

An Evaluation of Two Acid Hydrolysis Processes for the Conversion of Cellulosic Feedstocks to Ethanol and Other Chemicals

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ABSTRACT

The Tennessee Valley Authority (TVA) has been actively involved in the development of acid hydrolysis processes for the conversion of cellulosic feedstocks to ethanol since 1981. At that time, the TVA renewed earlier work conducted in the 1950s with the USDA Forest Products Laboratory to develop a dilute sulfuric acid hydrolysis process. Hydrolysis research at the TVA was further expanded in 1983 with the development of a concentrated sulfuric acid hydrolysis process for converting cellulosic feedstocks to sugars for ethanol production. Both processes are being developed in laboratory-, bench-, and pilot-scale studies. Ethanol yields from the two processes are 63 gal/t using dilute acid hydrolysis and 72 gal/t using the concentrated acid hydrolysis.

An economic assessment of the two processes has been conducted using a base-case, commercial-scale design for producing 11 M gal/yr of ethanol. Hardwoods and corn stover are used as feedstocks for the dilute and concentrated sulfuric acid hydrolysis processes, respectively. This paper will evaluate the effects of both internal and external factors on ethanol production costs. The sensitivity of these costs to technology, market, and economic changes will be presented.

Index Entries: Acid hydrolysis; sulfuric acid, dilute; sulfuric acid, concentrated; ethanol production.

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INTRODUCTION

Since 1980, the Tennessee Valley Authority (TVA) has been involved in the development of acid hydrolysis processes for the conversion of cellulosic feedstocks to ethanol. Two processes have evolved from this work—a dilute and a concentrated sulfuric acid hydrolysis process—and are being developed and evaluated in bench- and pilot-scale studies. Flow diagrams of the two processes are shown in Figs. 1 and 2. The dilute sulfuric acid process is a two-stage process that uses high temperatures (266°F) and pressures (10 atm) to convert hemicellulose and cellulose to sugars. The process has been evaluated using wood, resulting in sugar yields equivalent to 60 gal ethanol/t dry feedstock (1). The concentrated acid process is also a two-stage process; however, low temperatures (212°F) and pressures (1 atm) are used during hydrolysis. Evaluations of the concentrated acid hydrolysis process using corn stover for feedstock have resulted in sugar yields equivalent to 72 gal ethanol/t feedstock (2).

Economic evaluations of the two processes have been conducted to determine base-case capital and operating costs for commercial plant designs. The effect of potential process improvements on the economics of the base-case designs was also determined. This paper will present the results of these evaluations.

BASE-CASE COST ESTIMATES

Base-case capital and operating cost estimates were determined for two commercial-scale ethanol production facilities, each designed to process 500 t of feedstock/d. In the first design, dilute acid hydrolysis is used to convert Tennessee Valley hardwoods to fermentable sugars for ethanol production. In this design, 165,000 dry tons of hardwood are processed to product 11 M gal of fuel-grade ethanol (includes 5% denaturant). Annual byproducts from the process include 55 M kWh of electricity, 7.2 M lb of acetic acid, and 3.5 M lb of furfural (3).

The second design uses concentrated sulfuric acid to convert corn stover to fermentable sugars for ethanol production. Again, the plant is designed to process 165,000 t of feedstock annually. However, ethanol yield is higher, resulting in an annual production capacity of 12.5 M denatured gal of fuel-grade ethanol. A byproduct credit is taken for 43 M kWh of electricity produced/yr (4).

Cost estimates for the evaluations are based on preliminary engineering analysis of the dilute and concentrated acid hydrolysis processes. Mass and energy balances, equipment specifications, raw material requirements, utilities, usage rates, waste disposal, construction, and engineering costs were prepared. Capital cost estimates were integrated into a computer spreadsheet with operating costs and estimated revenues from the sale of ethanol byproducts to determine the base-case production costs.

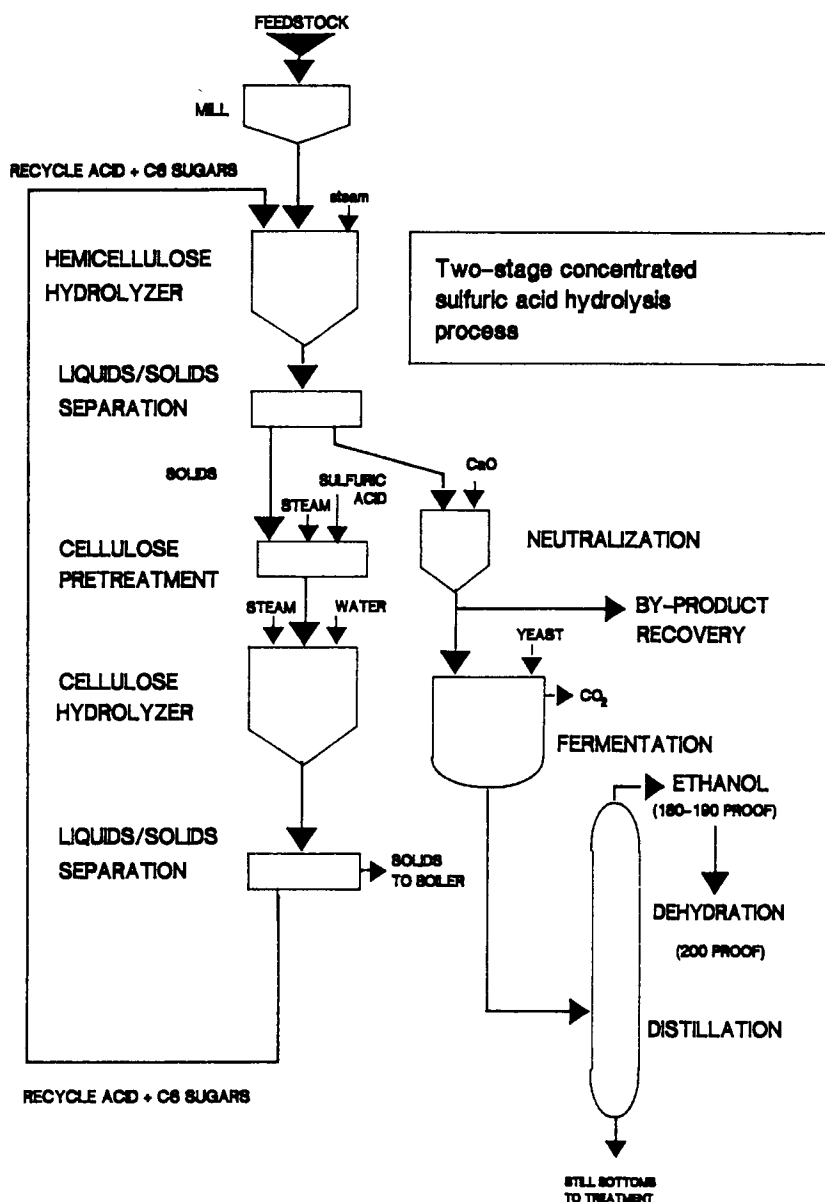


Fig. 1. The two-stage concentrated sulfuric acid hydrolysis process.

Total capital investments and annual operating cost estimates are shown in Tables 1 and 2, respectively. All costs are given in 1988 dollars. Capital cost-related items are based on a total capital investment of \$56 M for the concentrated acid process and \$81 M for the dilute acid process, with an annual capital recovery charge factor of 13%. Based on these costs and assumptions, the ethanol production cost for the base-case system designs, using concentrated acid and dilute acid processes, are \$1.69 and \$1.81/gal, respectively.

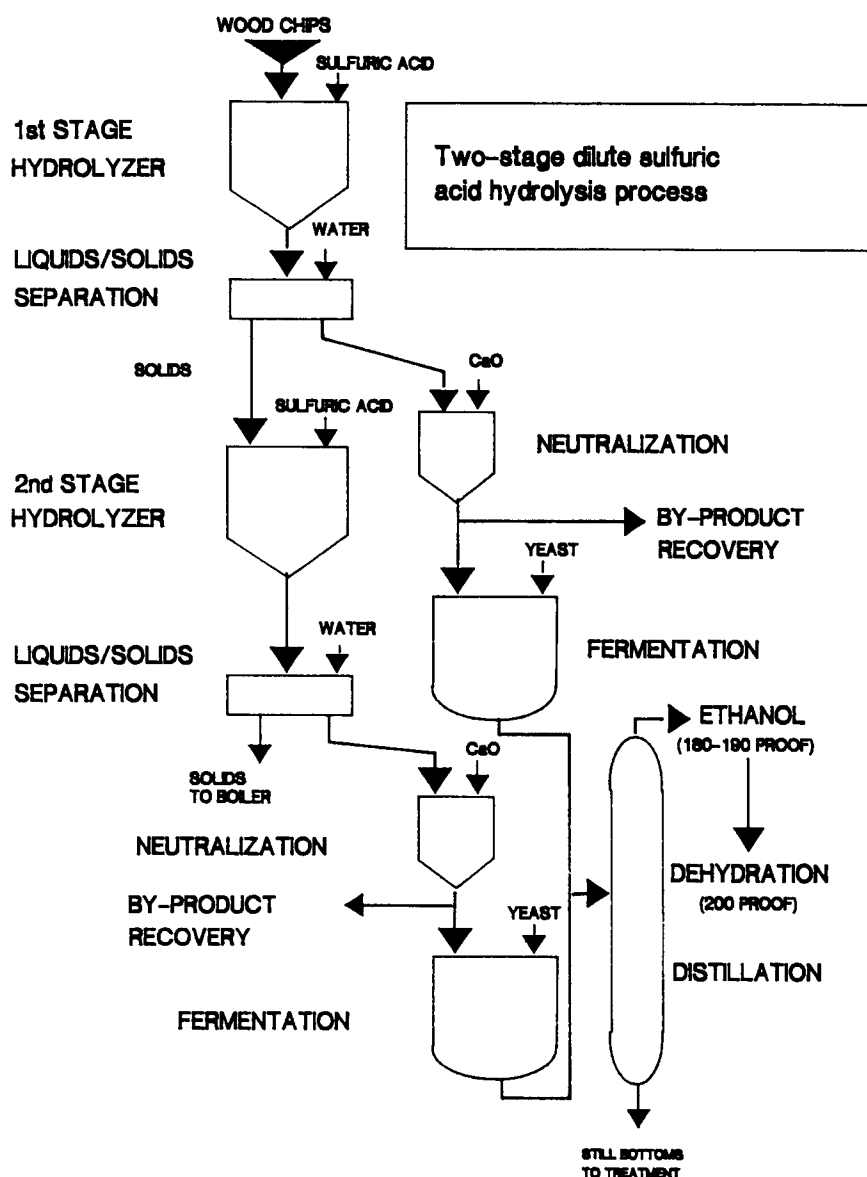


Fig. 2. The two stage dilute sulfuric acid hydrolysis process.

EFFECT OF SYSTEM VARIATIONS ON BASE-CASE COST ESTIMATES

Several process improvements and coproduct options that have the potential to reduce base-case ethanol production costs in the two plant designs have been identified in TVA research. The potential impact of acid recovery, increased fermentation efficiency, furfural production, and integration of ethanol production systems with other industries will be discussed.

Table 1
Total Capital Investment for 500 t/d Concentrated
and Dilute Acid Hydrolysis Facilities

| Plant section | Capital investment | |
|-----------------------------------|---------------------------------------|---------------------------------|
| | Concentrated acid hydrolysis facility | Dilute acid hydrolysis facility |
| Feedstock handling | \$ 1,597,000 | \$10,240,000 |
| Hydrolysis | 13,418,000 | 15,194,000 |
| Neutralization | 1,794,000 | 875,000 |
| Furfural and acetic acid recovery | - | 12,447,000 |
| C ₆ fermentation | 8,744,000 | 7,936,000 |
| C ₅ fermentation | 11,969,000 | 11,534,000 |
| Distillation | 3,261,000 | 5,466,000 |
| Waste Treatment | 5,492,000 | 5,857,000 |
| Utilities | 4,892,000 | 4,668,000 |
| Offsites | 5,312,000 | 5,621,000 |
| Total | \$56,479,000 | \$80,838,000 |

Table 2
Production Cost Estimate for 500 t/d Concentrated
and Dilute Acid Hydrolysis Facilities

| | Production cost, \$/gal | |
|--------------------------|------------------------------|------------------------|
| | Concentrated acid hydrolysis | Dilute acid hydrolysis |
| Raw materials | | |
| feedstock | \$0.33 | \$0.38 |
| Acid | 0.27 | 0.04 |
| Lime | 0.15 | 0.02 |
| Chemicals | 0.12 | 0.09 |
| Utilities | 0.05 | 0.05 |
| Labor | 0.19 | 0.25 |
| Overhead and maintenance | 0.17 | 0.54 |
| Waste disposal | 0.03 | - |
| byproducts | | |
| Electricity | (0.21) | (0.20) |
| Furfural | - | (0.16) |
| Acetic acid | - | (0.16) |
| Annual operating cost | \$1.10 | \$0.85 |
| Capital charges | 0.59 | 0.96 |
| Ethanol production cost | \$1.69 | \$1.18 |

Table 3
Comparison of Capital Costs by Plant Section for a 12 M gal/yr Ethanol Facility
Using Solvent Extraction, Adsorption, and Ion Exclusion for Acid Recovery

| Plant section | Capital Investment | | |
|-----------------------------|--------------------|--------------|---------------|
| | Solvent extraction | Adsorption | Ion exclusion |
| Feedstock handling | 1 1,597,000 | \$ 1,597,000 | \$ 1,597,000 |
| Hydrolysis | 13,418,000 | 13,418,000 | 13,418,000 |
| Acid recovery | 4,220,000 | 5,000,000 | 5,295,000 |
| Neutralization | 449,000 | 1,794,000 | 449,000 |
| C ₆ fermentation | 8,744,000 | 8,744,000 | 8,744,000 |
| C ₅ fermentation | 11,969,000 | 11,969,000 | 11,969,000 |
| Distillation | 3,261,000 | 3,261,000 | 3,261,000 |
| Waste treatment | 5,492,000 | 5,492,000 | 5,492,000 |
| Utilities | 4,892,000 | 4,892,000 | 4,892,000 |
| Offsites | 5,312,000 | 5,312,000 | 5,312,000 |
| Total | \$59,354,000 | \$61,479,000 | \$60,429,000 |

Acid Recovery

The base-case concentrated acid hydrolysis design assumes no recovery of sulfuric acid. Research indicates that the potential does exist to efficiently recover a substantial amount of acid for recycle to the process (5–7). Acid recovery research is being conducted to determine the potential of using solvent extraction, adsorption, or ion exclusion for the recovery of sulfuric acid in the concentrated acid hydrolysis process.

Capital and production costs have been determined, based on the incorporation of each of these technologies into the current base-case design, and are shown in Tables 3 and 4. Capital costs for the solvent extraction process were calculated to be \$4.2 M (5). Production costs for the process are based on the recovery and recycle of 93.2% of the sulfuric acid used. Solvent losses were estimated to be 176 t/yr for a total cost of \$464,904/yr. Based on these assumptions, total capital investment for the ethanol-from-corn stover facility, incorporating solvent extraction, was determined to be \$59 M. Ethanol production costs were calculated to be \$1.33/gal, a savings of about \$0.36/gal over the base-case design (Table 4).

Capital costs for the adsorption process are estimated to be \$5 M. Ethanol production costs, based on the recovery of 30% of the acid used in the process (6), were calculated to be \$1.61/gal (Table 4). Lower production costs have been reported by the University of Missouri, using a modified concentrated acid hydrolysis process.

Total capital investment for the ion exclusion process was calculated to be \$5.3 M (7). The unit is designed to recover 95% of the acid used in the process. Based on these assumptions, ethanol production costs were

Table 4
Comparison of Ethanol Production Costs Using Adsorption, Solvent Extraction,
and Ion Exclusion for Acid Recovery

| Cost component | Production cost, \$/gal | | |
|--------------------------|-------------------------|------------|---------------|
| | Solvent extraction | Adsorption | Ion exclusion |
| Raw materials | | | |
| Corn stover | \$0.33 | \$0.33 | \$0.33 |
| Acid 0.02 | 0.19 | 0.01 | |
| Line 0.01 | 0.11 | 0.01 | |
| Chemicals | 0.16 | 0.14 | 0.14 |
| Utilities | 0.05 | 0.05 | 0.05 |
| Labor | 0.17 | 0.17 | |
| Overhead and maintenance | 0.18 | 0.17 | 0.18 |
| Coproducts | 0.00 | 0.02 | 0.00 |
| Electricity | -0.21 | -0.21 | -0.21 |
| Annual operating cost | \$0.71 | \$0.97 | \$0.68 |
| Capital charges | 0.62 | 0.64 | 0.63 |
| Ethanol production cost | \$1.33 | \$1.61 | \$1.31 |

estimated to be \$1.31/gal (Table 4) when ion exclusion is incorporated into the base-case concentrated acid hydrolysis design.

Increased Fermentation Efficiency

Research is being conducted to identify ways to improve fermentation of sugars produced by acid hydrolysis to ethanol. Xylose fermentation research has increased ethanol yields from xylose from zero to about 20 gal of ethanol/dry t of wood. This higher yield represents a conversion efficiency of 50% of theoretical. Conversion efficiencies as high as 70% have been achieved in laboratory tests using hydrolyzate from both processes, and further improvements are expected.

Figure 3 shows the sensitivity of ethanol production cost to improvements in xylose fermentation efficiencies. An increase in fermentation efficiencies from 50% (used in base-case design) to 70% will reduce the cost of ethanol production by \$0.21/gal in both processes. This increase assumes that no additional processing or capital costs are incurred. In addition to yield improvement studies, fermentation research is identifying and developing ways to increase process efficiency.

Furfural Production

Ethanol production costs for both facilities also can be reduced through the coproduction of furfural. The base-case dilute acid hydrolysis process is designed to maximize ethanol yield; however, 23.7 lbs of byproduct

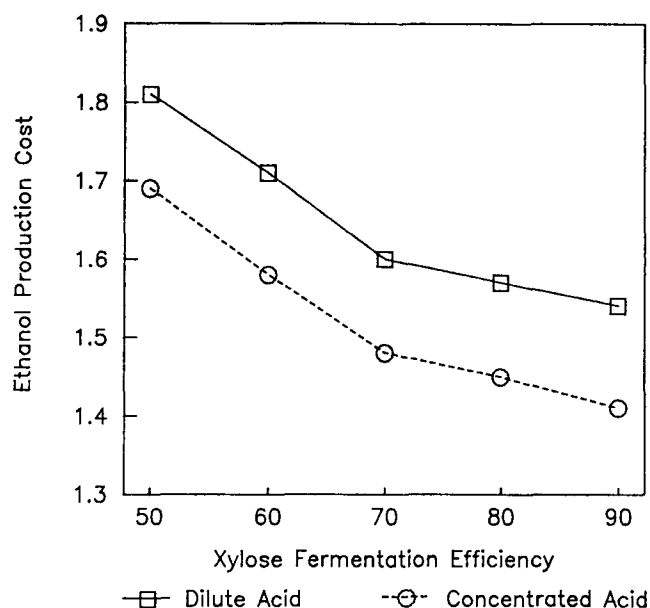


Fig. 3. The estimated effect of xylose fermentation efficiency on ethanol production costs.

furfural are also produced per ton of hardwood processed. However, even though the amount of furfural produced in the base-case is small (3.5 M lbs/yr), a credit of about \$0.16/gal of ethanol produced is provided to the process based on a furfural market price of \$0.50.

If the xylose was used to produce furfural (rather than ethanol), 181 lbs of furfural could be produced and recovered per ton of hardwood processed (assuming the furfural yield is 60% of theoretical, which is 0.73 lb furfural/lb xylose) (8). Recovery of furfural from the hydrolysis unit should be 96% efficient, and the recovery efficiency of the furfural purification unit is 90%. If furfural is sold for \$0.50/lb, additional revenue of \$65.25/t of hardwood can be generated. In addition, substitution of the xylose-to-ethanol fermentation plant section with a furfural production section would reduce capital costs from \$80.8 to \$72.6 million. The combination of higher revenue and lower capital cost is equivalent to reducing ethanol production costs to \$0.73/gal (Table 5).

Furfural can also be produced from the xylose remaining in the stillage from the concentrated acid process. In the base-case scheme, the unfermented xylose (50% of initial amount) in the stillage is concentrated by evaporation and burned along with other organics. If this xylose was used to produce furfural (rather than burned), 88 lbs of furfural could be produced per ton feedstock processed. If furfural was sold for \$0.50/lb, a credit of about \$0.52/gal of ethanol produced would result. Ethanol production costs would be reduced to \$1.17/gal by the production of 88 lbs of furfural/t corn stover (Table 6).

Table 5
Ethanol Production Costs Estimate
for a Dilute Acid Hydrolysis Ethanol
Production Facility with Coproduct Furfural

| | \$/gal of ethanol |
|--------------------------|-------------------|
| Raw materials | |
| Corn stover | \$0.54 |
| Acid | 0.06 |
| Lime | 0.03 |
| Chemicals | 0.13 |
| Utilities | |
| Water | 0.07 |
| Steam | 0.01 |
| Labor | 0.36 |
| Overhead and maintenance | 0.76 |
| Byproducts | |
| Electricity | -0.29 |
| Acetic acid | -0.23 |
| Coproducts | |
| Furfural | -1.94 |
| Annual operating cost | -0.50 |
| Capital charges | 1.22 |
| Ethanol production cost | \$0.73 |

Table 6
Ethanol Production Costs Estimate
for a Concentrated Acid Hydrolysis Ethanol Facility
with Coproduct Furfural

| | \$/gal of ethanol |
|--------------------------|-------------------|
| Raw materials | |
| Corn stover | \$0.33 |
| Acid | 0.27 |
| Lime | 0.15 |
| Chemicals | 0.12 |
| Utilities | |
| Labor | 0.05 |
| Overhead and maintenance | 0.17 |
| Waste disposal | 0.03 |
| Byproducts | |
| Electricity | (0.17) |
| Furfural | (0.58) |
| Annual operating cost | 0.56 |
| Capital charges | 1.61 |
| Ethanol production cost | \$1.17 |

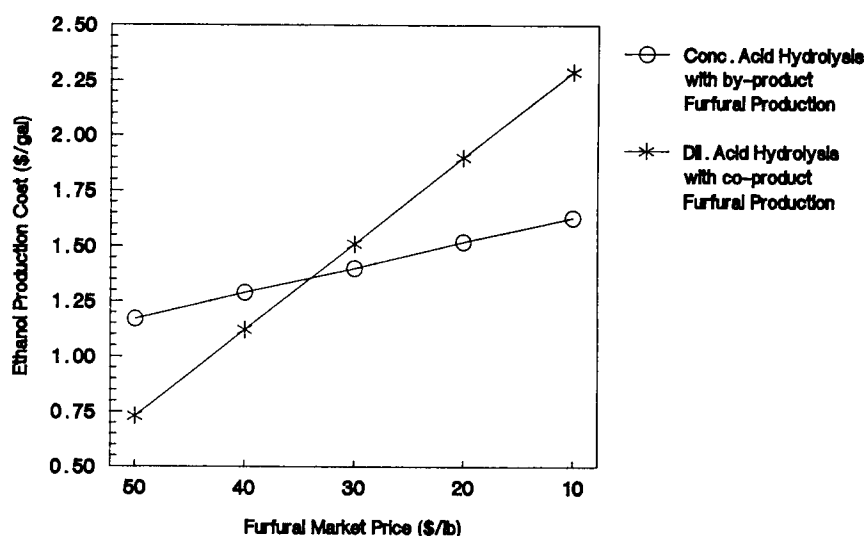


Fig. 4. The effect of furfural market price on ethanol production costs.

A furfural selling price of \$0.50/lb, used in both acid hydrolysis scenarios, represents the high end of the potential range of selling prices for the coproduct. An increase in the supply of furfural, as produced by an acid hydrolysis facility, would result in a decrease in the furfural market price. Furfural prices could be reduced to about \$0.10/lb, depending on the supply. The effect of market price on ethanol production costs is shown in Fig. 4. In the dilute acid hydrolysis process, a 10-cent change in the market price of coproduct furfural results in a 39-cent change in ethanol production costs. Production costs for the dilute acid hydrolysis process range from \$2.28/gal (furfural at \$0.10/lb) to about \$0.73/gal (furfural at \$0.50/lb). In the concentrated acid hydrolysis process, a 10-cent change in the market price of the by product, furfural, is reflected by a 12-cent change in ethanol production costs. Production costs in the concentrated acid hydrolysis process range from \$1.63, with furfural at \$0.10/lb, to \$1.17/gal, with furfural at \$0.50/lb.

System Integration

The economic feasibility of acid hydrolysis technology can also be improved by integrating biomass processing facilities with existing industrial facilities. Often, construction and financing costs and other problems can be minimized by using facilities that already exist (9). Substantial cost savings can occur by sharing management, maintenance, and capital equipment. For example, cellulose-to-ethanol processing can be integrated with pulp and paper production. Since paper mill sludge is high in cellulose, the use of this waste product would eliminate feedstock costs and reduce ethanol production cost by as much as \$0.38/gal. In addition, dis-

posal costs for the facility's "waste product" would be significantly reduced. Integrated with other wood processing, ethanol production, and agricultural processing industries is also possible.

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