fuel additive that can compete favorably with the performance and properties of gasoline. However, modifications (e.g. reformulated gasoline) are continually being made to gasoline formulations to maintain competitiveness and blur the advantages of alternative fuels such as ethanol.

OVERVIEW OF ETHANOL TECHNOLOGY

Current Production from Sugar and Starch Crops

About 3.4 billion gallons (gal.) of ethanol are made annually from cane sugar in Brazil (32), but at currently controlled levels, prices are too high for sugar to be a viable feedstock in the United States. Even in Brazil, cyclical world sugar prices result in widely fluctuating ethanol production, disrupting supplies and prices in the fuel market. In 1998, ~1.3 billion gal. of fuel ethanol made from starch crops, mostly corn, were consumed in the United States (33, 34). However, competing demands for corn, its greater value for food and feed, and limitations in coproduct uses are projected to limit the market to ~3–5 billion gal. (35). In

¹Jeffrey Bentley, vice president of Arthur D. Little, Inc. a company recently honored by the United States government for its novel fuel-cell technology, stated that “ethanol provides higher efficiencies, fewer emissions, and better performance than other fuel sources, including gasoline ... Where ethanol is available, it would be the fuel of choice by consumers” (31a).

addition, federal and state incentives are required even at current production levels to support ethanol use, and controversy continues to surround these subsidies even though such practices were common in the emergence of the oil industry from one dedicated to making kerosene for lighting homes to the production of a full slate of fuels and petrochemicals (29). It is important to realize that the widespread use of corn ethanol has fostered an acceptance and infrastructure that is poised for and vital to major expansions in ethanol use.

Lignocellulosic Biomass

Although not yet practiced commercially because of the greater recalcitrance of biomass, ethanol can also be made from plentiful lignocellulosic materials such as forestry and agricultural residues, significant portions of municipal solid waste (e.g. waste paper and yard waste), and woody and grassy crops grown to support fuel production. Because the potential supply of these sources of biomass is far greater than for food crops, competing uses for biomass are limited, and the demand for coproducts is expected to be compatible with the fuel markets, as we discuss below, bioethanol should be able to make a major impact on transportation fuel markets.

Biomass is a complex material made up of three major organic fractions with representative compositions on a dry-weight basis being as follows: 35%–50% cellulose, 20%–35% hemicellulose, and 12%–20% lignin (1). Biomass also contains smaller amounts of minerals (ash) and various so-called extractives. Cellulose comprises long chains of glucose sugars that can be broken apart by a hydrolysis reaction with water when catalyzed by enzymes known as cellulase or by acids. However, hydrogen bonds hold the long cellulose chains tightly together in a crystalline structure, impeding breakdown to glucose. Hemicellulose is an amorphous chain of a mixture of sugars, usually including arabinose, galactose, glucose, mannose, and xylose, as well as smaller amounts of a few other compounds, such as acetic acid. Hemicellulose chains are more easily broken down to form their component sugars than is cellulose. Lignin is not a sugar-based structure but is instead a heterogeneous substance based on a phenol-propene backbone.

Enzymatic Conversion of Biomass to Ethanol

The focus of this chapter is on biomass ethanol technology based on enzymatic hydrolysis of cellulose because the application of modern biotechnology offers the greatest potential for cost reductions that could make ethanol ultimately competitive with conventional fuels on a large scale without subsidies. To keep the length of the chapter manageable, the emphasis is on technologies, process steps, and configurations used in similar studies by the National Renewable Energy Laboratory (NREL) and Chem Systems (12, 13); although those selected are believed to be frontrunners, a variety of other options could prove equally or more cost effective with further development. Those interested in other technologies to use in association with enzymatic conversion of biomass to ethanol, information on

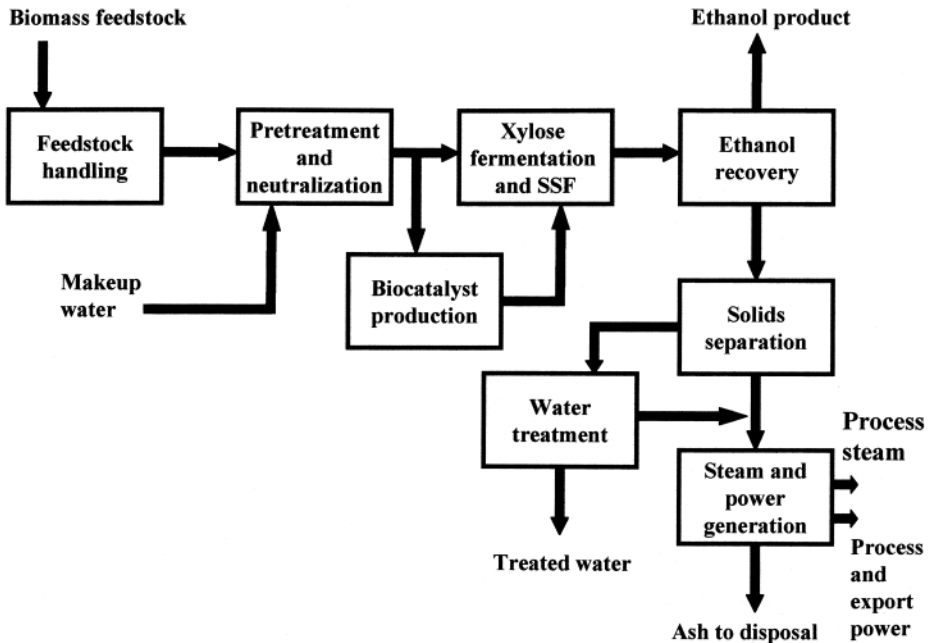


Figure 1 Block flow diagram for conversion of biomass to ethanol by the NREL process configuration. SSF, Simultaneous saccharification and fermentation.

alternative cellulose hydrolysis approaches such as dilute or concentrated acid-based technologies, or more details on technology than can be presented here should consult the literature (e.g. 1).

As summarized for the overall process in Figure 1, a material-handling operation brings feedstock into the plant, where it is stored and prepared for processing. Solids-handling operations such as these require considerable engineering attention to ensure that they work properly, because failures in this area have crippled entire plants. Design and operation of any biomass storage must be properly addressed to ensure that the feedstock will maintain its cellulose and hemicellulose content (36).

Next, biomass is pretreated to open up its structure and overcome its natural resistance to biological degradation. First, NREL and Chem Systems used a disc refiner to produce 1- to 3-mm wood chips to ensure adequate heat and mass transfer in the pretreatment step. About one-third of the power of the entire plant is expended in this operation, and it is important not to grind the material any more than needed. Then the milled chips are soaked in dilute sulfuric acid for 10 min. at 100°C followed by heating to 160°C for 10 minutes to break down the hemicellulose to form its component sugars, typically arabinose, galactose, glucose, mannose, and xylose. The pretreated biomass liquid hydrolyzate is neutralized and conditioned to remove or inactivate any compounds naturally released from the material

(e.g. acetic acid or lignin) or formed by degradation of biomass (e.g. furfural) that are inhibitory to fermentation.

Although historically the five sugars derived by hemicellulose hydrolysis could not be fermented to ethanol at high yields, several bacteria have been genetically engineered to ferment all of these sugars in a breakthrough achievement for ethanol technology (37–39). Thus, the hydrolyzate is sent to the five-carbon sugar fermentation step in which genetically engineered *Escherichia coli* or other suitable organisms convert the free sugars to ethanol, as again shown in Figure 1.

A portion of the hydrolyzate is sent to a separate enzyme production step in which ~2% of the total sugars is consumed by an organism such as the fungus *Trichoderma reesei* to make cellulase. The entire broth from enzyme production, including cellulase, the organism that produced it, and unconverted substrate, passes to the cellulose hydrolysis process, eliminating enzyme-processing steps, reducing the possibility of introducing invading organisms, using enzyme associated with fungal biomass, and converting any cellulose left after cellulase production into ethanol (40, 41).

As mentioned previously, cellulase catalyzes the breakdown of cellulose to release glucose, which many organisms, including common yeasts, ferment to ethanol. Although the hydrolysis step can be carried out first followed by fermentation in a separate vessel, most workers in the field prefer the simultaneous saccharification and fermentation (SSF) route, in which enzyme and fermentative organism are added to the same vessel to produce ethanol from sugars as soon as they are released (40, 42–53). Because glucose and the short cellulose chains (cellulose) formed during hydrolysis are strong inhibitors of enzymatic action, whereas ethanol has a much weaker impact on enzyme activity (54), the rates of reaction are actually faster for the SSF configuration than for a separate hydrolysis and fermentation approach, even though the temperature must be reduced from optimum levels for cellulase activity to accommodate the fermenting organism (43, 44, 47). In addition, the SSF process cuts equipment and other vessel-related costs by about half, and the presence of ethanol in the fermentation inhibits invasion by organisms that would thrive in a dilute sugar stream and divert sugars to unwanted products such as lactic acid.

In the NREL and Chem Systems designs, SSF broth is transferred to a series of distillation columns to recover ethanol as the overhead product, and the ethanol product is taken off at the azeotropic composition with ~5% water left in it for use as a neat fuel. The lignin, water, enzymes, organisms, and other components leave with the column bottoms, and the solids are concentrated to feed the boiler that provides all of the heat and electricity for the entire process, with any excess electricity sold. No other coproducts are taken from the system because it is assumed that only the electricity market is compatible with large-scale penetration of bioethanol for fuel use. The liquid not retained with the solids is processed through a combined anaerobic and aerobic waste treatment process, with the clean water discharged from the plant or recycled to the process, the sludge disposed of, and the methane fed to the boiler. The ash from the boiler is taken to a landfill.

ECONOMIC PRO FORMA ANALYSIS FOR BIOETHANOL

The goal of the NREL and Chem Systems studies was to estimate the cost of producing ~58 million gal./year of denatured ethanol (90.3% by weight ethanol, 4.7% water, and 5.0% gasoline as a denaturant) from 1920 tons/day of dry wood. Therefore, material and energy balances were developed for the configuration discussed above, and the costs of raw materials, utilities, labor, and other cash costs of production were derived based on quantities of materials required and published prices. In addition, equipment was sized to carry out the operations described based on the best available performance data in the literature, and equipment costs were determined from computer tools and vendor quotes. The overall information was then combined to determine the price at which bioethanol must be sold to cover all the operating costs and realize a targeted return on investment. In this section, these results are summarized to provide a perspective on the costs of producing ethanol from biomass. The projected costs for the NREL and Chem Systems studies were quite similar, but the NREL estimates are primarily used here for consistency and because they were the more recent of the two, even though they were published first. All results are in 1990 dollars.

The cost of equipment was estimated for the base-case ethanol plant described earlier, as summarized in Table 1 (13). Equipment was included for all areas,

TABLE 1 Estimated capital investment for bioethanol production for National Renewable Energy Laboratory reference case in 1990 dollars

Plant area	Million \$
Wood handling	7.16
Pretreatment	23.68
Xylose fermentation	6.16
Cellulase production	2.76
Simultaneous saccharification and fermentation	20.93
Ethanol recovery	3.99
Off-site tankage	4.09
Environmental systems	3.96
Utilities	53.14
Miscellaneous	<u>2.52</u>
Fixed capital investment	128.39
Start-up costs	6.42
Working capital	<u>6.40</u>
Total capital investment	<u>141.22</u>

including wood handling, pretreatment, fermentation of hemicellulose sugars, cellulase production, SSF, ethanol recovery, off-site tankage for raw material and product storage, environmental systems, utilities, and other miscellaneous items. Installed costs were factored with estimates based on purchased equipment costs. Provisions were also incorporated into the capital costs for startup and working capital. The result was an installed-equipment cost of \$128.4 million and a total capital cost of \$141.2 million or \$2.41/gal. of installed annual ethanol capacity.

Table 2 lists the cash costs of production for the base-case plant, again based on 1990 dollars. Raw material costs include those for wood at \$42/dry ton, sulfuric acid for pretreatment, lime for neutralization of the acid and conditioning, nutrients for the organisms, including ammonia, corn steep liquor, and other such ingredients, corn oil for controlling fermentor foaming, glucose for growth of seed cultures, gasoline to denature the final product, and other chemicals. Costs were also included for disposal of residual ash and other solids and for well water, but a credit resulted from the sale of excess electricity beyond that needed to power the plant. Labor costs were included for operating personnel, forepersons, supervisors, maintenance, and direct overhead. General plant overhead, insurance, and property taxes completed the cash costs for the plant. The sum of these costs resulted in a projected cash cost of production of \$0.734/gal. of denatured ethanol produced.

To calculate the projected total cost of bioethanol, the capital costs for the plant were annualized at a rate of 20% of the initial investment. This fixed-charge rate reflected a 10% after-tax rate of return on capital and included income taxes at 37%,

TABLE 2 Estimated cost of bioethanol production for National Renewable Energy Laboratory reference case in 1990 dollars

Item	Million \$/year	Cents/gal
Wood	26.88	45.9
Other raw material	8.14	14.1
Gypsum disposal	0.40	0.7
Electricity	(4.15)	(7.1)
Water	0.14	0.2
Labor/supervision	1.57	2.7
Maintenance	3.85	6.6
Direct overhead	0.71	1.2
General overhead	3.52	6.0
Insurance, property taxes	1.93	3.3
Total cash costs	42.99	73.4
Annualized capital charge	28.24	48.3
Total cost of production	71.23	121.7

15-year plant life, 3-year construction period, 3-year period to achieve full capacity, and straight-line depreciation. The result was a capital charge of \$0.483/gal., and combining this value with the cash cost of production gave a projected selling price of \$1.22/gal., as shown in Table 2. At this price, bioethanol would be competitive with the current market price of corn. Furthermore, if advantage is taken of niche market opportunities such as use of inexpensive waste biomass as feedstock, low-cost debt financing, production of higher-value coproducts, or integration into an existing facility, a much lower projected cost results (10). As we demonstrate below, these special markets can be particularly important in compensating for the risk of introducing technology in the first few plants.

These cost projections are for the *n*th plant and not the first. Thus, they assume that the technology is fully mature and the costs have evolved to virtually the lowest possible for the particular process configuration applied. These projections also assume that scale-up risks are negligible because of the experience of building many identical plants previously. However, they are still constrained by the particular choice of unit operations, biological components, materials of construction, and other system choices, and changes in this underlying framework could dramatically reduce processing costs for both *n*th and first plants, as is shown below.

HISTORIC PROGRESS

Bioethanol cost analyses such as those just described actually began with several process designs by selected engineering and consulting firms for different enzymatic and dilute-acid-based pathways to bioethanol production (e.g. 55–58), and the approach was extended to other systems such as use of concentrated acids to hydrolyze biomass to sugars (59, 60). Based on such cost projections and in light of tightening federal research budgets in the 1980s, a decision was made to focus on enzymatically based bioethanol production technology.

Prior to the study reported, NREL used a similar cost estimation methodology to track the progress of research advances for enzyme-based processes and define opportunities to lower the cost of ethanol production further (61, 62). However, there are several differences in the basis for these historic cost projections compared with the NREL and Chem Systems studies reported above, with the use of a capital recovery factor of 0.13 instead of 0.20 to annualize capital costs being the most significant (61, 62). Therefore, the costs from the historic studies have been adjusted to apply the same capital recovery factor and year dollars as for the NREL and Chem Systems studies, discussed earlier with the costs originally reported in 1988 dollars shown in parentheses to aid in following the references cited.

Initially, a sequential hydrolysis and fermentation route was used for breakdown of cellulose to glucose and subsequent fermentation to ethanol. The result was a projected selling price of \$4.63 (\$3.60)/gal. for 1979 technology based on the use of a fungal strain known as QM9414 for cellulase production. Three years later, a

strain known as Rut C30 could be used with a cost of \sim \\$3.49 (\\$2.66)/gal., because of a better balance in enzyme activity components and lower end product inhibition. A different cellulase, known as 150L and developed by Genencor, improved hydrolysis results further and lowered the projected cost to \\$2.90 (\\$2.25)/gal. for the year 1985. When this same cellulase enzyme was applied to the SSF configuration, the estimated cost of bioethanol manufacture dropped to \\$2.28 (\\$1.78)/gal. in the year 1986. If the biomass feed rate is kept constant with more efficient cellulase rather than reducing the plant size to maintain a fixed ethanol capacity, the cost drops to \sim \\$2.00 (\\$1.65)/gal.

Figure 2 presents the history of bioethanol cost reductions, including the more recent NREL projections of \\$1.22/gal. discussed previously. The descriptions that follow summarize the technology advancements that led to these cost reductions.

Hemicellulose Hydrolysis/Pretreatment

Although not obvious in the above economic summary, a key element underlying bioethanol cost reductions has been improvements in pretreatment technology. Without pretreatment, sugar yields are low because cellulose is not readily accessible to the large cellulase enzyme protein structures. Over the years, various biological, chemical, and physical pretreatment approaches have been studied to increase the susceptibility of cellulose to attack by enzymes (63, 64). Physical techniques include comminution and irradiation, and, although mechanical methods

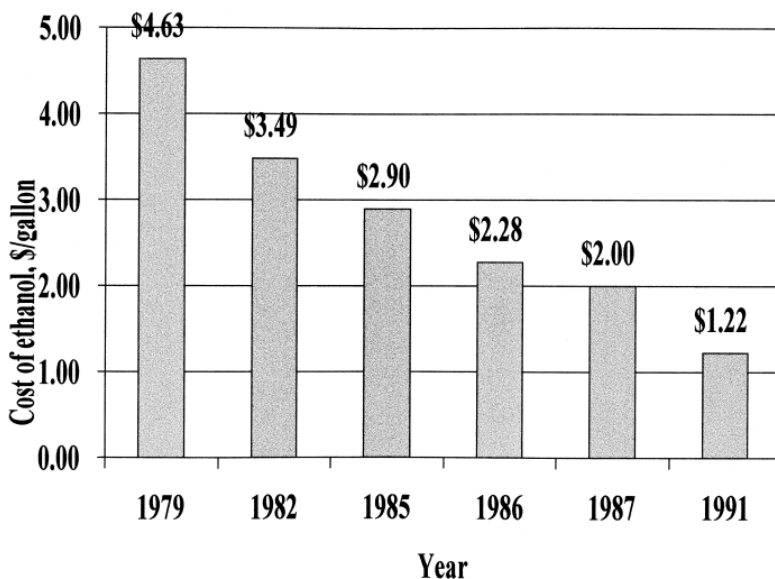


Figure 2 Progress in reducing the cost of producing ethanol from biomass based on enzymatic cellulose hydrolysis technology, as shown in 1990 dollars.

such as extensive ball milling were somewhat effective, the energy requirements were too great to be viable. Irradiation approaches such as exposure to electron beams or microwave heating have not proven to be effective owing to cost, efficiency, and/or performance limitations. Biologically based technologies could greatly simplify pretreatment, but the rates are slow, yields are low, and little experience has been developed with such approaches.

Chemical methods have become the generally preferred route to improve the enzymatic digestibility of cellulose (63). In particular, building off early work on plug flow systems by Converse et al (65) and Knappert et al (66), dilute acids, and particularly sulfuric acid, have proven to be very effective for hemicellulose removal at relatively low costs (12, 13, 67). Steady progress has been made over the years in refining the technology further to remove hemicellulose with high yields and achieve good digestibility of cellulose, and the process has been demonstrated to be effective on a variety of biomass feedstocks (68–72). Consequently, the kinetics of hemicellulose removal are reasonably known and modeled (65, 66, 73), and the severity parameter has been particularly effective in correlating performance over a wide range of temperatures, times, and acid concentrations (74). High yields of ~85% to $\geq 90\%$ of the sugars can be recovered from the hemicellulose fraction with temperatures of $\sim 160^\circ\text{C}$, reaction times of ~ 10 min, and acid levels of $\sim 0.7\%$, and $\sim 85\%$ to $>90\%$ of the remaining solid cellulose can be enzymatically digested to produce glucose (68–72). However, we demonstrate below that dilute acid pretreatment is still a major cost element that introduces technically significant challenges to the process.

Alternatively, sulfur dioxide can be used in place of sulfuric acid to some advantage, although its performance is not as well characterized and its use introduces some safety concerns (67, 75, 76). Ammonia is a promising alternative to sulfuric acid and offers some advantages for materials of construction and compatibility with fermentations (77). There has also been interest in using carbon dioxide to form carbonic acid for catalyzing hemicellulose hydrolysis, but results to date have not been encouraging. Pretreatment by water and steam alone in a steam explosion process relies on release of natural acids from hemicellulose to break down the hemicellulose, followed by rapid pressure release to quench the reaction and disrupt the fibrous structure. Although conceptually simple, the yields of sugars from hemicellulose are low at $<65\%$ for these so-called batch steam explosion techniques, and such yields are too low to be attractive (78, 79). Alkaline materials such as sodium hydroxide are particularly effective at removing the lignin from biomass along with solubilization of much of the hemicellulose, but the cost of chemicals is excessive for production of low-value, high-volume products such as fuels. Solvents such as methanol or ethanol can be used in an organosolv approach to remove lignin, often with the addition of acids to improve the removal of hemicellulose. Such lignin removal technologies provide good separation of the major biomass components (i.e. cellulose, hemicellulose, and lignin), but current costs are too high for these technologies to be used for other than production of high-value products such as high-grade cellulose (63, 64).

Fermentation of Five-Carbon Sugars

Without a profitable use of the five-carbon sugars xylose and arabinose, bioethanol is too expensive at \$2.00/gal. to compete in commercial markets. To increase revenues, various studies were undertaken to identify coproducts that could be made from these sugars, such as furfural and its derivatives (80), but none of their markets was sufficient to use the volume of such coproducts that would accompany large-scale bioethanol production. In the final analysis, manufacture of more ethanol from pentose sugars is the best option for enhancing revenues and marketing products. Unfortunately, natural organisms do not achieve high enough ethanol yields to be economically viable and even then typically require careful control of dissolved-oxygen levels, which is difficult to accomplish in gigantic commercial fermentors (81–83).

The critical achievement in reducing ethanol production costs to the \$1.22/gal. value projected by NREL was the genetic engineering of several bacteria to allow them to ferment all five sugars found in biomass to ethanol (37–39). To achieve this breakthrough, two genes from the ethanol-producing bacterium *Zymomonas mobilis* were inserted into any one of a number of new bacterial hosts, such as *E. coli* or *Klebsiella oxytoca*. These genes code for the enzymes pyruvate decarboxylase and alcohol dehydrogenase, which divert the intercellular compound pyruvate into ethanol, draining the pyruvate pool enough that it no longer forms appreciable quantities of natural products such as acetic acid. Because the host organisms take up arabinose, galactose, glucose, mannose, and xylose sugars to produce pyruvate, the result is use of all sugars at yields that are very close to theoretical (84). The significance of this invention to commercialization of bioethanol technology was recognized by award of the landmark patent 5,000,000 after a several-year search by the U.S. Patent Office (37). A number of patents have been subsequently issued to those inventors who substantially broaden the scope of the original claims.

More recently, a few additional organisms have been genetically engineered to ferment five-carbon sugars to ethanol at high yields (82, 83). These are based on broadening the range of sugars used by organisms that already make ethanol. One such bacterium, *Zymomonas mobilis*, now uses arabinose and xylose in addition to the glucose it naturally metabolizes (85), whereas a strain of the yeast *Saccharomyces cerevisiae* has been genetically modified to ferment xylose in addition to its normal uptake of galactose, glucose, and mannose (87–89). Overall, an important feature for such organisms to be commercialized is the ability to ferment all biomass sugars to ethanol with yields of about 90% of theoretical and to establish that they can be successfully applied to low-cost hemicellulose hydrolyzates.

Cellulose Hydrolysis

Although hemicellulose can be readily hydrolyzed to sugars at high yields and its sugars are not easily fermented by native organisms, cellulose is very difficult to hydrolyze to glucose, its component sugar, which in turn is quite readily fermented to ethanol with high yields and at high concentrations by common yeasts. Because

cellulose is the largest single fraction of biomass, one of the major challenges in bioethanol technology development is to improve the technology for hydrolysis of recalcitrant cellulose. In fact, all of the historic cost reductions reported from 1979 to 1986 resulted from improvements in enzymatic hydrolysis of cellulose in conjunction with acid hydrolysis of hemicellulose (i.e. pretreatment) (61, 62).

In the early stages of technology development for cellulose hydrolysis, considerable attention was devoted to dilute-acid-catalyzed breakdown of cellulose, but unfortunately the yields were low owing to excessive degradation of glucose at the highly severe conditions of $\sim 240^{\circ}\text{C}$ used for cellulose hydrolysis (90, 91). In addition, there were concerns about the formation of undesirable tars that would cause operational problems as well as yield losses, and the very short residence times of ~ 6 s required to realize reasonable yields are so low as to be considered impractical by many. Alternatively, concentrated acids could achieve virtually theoretical yields, at least in principle, but acid concentrations are so high that it is essential to recover and recycle the acid. Unfortunately, the capital and operating costs for acid recycling schemes are so high that exceptional coproduct revenues or feedstock tipping fees are essential to financial success, and this demand limits market potential greatly (59, 60).

During World War II, considerable attention was devoted to combating an organism that degraded cotton clothing and gear in tropical areas. It was found that this fungus produced an enzyme known as cellulase that weakened the cotton in uniforms, web belts, tents, and similar items. During the energy crisis of the 1970s, it was recognized that this same enzyme could hydrolyze cellulose in biomass to glucose at very high yields for ethanol production. Thus, substantial efforts were exerted to understand how to use the enzyme effectively, and one of the fungi that produced the enzyme was named *Trichoderma reesei* in honor of Edwin Reese of the U.S. Army Natick Laboratory where much of the early cellulase work was carried out (92).

One of the early strains of *Trichoderma reesei* was designated as QM9414, in which the QM designation referred to the U.S. Army Quartermaster Corps. Although its enzymes broke down cellulose, the rates and concentrations of ethanol produced by QM9414 were limited owing to inhibition of cellulase by glucose and soluble chains of glucose known as oligomers, formed during the breakdown of cellulose. It was found that cellobiose, a glucose dimer, is particularly inhibitory to enzyme action (54). The performance of other early strains was improved by classical mutations and strain selection, with one variety known as Rut C30 developed at Rutgers University proving superior (93). A cellulase known as 150L produced by Genencor was very effective at cellulose hydrolysis because of enhanced levels of an enzyme component known as β -glucosidase that converted cellobiose into glucose (46, 48, 52, 53). Furthermore, even though the fermentation temperature must be reduced below that considered optimum for cellulase action to accommodate temperature limitations of known fermentative organisms, accumulation of glucose was minimized when 150L cellulase was used in an SSF configuration, further reducing end-product inhibition of the enzyme and improving the

rates, yields, and concentrations of ethanol production (47, 49). Nonetheless, cellulase action is still slow, with SSF reaction times of ~ 5 – 7 days needed to achieve modest ethanol concentrations of $\sim 4.5\%$ – 5.0% at affordable cellulase loadings (94–98).

Glucose Fermentation

Glucose can be fermented by using well-established technology developed over centuries for such applications as wine making, brewing, food processing, and ethanol production from sugar and corn, and ethanol concentrations of $\sim 10\%$ to 12% and more are achieved in ~ 48 h. Although improvements can be made in areas such as increasing the temperature tolerance of yeasts to reduce cooling costs, fermentation costs are already quite low, and the impact of such developments will be relatively small as well as difficult to achieve.

On the other hand, after the invention of the SSF configuration for cellulose conversion by Takagi and coworkers in the mid 1970s (40, 42), it became important to identify fermentative organisms that could tolerate the greater stress associated with the combined effects of high temperatures desired to increase rates of enzymatic hydrolysis, low glucose levels from rapid sugar metabolism by the fermenting organism, and high ethanol concentrations. A number of investigations followed to find the best organism-enzyme combinations, with particular emphasis on thermotolerant yeasts, and several organisms were identified that improved the rates, yields, and concentrations of ethanol formation (46–53). However, it was found that rapid conversion of cellobiose to glucose was more important than the fermentation temperature. Thus, the best results were with a cellulase such as Genencor 150L, which is higher than many in β -glucosidase (46, 49). Alternatively, an organism such as *Brettanomyces custerii* that can ferment cellobiose into ethanol either directly or in coculture with a more ethanol-tolerant yeast enhances performance (46, 52, 53). Some of the bacteria genetically engineered to ferment xylose to ethanol also have the ability to ferment cellobiose to ethanol, and genes have been inserted in others to impart this trait (39), reducing enzyme requirements.

Enzyme Production

Cellulase is produced commercially, but existing preparations are directed at low-volume, high-value specialty markets such as stone-washed jeans, with the primary interest in providing carefully balanced properties that command high prices. Furthermore, cellulase production research has been very limited for applications to production of low-cost sugars from cellulose for conversion to fuels and commodity chemicals (99). Thus, although the cost of cellulase production is not a major element in the particular projected economic studies presented above, the technical performance is based on relatively limited data and some major extrapolations of costs that need to be verified. For instance, recent investigations project higher

costs of ~\$0.50/gal. of ethanol produced if cellulase is manufactured on site or \$3.00/gal. if it is purchased (100). Overall, these differences reflect the uncertainty in both the performance and choice of technology.

Features that differentiate cellulase production applications for bioethanol production from current markets include the substrate used and the direct addition of whole broth to the SSF process. Production of cellulase on mixed liquid/solid hydrolyzate from pretreatment instead of lactose and other more costly and limited carbon sources typically used commercially shows promise to reduce the cost of cellulase production and simplify the integrated production system (101, 102). In contrast to enzyme production for specialty markets, in which cellulase is typically removed from the fungal source and then concentrated before shipment to the user, adding the entire cellulase production broth to SSF vessels improves performance because fungal bodies retain some cellulase and, particularly, β -glucosidase activity (40, 41). This approach also saves on capital investment by eliminating costly equipment and reduces the opportunity for microbial invasion by simplifying the process. Furthermore, any substrate not used for enzyme production passes to the SSF process and is converted to ethanol, increasing yields. The team who originally developed the SSF process termed whole-broth cellulase addition a koji technique (40).

Product Recovery

Product recovery in the NREL/Chem Systems studies is based on conventional distillation technology. Although there has been some controversy in the past about high energy use for ethanol purification, these concerns were based on inefficient, outdated technology used by some firms during the emergence of the corn ethanol industry. Such firms have now either switched to modern, efficient equipment or are no longer in business. The cost of and energy use by new distillation equipment are not significant in the production of bioethanol, and given the tremendous experience curve for distillation, the prospects for advances that will have a significant impact on bioethanol production costs are not high (7). The key is to use state-of-the-art technology.

OPPORTUNITIES FOR TECHNOLOGY IMPROVEMENTS

As pointed out by the historic cost projections, sustained, although very cyclical, government funding for research and development has reduced the projected cost of bioethanol manufacture by a factor of ~4, to a level that is now competitive with ethanol from corn for direct blending with gasoline. Although its cost is still high enough to require tax incentives, particularly for implementation with nonwaste feedstocks, the cost of production can be reduced further to the point that bioethanol will be viable on the open market for blending and use as a neat

fuel. This potential has been confirmed through several distinct approaches, three of which will be reviewed in this section of the chapter to define the impacts of improvements and specific opportunities for research.

Sensitivity Studies

Once tools have been set up to close material and energy balances and estimate operating and capital costs for a particular process configuration, it is relatively straightforward to investigate the impact of changes in key performance parameters on process economics. One simply determines how the costs change as yields, rates, concentrations, and other parameters are varied over a realistic range. The primary drawback to this approach is that it is only used easily if the process configuration remains fixed, and advanced schemes with different processing sequences that could substantially reduce costs are not easily studied.

The NREL and Chem Systems studies examined the sensitivity of the projected costs to several key cost and performance parameters: feedstock costs, plant size, electricity revenue, revenue from other coproducts, decreasing capital-related costs, decreasing noncapital-related costs, and yield of ethanol from carbohydrates (12, 13). Ethanol yield was further broken down based on each process step, including hydrolysis of hemicellulose to sugars, fermentation of hemicellulose sugars to ethanol, hydrolysis and fermentation in SSF, and cellulose consumption for cellulase production and growth of organisms.

The results of the NREL sensitivity studies are summarized in Table 3. The largest single impact would be a $\sim 38\%$ cost reduction if we could obtain free feedstock, but it is very unlikely that a large supply of feedstock can be obtained at no cost, with transportation costs being covered as a minimum. For large-scale impact of bioethanol technology, a more reasonable feedstock cost would be on the order of \$34/dry ton, the goal for the Department of Energy Biomass Production Program, resulting in a cost reduction of $\sim 7.4\%$ from the NREL base case. The largest plausible research impact in the NREL study was an $\sim 12.3\%$ cost reduction through improving the yield from the SSF step. After this, increasing the plant size by about a factor of 5 reduces the cost by $\sim 11.5\%$, assuming that only the distillation and plant offsites benefit from economies of scale. Reducing the SSF fermentation time to 2 from 7 days drops the cost of ethanol by $\sim 5.5\%$, whereas improvements in yields of sugars from hemicellulose and the subsequent fermentation step decrease costs by 2.9% and 2.0%, respectively. Increasing on-stream time has a similar impact to that of the latter two variables, resulting in a cost reduction of 2.1%. About 1.1% cost reductions can be achieved by cutting the xylose fermentation time in half, reducing the cellulase production time by a factor of 3, and decreasing milling power needs by 35%. Using 10,000 tons/day of feedstock costing \$34/dry ton coupled with all of the other improvements summarized above results in a 40% cost reduction to $\sim \$0.74/\text{gal.}$ of ethanol, a value competitive with gasoline selling for $\sim \$0.92/\text{gal.}$ at the plant gate, assuming bioethanol is used in a properly optimized spark ignition, internal combustion engine.

TABLE 3 Results from National Renewable Energy Laboratory sensitivity study of impact of process performance on costs^a

Process element	Units	Change from	Change to	Percent impact ^b
Feedstock cost	\$/Ton	42	34	7.4
Feedstock cost	\$/Ton	42	0	37.7
Plant size	Dry tons/day	1920	10,000	11.5
SSF yield	% of theoretical	72	90	12.3
Xylose to ethanol	% of theoretical	85	95	2.0
Hemicellulose to sugars	% of maximum	80	90	2.9
SSF reaction time	Days	7	2	5.5
Xylose fermentation time	Days	2	1	1.1
Cellulase production time	Days	6	2	1.1
Milling power	% of reference case	100	65	1.2
Onstream time	% of total hours	91.3	95.0	2.1

^aSSF, Simultaneous saccharification and fermentation.^bPercent change in estimated total cost of production of \$1.22/gal.

The Chem Systems study took a more aggregated look at technology improvements and did not attempt to subdivide their impact. For example, they showed that a drop in capital costs of ~27% would lower ethanol costs by 21%. They also showed that an overall yield increase from 68% in the base case to 90% would lower costs by about 25%. Changes in feedstock costs and plant size had similar effects on ethanol production costs as shown by the NREL study.

Other improvements in ethanol technology could be readily included in such studies, such as use of feedstocks with higher carbohydrate content, further reductions in milling power, less power for mixing, lower-cost pretreatment reactors, reduced air compression needs, higher-efficiency boilers/turbogenerators, improved heat integration, reduced costs for preparation of inoculum, and use of less chemicals and nutrients. Additional improvements such as advanced bioreactor and pretreatment vessel designs and combining process steps through a consolidated bioprocessing arrangement would also lower costs but require substantial changes in the process configuration and flow-sheet modeling.

As part of a study to define more specific opportunities for improvement that will be discussed in a later section, slightly updated cost projections from the NREL analysis were broken down based on the key process steps, as summarized in Figure 3 (9). Consistent with the sensitivity studies discussed above, the feedstock is the single most costly element, at ~39% of the total, but as mentioned above, it is difficult to impact feedstock costs substantially for eventual large-scale bioethanol

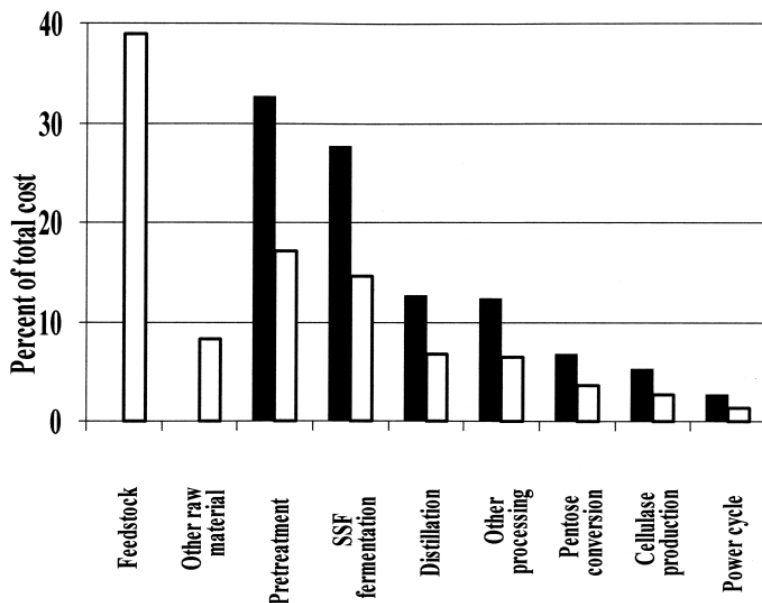


Figure 3 Contribution of major cost elements to overall ethanol production costs for the NREL reference case. Cost reductions based on the total production cost are shown as *open bars*, whereas the impacts on processing costs alone are presented as *solid bars*. SSF, Simultaneous saccharification and fermentation.

production. However, the costs of the processing steps can be reduced further, and the most expensive of these steps is for pretreatment, representing almost one-third of the total processing costs. The second most costly operation is the SSF process, accounting for ~28% of the total. Thus, hydrolysis to sugars in the pretreatment and SSF steps accounts for >60% of the total processing cost, and better pretreatment technology could have an impact both by lowering the cost to break down hemicellulose and by improving the rates and yields in the SSF process. The third most costly operation is product recovery, but at a far lower 12.6% of the total processing cost with a similar contribution by the remaining process steps including waste recovery. The costs for pentose conversion and cellulase production are about half the cost of distillation, with a far lower net value projected for power generation after taking credit for power exports.

Technology Advances

The process studies were taken further to define more specific technical opportunities to lower bioethanol production costs and estimate the resulting cost of production (9). For this analysis, an advanced process configuration was chosen that focused on improved pretreatment technology in conjunction with consolidated bioprocessing that combined the cellulase production, cellulose hydrolysis,

cellulose sugar fermentation, and hemicellulose sugar fermentation steps in a single fermentor. The latter arrangement eliminates equipment and reduces operating costs.

Complete material and energy balances were applied just as for the Chem Systems and NREL studies, and two levels of performance parameters were integrated into the system: one being for the best performance conceivable and the other representative of advanced technology that is believed to be the most likely achievable by analogy with similar systems. Capital and operating costs were then estimated from the process conditions, flow rates, and vessel sizes to support the estimate of the overall cost of bioethanol production including capital recovery, as above.

The advanced technology scenario considered technology improvements only for the pretreatment and biological-processing steps. The advanced pretreatment technology characteristics were based on expectations for liquid-hot-water pretreatment technology, with elimination of acids, conditioning, and biomass milling (103). Higher yields of hemicellulose sugars were also forecast for this approach, and lower-cost materials of construction and other cost reductions were expected. Advances in other pretreatment technologies also show promise to realize similar gains (104, 105). The consolidated biological-processing operations were projected to increase cellulose hydrolysis yields to 92% with subsequent fermentation to ethanol at a 90% yield. The ethanol concentration was set at 5% by weight, and the fermentation time was taken as 36 h. Continuous fermentation was used, and, as a result, costly seed fermentors were eliminated. Combining these advances resulted in a projected total bioethanol cost including return on investment of ~\$0.50/gal. in the advanced technology scenario for a plant using ~2.74 million dry tons/year of feedstock costing \$38.60/delivered dry ton. More aggressive performance taken for the best possible technology reduced the projected total cost to about \$0.34/gal.

The influence of the individual factors on reducing processing costs for the very plausible advanced technology scenario is summarized in Figure 4. This Figure clearly indicates that the most significant impact would result from advances in biological processing and pretreatment and that these areas even outweigh substantial scale-up in plant capacity. Enhancement of technical performance also reduces the cost but would not be sufficient without changing to advanced process configurations to achieve the projected low bioethanol costs. Although lowering the cost of the biomass feedstock has one of the smallest impacts on cost and that impact will drop even more as plant yields increase, higher-productivity crops will reduce transportation distance and costs to the plant, making it feasible to increase plant scale toward that considered in the study. Higher feedstock productivities also increase the supply of biomass that can be produced on a given land area and reduce environmental impacts. Interestingly, these results show that even though advances in pretreatment can have one of the most significant impacts on bioethanol economics of all the technology options considered, pretreatment remains the most costly step of the advanced process at about two-thirds of the advanced-technology cost, begging the question of what other configurations could be devised that would reduce the cost even more.

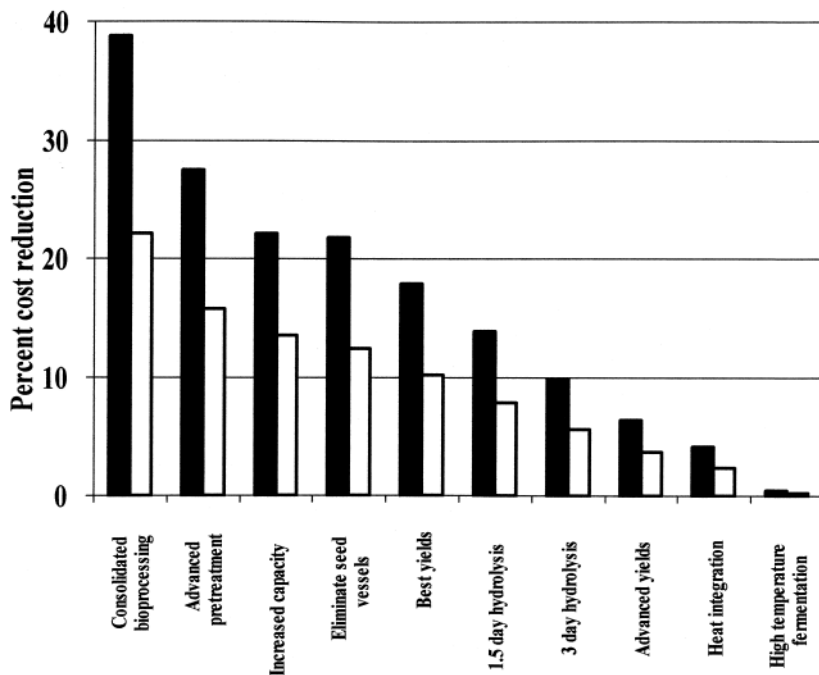


Figure 4 Impact of advances in key process step configurations and performance parameters on reducing the cost of producing ethanol from biomass based on the advanced-technology scenario. Again, cost reductions compared with the total production cost are shown as *open bars*, whereas the impacts on processing costs alone are presented as *solid bars*.

Allowable Cost Projections

Although detailed process designs and economic evaluations such as those described provide useful estimates of the cost of production of bioethanol and identify targets for continued cost reductions, these studies are highly dependent on the specific process designs chosen, and their complexity makes them time consuming to both apply and understand. Furthermore, different studies often show decidedly different results, and poor economics are more often the consequence of a poor process design than a measure of the economic viability of the technology. In other words, a negative result in process design can be as much a reflection of the design engineer as it is of the technology, and it is dangerous to conclude, as all too many studies have, that bioethanol technology is not economically viable based on a particular process configuration that may be poorly conceived.

A useful perspective on the economic viability of bioethanol technology can be gained by a macroscopic process model, and one such approach calculated an allowable capital cost based on estimates of revenues and all process costs and benchmarked the result against capital costs typical for corn ethanol plants

(106). This analysis began with a determination of the contribution of feedstock costs alone to the cost of bioethanol production as a function of overall ethanol yield. Other so-called unavoidable costs for chemicals and nutrients, utilities, labor and supervision, and direct and general overhead were estimated and added to the feedstock cost to provide a total cash cost of production. Next, the revenue from sale of ethanol at competitive prices for use as a pure fuel was calculated and added to estimates of the revenue derived from sale of electricity available in excess of process heat and power demands. The difference between the total revenues and total costs provided the funds available to cover the cost of capital recovery including return on capital. The acid test at this point is that the funds available must be positive or the technology cannot support itself, at least based on the product mix and feedstock strategies chosen. The funds available were divided by the appropriate combination of capital-weighting factors to account for installation of equipment, fixed charges, startup costs, maintenance including general plant overhead, insurance and property taxes, and the annualized capital recovery factor to calculate an allowable capital investment that could be covered by sale of ethanol and power.

This analysis led to an allowable capital investment of \sim \\$1.33/gal. of annual ethanol production capacity to compete in the pure fuel market, a value close to capital costs typical of modern corn ethanol processes. Thus, such costs appear reasonable and within the range achievable through continued advancements in bioethanol technology. Furthermore, for regions of the country that have imposed more strict limitations on gasoline vapor pressure to combat air pollution, the low emission characteristics of ethanol become more of an economic advantage, and the allowable capital cost increases to \sim \\$1.90/gal. of ethanol or more. For the short term, ethanol is even more valuable for blending with gasoline owing to various tax incentives, an invaluable factor that will allow even greater capital investments and/or operating costs for introductory plants.

These results amplify the importance of full feedstock utilization to produce bioethanol and any coproducts such as electricity, if the technology is to be economically viable. However, they also demonstrate that there appear to be no fundamental barriers to achieving competitive costs, even though continued advances are required to improve overall yields and lower costs enough to meet the minimum levels assumed in this study. The key is to invest more in research to accelerate advances in technology.

CHALLENGES IN COMMERCIALIZING BIOETHANOL TECHNOLOGY

Although bioethanol technology has advanced to the point that it has tremendous potential for commercialization based on the process studies summarized, bioethanol plants must actually be built before any of its substantial environmental, economic, and strategic benefits for humanity can be realized. Given the long lead times for large-scale technology implementation, there is an urgency to move to

this next stage in technology evolution, but more than technology alone is needed to realize commercial success. In this section, some of the important demands that must be met for large-scale implementation of bioethanol technology are summarized. The discussion is based on typical project-financing considerations (107), but the ideas should be relevant to obtaining the large sums needed from any reputable source.

Feedstock and Offtake Agreements

Although financial institutions that invest in new technology expect a larger return than normal to compensate for the greater risk, they must still mitigate that risk before they will invest large amounts of capital (108). A typical approach is to contract risk away. Because feedstock costs directly impact the bottom line, contracts must be in place for enough feedstock to supply the plant at its nameplate rating. These contracts have to be intermediate- to long-term commitments, generally valid over the financial life of the plant. Similarly, assurances are needed that the costs of all chemicals, nutrients, or other purchased supplies are either historically very stable or contracts are in place that guarantee they can be purchased at the prices required to justify plant economics (107).

Financiers are also concerned about price fluctuations in the product market and will demand that much if not all of that risk be contracted away. Thus, the plant operator must develop long-term contracts for the plant offtake, probably at less than market prices to make this obligation attractive to the customer. Because the contracts will generally impose quality demands on the product, the developer must demonstrate to the financial institution that the product can meet user specifications when made from biomass feedstocks. Such demonstrations are typically costly and time consuming (107, 108).

Feedstock Quality

The composition of the feedstock is very important to the yields of ethanol, and thorough data are needed to convince financial institutions that the feedstock quality will be as forecast throughout the economic life of the plant. For bioethanol, maintaining cellulose and hemicellulose content is critical to achieving target yields, whereas changes in lignin and ash content can impact downstream operations such as the boiler/generator. High moisture content will increase shipping and handling costs and can accelerate degradation. Storage of feedstock will probably be required to supply the plant year round and amortize the large capital cost over as much throughput as possible. However, biomass will likely deteriorate during storage, and data are essential to show that the feedstock will meet quality expectations throughout the year (107).

Coproducts

Coproducts can be extremely important to enhancing revenues and can make the difference in carrying a plant financially, particularly for initial plants (10, 109,

110). However, the market must again be contracted in advance if this income is important to economically justify a plant. Such a requirement can be very difficult to meet and places additional burden on the developer to demonstrate that product quality expectations can be achieved and that the coproduct volume and timing are consistent with the overall plant strategies.

Process Guarantees and Financing

The risk element of process scale up is particularly important to understand for those interested in technology development and innovation (107). Financial institutions typically seek to contract away technical risk by holding vendors and engineering and/or construction firms financially responsible for the plant meeting some minimum performance expectations through process guarantees. However, studies such as those cited in this paper are primarily intended to benchmark technology progress and therefore are focused on the cost of the core technology. Accordingly, they assume mature technology as applied to an *n*th plant, or in other words, the costs have been reduced to nearly the lowest level possible for the particular technology chosen via a substantial learning curve based on experience with a large number of previous plants. In addition, such cost projections are often based on factored estimates and by extrapolation from laboratory and bench scale data to predict how a fully integrated, large-scale system will perform. They are not meant to be in the detail required for the rigorous due-diligence process demanded for financing and constructing commercial plants. In a similar vein, it is worth noting that initial estimates of plant costs by engineering and consulting firms are often optimistic for new technology and may underestimate capital costs by multiples of two or more compared with a final cost that includes process guarantees.

Unfortunately, a first plant must be built well before the *n*th can be, and it will cost far more owing to lack of experience coupled with a tendency to overdesign first plants to compensate for unknowns and risk. In effect, costs will be layered on top of the basic cost of the core technology used. One type of incremental cost will be for equipment that will subsequently be shown to be not required but that was applied initially to ensure that the first plant will operate as planned. In addition, lower-cost equipment will evolve through information gained from running the first plants in areas such as materials of construction requirements, physical properties of key streams, and equipment size needs, and performance will also improve over time, improving profitability. Substantial contingency costs, in addition to those typically used to cover unforeseen events such as price increases, weather, and hidden underground obstacles, are also added in to pay for unexpected costs and delays that can arise during startup of a first-of-a-kind plant. Because ethanol technology tends to be site specific, the plant design could vary from one location to the next to capitalize on any existing infrastructure, low-cost biomass sources, community needs, and other factors that can improve the economics but complicate process guarantees as well (10).

Owing to the layering of costs to compensate for risk, proven technology may actually cost less to commercialize than more advanced technology, even though

the cost of the core technology is greater for the former than the latter. Thus, although inventors may assume that a new technology they have devised will revolutionize a process and lead to unfathomable profits for some company, comprehensive data and analysis will be required to reduce the cost layers and convince those financially responsible for engineering and constructing the plant to take responsibility for the risk associated with new technology. Because scale-ups of more than two orders of magnitude are difficult (107), the result can be a drawn-out demonstration effort that is extremely costly with significant risk in its own right that few organizations may be able to undertake. In addition, process developers must be prepared to fully document and defend such laboratory testing and pilot plant work. Some have labeled the gap between technology innovation and its application the “valley of death,” whereas others have termed it the “mountain of doom” because of the difficulty in taking new technology to commercialization.

IMPLICATIONS FOR RESEARCH AND DEVELOPMENT

It must be remembered that bioethanol is targeting a well-established mature commodity fuels market that is valued at ~\$100 billion/year and is extremely efficient and competitive. In light of this, the technical progress achieved with annual budgets of ~\$20 million is remarkable and a tribute to the management and focus of the program. By comparison, one day of imported oil costs the United States ~\$150 million (21). With a much greater and more reasonable commitment to fund bioethanol technology development, the pace of technology application could be accelerated significantly with great benefit to society. Properly focused research can play a powerful role both in reducing the risk of technology application and improving technology for bioethanol production.

Enhancing Fundamentals

Developing a stronger foundation for bioethanol technology based on fundamental principles and statistical analysis can be an effective alternative or at least complement to large-scale demonstration in reducing scale-up risk and can significantly cut the time and costs in taking technology from innovation to application. All too often, limited data are presented to illustrate the benefits of a technical concept, but convincing information over a significant range of conditions that could be encountered commercially is lacking. Furthermore, problematic data that show some possible deficiencies may be attributed to experimental errors and not reported. It is important to assemble full data sets over a range of operating conditions expected in actual use and clearly explain all of the data fully and carefully.

Developing fundamentally based models with demonstrated statistical accuracy is a particularly powerful tool for interpretation and application of experimental data that deserves far more attention for biomass processing. Such models are invaluable in gaining insight and developing useful correlations and other approaches that facilitate reliable and timely process scale-up. Proper design of experiments

will reduce the number of experiments required to gather meaningful results and clearly show statistically significant trends and differences. Through proper interpretation based on fundamental principles and statistical design, even seemingly problematic data will often reinforce important cause and effect relationships that give the engineers and financiers comfort in scaling up a process. With so much money at stake, it is important to realize that a due-diligence process will definitely proceed scale up, and proven analysis and design tools will be invaluable in supporting technical and economic proforma analyses (107).

A related need is to accurately close all energy and particularly material balances during experimentation. No process will be taken to commercial scale if the fate of all materials cannot be predicted. First, as shown previously, product yield has a pervasive impact on process revenues, and any margin in interpretation of yield will be assumed to favor the worst case unless proven otherwise. Second, any material that does not become product undoubtedly ends up in the waste stream, affecting the size and cost of waste treatment facilities. Material balance closure is very difficult with biomass systems, owing at least in part to the extreme difficulty of measuring solid flow rates and compositions, but this is an area that deserves considerable attention. Predictive models based on fundamental principles and statistical experimental design will again prove invaluable in supporting convincing material and energy balances.

Advancing Technology

The economic studies clearly indicate that the cost of bioethanol production can potentially be reduced further to be competitive without tax incentives and that no fundamental barriers block attainment of such a goal. Improvements in yield will reduce costs, and it is important to devise process steps that are as efficient as possible. However, advanced process configurations must be developed if bioethanol costs are to be competitive for use as a pure fuel.

Advances in pretreatment and biological-processing steps clearly provide the greatest opportunity to reduce bioethanol costs, and much more emphasis is needed in these areas. For pretreatment, improved process configurations are needed that reduce chemical costs for hemicellulose hydrolysis and subsequent conditioning for biological processing. In addition, energy requirements for biomass milling and heating must be reduced, and less corrosive environments are desired to reduce the cost of vessels. Furthermore, these improvements are needed while still maintaining and preferably increasing product yields.

A particularly promising pretreatment approach has been defined as low acid to no acid (known as liquid-hot-water pretreatment) systems (103–105, 111, 112). Such processes achieve high yields of sugars from hemicellulose and produce very reactive cellulose that enzymes hydrolyze much faster than for other pretreatment options. Less size reduction is needed before pretreatment, and the hydrolyzate can be fermented to ethanol without conditioning, cutting chemical and capital costs and avoiding generation of problematic wastes. Because of the low acid levels, less

exotic materials of construction are needed, reducing capital costs substantially. However, process configurations studied at the bench are difficult to scale up, and it is not clear whether sufficiently concentrated sugar streams can be realized for economic fermentation and product recovery. Further study is also needed on how to hydrolyze the high proportion of oligomers typical of advanced pretreatment to simple sugars for fermentation.

It is clear that a consolidated bioprocessing configuration would greatly cut costs by producing sugars from cellulose and fermenting all sugars to ethanol in the same vessel. Such an approach would also reduce the opportunity for contamination of fermentations by unwanted organisms that can enter the process during transfers among vessels. Some progress has been made in this direction (39), but substantially more funding is needed to develop such sophisticated technology.

Teaming of Expertise

Developing a solid understanding of mechanisms for key steps in biological conversion of cellulosic biomass to ethanol and other commodity products and applying that knowledge to facilitate commercialization and advancements of technology are challenging but eminently possible. Precisely because of the magnitude of the endeavor and the scope of the technology, experts working cooperatively in true teams can meet the challenge far more effectively than the classical approach of individuals attacking problems in isolated research organizations. The critical areas of biomass pretreatment and cellulose conversion can particularly benefit by assembling teams of those with established experience in each area to focus on understanding and improving each of these steps. In addition, tremendous benefits would be gained by interaction of separate teams to address interactions among steps that will be integral to a commercial process. These teams would be strengthened further by seeking advice from vendors, engineering and construction firms, financial institutions, and others responsible for technology commercialization to provide an applications perspective. If funded in a way that rewards cooperation, such teams would provide a powerful and talented resource that would accelerate successful introduction of low-cost bioethanol technologies into the marketplace, with tremendous environmental, strategic, and economic advantages for all.

CONCLUSIONS

Biomass ethanol is a versatile fuel and fuel additive that can provide exceptional environmental, economic, and strategic benefits of global proportions. Bioethanol can play a particularly powerful role in the quest to reduce greenhouse gas emissions that will be difficult for any other transportation fuel options to match. Because of the widespread abundance of biomass, bioethanol can also be invaluable for meeting the growing international demand for fuels by developing nations as well as enhancing the energy security of developed countries. Furthermore,

conversion of waste materials to ethanol provides an important disposal option as new regulations restrict historical approaches. It also is important to note that bioethanol is among the few options available for sustainable production of liquid fuels. Finally, although gasoline is continually being reformulated to reduce its environmental impact, ethanol has favorable properties that can provide air and water quality attributes comparable, if not superior, to gasoline and can provide particular benefits when used as a pure fuel in properly optimized engines and ultimately fuel cells.

Tremendous progress has been made in reducing the cost of enzymatic-based technology for bioethanol production, with current estimated costs showing the technology to be potentially competitive now, particularly for niche markets. A key to these advances has been in achieving higher yields, faster rates, and greater concentrations of ethanol through improved pretreatment technology, development of better cellulase enzymes, and synergistic combination of cellulose hydrolysis and fermentation steps that make progress in overcoming the natural recalcitrance of biomass. Genetic engineering of bacteria so that they ferment the diverse range of sugars in lignocellulosic materials to ethanol with high yields is a milestone achievement essential to economic success.

Although progress has been impressive, the cost of bioethanol production must be reduced further if it is to be competitive without special tax incentives on a large scale for the fuel market. Because enzyme-based systems can build off the emerging achievements of biotechnology, they show particular promise for further cost reductions, and sensitivity studies, process modeling, and macroscopic economic analyses reveal that there are no fundamental barriers to advancing the technology. Cost estimates reveal that pretreatment is a particularly expensive step, both directly and indirectly. From a technology perspective, the sensitivity studies clearly show that ethanol yield is a strong economic driver, and there are significant gains from improving the yields of all process steps. It is important that even greater cost reductions can result from improving pretreatment and biological-conversion-process configurations. In fact, specific advanced pretreatment and bioprocessing configurations based on continued progress in overcoming the recalcitrance of biomass have been identified that would reduce the cost of bioethanol production to levels that it can compete in a nonsubsidized market. However, even though the advanced pretreatment configuration chosen significantly reduces cost, it would represent about two-thirds of an overall advanced design scenario, suggesting that further improvements beyond those envisioned should be sought, with tremendous impact. This result also implies that emphasis on novel pretreatment technology with extremely low-cost potential is badly needed instead of pursuing relatively minor improvements over dilute sulfuric-acid approaches, and such advances will probably best come through improving our knowledge of how pretreatment works. Interestingly, although feedstock cost reductions are constrained to levels that will have moderate impact for large-scale bioethanol production, more productive and less expensive biomass would make it feasible to feed larger plants that realize significant economies of scale.

It is just as important to take the next step and commercialize bioethanol technology so that its tremendous benefits can be realized. However, because bioethanol plants must typically be large to be profitable, substantial capital outlay is required, and risk management is essential to attract investors to finance the introduction of first-of-a-kind technology. Although large pilot and perhaps even semi-works demonstration projects may be required to provide an adequate level of comfort, significantly more emphasis on developing solid fundamental principles for design of biomass processing operations would greatly reduce the tremendous costs and delays associated with technology scale-up. Building expert teams to work cooperatively to understand key bioethanol-processing steps in the context of applying and advancing the technology is the most effective approach to realize the low-cost potential of bioethanol and realize its benefits on a large scale. In the final analysis, researchers, research managers, program leaders, and funding authorities who have had the vision and courage to advance bioethanol technology to the point that it now has commercial potential need to facilitate advancing and applying the technology in the face of even greater challenges to achieve widespread impact. In addition, entrepreneurs, financiers, engineers, and contractors with equal vision and courage are needed to take the technology to its first commercial applications.

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