Processing and Economic Impacts of Biomass Delignification for Ethanol Production

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ABSTRACT

The need for chemical pretreatment of biomass for the enzyme-catalyzed production of ethanol from lignocellulosic feedstocks has been established. Past research in the Alternative Fuels Division of the National Renewable Energy Laboratory has focused on dilute-acid prehydrolysis processes as a means of hydrolyzing the hemicellulose component of biomass. Such processes provide a solid residue that is more easily hydrolyzable by cellulase enzymes, as well as a hemicellulose-sugar component that can be converted by pentose-fermenting microorganisms.

This work investigates the technical and economic feasibility of including a separate biomass delignification/fractionation step, either in conjunction with dilute acid prehydrolysis or as an independent pretreatment process. These alternatives would not only solubilize the hemicellulose component of a biomass feedstock, but the lignin fraction as well. The resulting residual solids would be primarily composed of cellulose. The benefits found in converting such material to ethanol may include lower cellulase requirements, shorter bioconversion times, higher effective cellulose concentrations resulting in higher ethanol concentrations, smaller reactor volumes, and more efficient enzyme recycle options. A technoeconomic assessment indicates that improvements in these process parameters can lead to significant savings that can cover the costs of such process additions.

Index Entries: Ethanol from biomass; pretreatment; delignification; fractionation; process economics.

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INTRODUCTION

Background

The significant use of ethanol as an alternative transportation fuel in the United States can decrease the dependence on foreign oil imports, improve energy security, and reduce the balance-of-payments deficit. Lignocellulosic materials are a renewable resource that are potentially available in very large quantities, both as "wastes" from a wide variety of industrial, agricultural, and municipal activities, as well as from dedicated "energy crops," such as fast-growing herbaceous and woody plant species. Previous studies have indicated that sufficient quantities of such substrates may be available in the United States to produce enough ethanol to displace current and projected demands completely for transportation fuels in a sustainable manner (1).

The development of processes to produce ethanol from lignocellulosic biomass has been the subject of ongoing analysis for many years. Such processes typically hydrolyze the polymeric carbohyrate-based components in lignocellulosic biomass, namely cellulose and hemicellulose, to fermentable sugars using chemicals and/or enzymatic hydrolysis methods, followed by fermentation to produce ethanol. Advances in various conversion technologies has decreased the projected cost of ethanol production from a hardwood energy crop from about $0.95/L ($3.60/US gal) in 1980 to an estimated $0.32/L ($1.22/US gal) in 1992 (2).

Pretreatment Alternatives

One of the key steps in the conversion of lignocellulosic biomass to ethanol involves pretreatment of the substrate. The heterogeneous nature of such materials, with hemicellulose and lignin intertwined with the cellulose fibers, greatly limits the ability of cellulose-degrading enzymes to hydrolyze the cellulose fibers rapidly. Various pretreatment methods have been developed that physically and/or chemically disrupt this structure, resulting in substrates that are more susceptible to degradation by cellulases. General methods that have been reported include dilute acid prehydrolysis (3), autohydrolysis steam explosion (4), acid-catalyzed steam treatment with (5) or without (6) explosion, various alkali-based methods (7–10), and solvent-based "organosolv" processes (11).

In general, acid-based pretreatment processes are effective in solubilizing the hemicellulose component of biomass. Proper combinations of pH, temperature, and reaction time can result in high yields of fermentable sugars, primarily xylose from the hemicellulose, but little cellulose is generally hydrolyzed under such conditions (12). Processes of this nature can utilize the hemicellulose-based sugars to increase the ethanol yield from biomass. Acid-based processes under more severe conditions can result in high degrees of hydrolysis of cellulose, but can cause degrada-

tion of the sugars to unfermentable furfurals, tars, and organic acids (*13*). These types of processes are referred to as acid-hydrolysis processes.

Alkali-based pretretment processes generally result in more solubilization of the lignin fraction of biomass than their acid-based counterparts. Similar processes are used in the pulp and paper industry to produce high-quality, low-lignin content pulps. Such processes may be most sensible for converting municipal solid waste-type substrates, which have a large proportion of low-grade papers that are relatively high in lignin content and relatively low in the hemicellulose content. Many of the alkali-based pretreatment processes reported address the conversion of such substrates (*14-16*) and, in a number of cases, in combination with other pretreatment techniques (*17-20*).

In addition, pretreatment processes have been proposed to achieve full biomass fractionation (*21,22*), or separation of the biomass into individual cellulose-, hemicellulose-, and lignin-based streams. Fractionation processes offer the potential of producing a lignin-based coproduct stream, which may ultimately lead to higher revenues than the use of unconverted lignin as a boiler fuel. They may also result in improvements to ethanol production processes by providing fairly pure carbohydrate streams. Possible benefits found in converting such streams to ethanol may include lower cellulase requirements for enzymatic hydrolysis owing to less enzyme adsorption onto insoluble lignin and increased accessibility of the cellulose fraction by the enzymes, potentially shorter hydrolysis, and fermentation times resulting in smaller required reactor volumes, higher effective cellulose concentrations resulting in potentially higher ethanol concentrations and reduced ethanol recovery costs, lower mixing and pumping power requirements, and more efficient enzyme recycle options owing to decreased adsorption of enzymes on unreactive, insoluble lignaceous material.

The primary purpose of this work is to examine the potential benefits of conceptual "black box" biomass delignification/fractionation steps to the overall economics of a biomass-to-ethanol conversion process in a quantitative, predictive manner. This type of analysis can be used to determine the areas to emphasize research and development efforts for maximum economic benefit.

METHODOLOGY

Process Basis

A detailed conceptual design for a hardwood-to-ethanol process has been described by Hinman et al. (*2*). A process flow diagram for this design is presented in Fig. 1. Briefly, this design calls for a hardwood feedstock to undergo a dilute-acid prehydrolysis. A large fraction of the hemicellulose is solubilized during this pretreatment, but the cellulose and
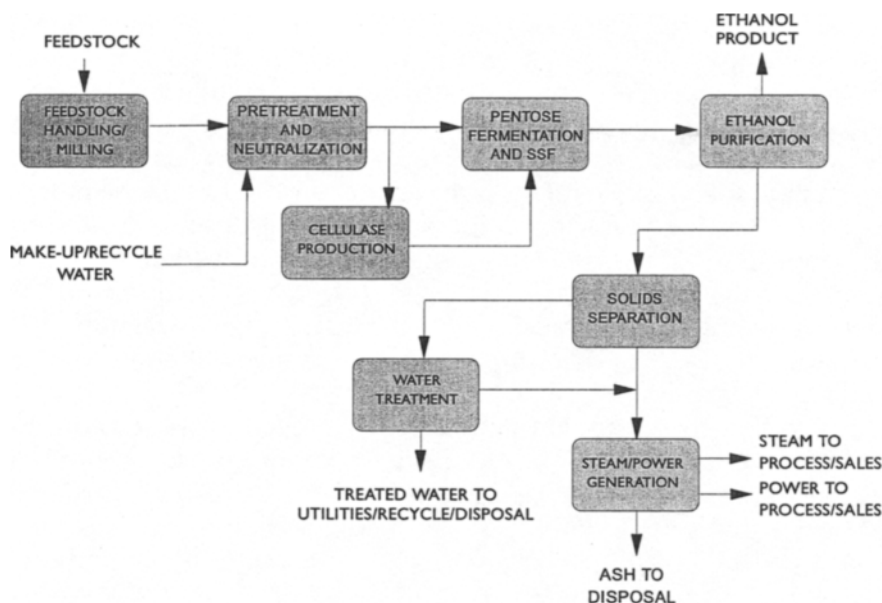
Fig. 1.   Conceptual biomass-to-ethanol process utilizing dilute-acid prehydrolysis.

lignin fractions are largely unaffected. The pentose sugars produced from hemicellulose are converted to ethanol in the pentose fermentation step, whereas a sidestream diverts a portion of the pretreated substrate to serve as a carbon source and inducer for cellulase enzyme-production. This enzyme is then added to the remaining pretreated feedstock to catalyze the hydrolysis of cellulose to glucose, which is concurrently fermented to produce ethanol in the simultaneous saccharification and fermentation (SSF) step. The lignin contained in the feedstock is largely unaffected during these steps. The lignin is ultimately recovered from the stillage stream following ethanol recovery and, along with methane produced during anaerobic digestion of unconverted soluble organics, is used to fire a boiler/turbogenerator system. The energy content in boiler feed streams is sufficient to supply all of the process steam necessary for the entire process. In addition, excess steam is produced, which is converted to electricity by the turbogenerator. There is enough electricity to supply all power needs to the process, with excess available to be sold as a byproduct, adding a positive revenue flow to the overall process. For a plant capable of processing 1745 dry tonnes (1920 US t) of 25 mm (1 in) hardwood chips a day, this process produces 221 million L/yr (58.5 million US gal/yr) of azeotropic, denatured ethanol (containing 5% [wt] unleaded gasoline) at an overall cost of $0.32/L ($1.22/US gal).

In the work described here, the feedstock of interest is switchgrass (*Panicum virgatum*), a rapidly growing herbaceous species that is considered a prime candidate for use as a dedicated energy crop. Since much of the process design used in this analysis is similar to the study of Hinman
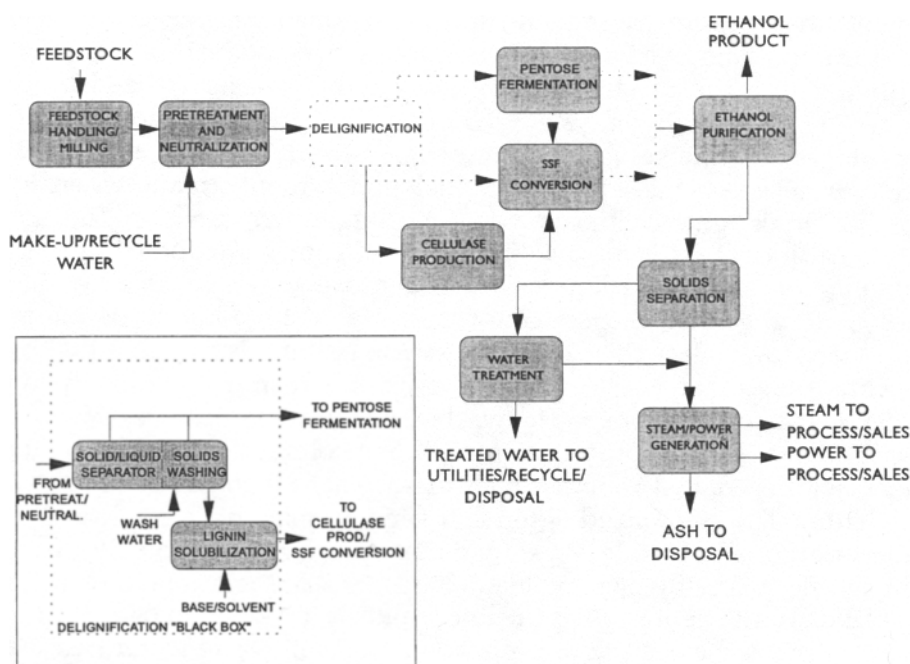
Fig. 2. Conceptual biomass-to-ethanol process utilizing biomass delignification in conjunction with dilute-acid prehydrolysis. Dashed arrows indicate possible process flow alternatives.

et al. (2), a case using this basic design, but employing switchgrass as a feedstock, was developed.

Biomass Delignification

Since the purpose of this work is to determine the potential impact of delignification/fractionation steps on the overall biomass-to-ethanol process, conceptual designs that would allow for such operations were developed. One example, which retains the dilute-acid prehydrolysis step, is presented in Fig. 2. This step serves to solubilize the hemicellulose component of the feedstock, leaving the cellulose and lignin fractions largely intact. A subsequent step that solubilizes lignin would leave a substantially pure cellulose substrate available for cellulase production and SSF conversion. Because limited laboratory data are available related to the specific reaction parameters for such a delignification procedure, this step is treated as a "black box" in terms of the process engineering analysis. The lignin is assumed to be converted to a soluble organic, which is then converted to methane in the waste-water treatment section via anaerobic digestion, assuming the lignin is fully degraded to monomeric compounds (23). Although the specifics of the delignification procedure are largely unknown with respect to reaction conditions, reagents, and so forth, some generalized assumptions that will affect the general

flow of materials to subsequent unit operations and, hence, the overall material and energy balance of the process, must be made. As shown in Fig. 2, within the delignification "black box," the neutralized product from dilute acid prehydrolysis is fed to a solid/liquid separation and solids washing step. The soluble pentose sugars produced during dilute acid prehydrolysis exit the separator in the liquid effluent stream, whereas insoluble lignin and cellulose would be largely captured in the solids stream. Since it is likely that the solids stream will contain significant quantities of entrained liquor rich in pentose sugars, a solids washing step, either within the separator or as a distinct unit operation, is necessary to displace this liquor. The wash effluent is combined with the separator liquid supernatant. This combined stream is fed directly to the pentose fermentation step. The washed solids are largely free of pentose sugars, and are composed primarily of insoluble lignin and cellulose along with entrained water. A base or solvent is then added to solubilize the lignin. The solubilized lignin is treated as a soluble organic in subsequent unit operations. It is assumed that these organics do not adversely impact the following bioconversion steps, and are not able to be utilized as carbon or nutrient sources in either cellulase production or SSF conversion. They can be utilized to produce methane in waste-water treatment. No additional revenue, such as those associated with products derived from lignin, is credited to the process.

The general process scenario of Fig. 2 was used to construct a delignification process base case, which can be compared to the standard dilute-acid base case. Since so little is known about the specific reaction conditions involved with delignification, no capital or operating costs were estimated for the operations described with the delignification "black box." Instead, a cost of ethanol production for the delignification process base case was calculated without these costs included. By comparison with the standard dilute-acid base case, it is possible to determine the maximum revenue that can be allocated to the delignification step in order to break even with the standard process.

Because so little is known concerning the reaction performance of the delignification step or its impact on the performance of other unit operations, the values assumed in the delignification base case may be inaccurate. Thus, it is useful to conduct a series of sensitivity analyses over a broad range of selected key parameters. This type of analysis not only addresses the possible inaccuracies of the assumed base-case values for these variables, but also give an indication as to which parameters have the most significant impact on the overall process.

Biomass Fractionation

A full biomass fractionation process may or may not include dilute acid prehydrolysis as a component. Therefore, a scenario examining a generalized fractionation process was created to determine its potential
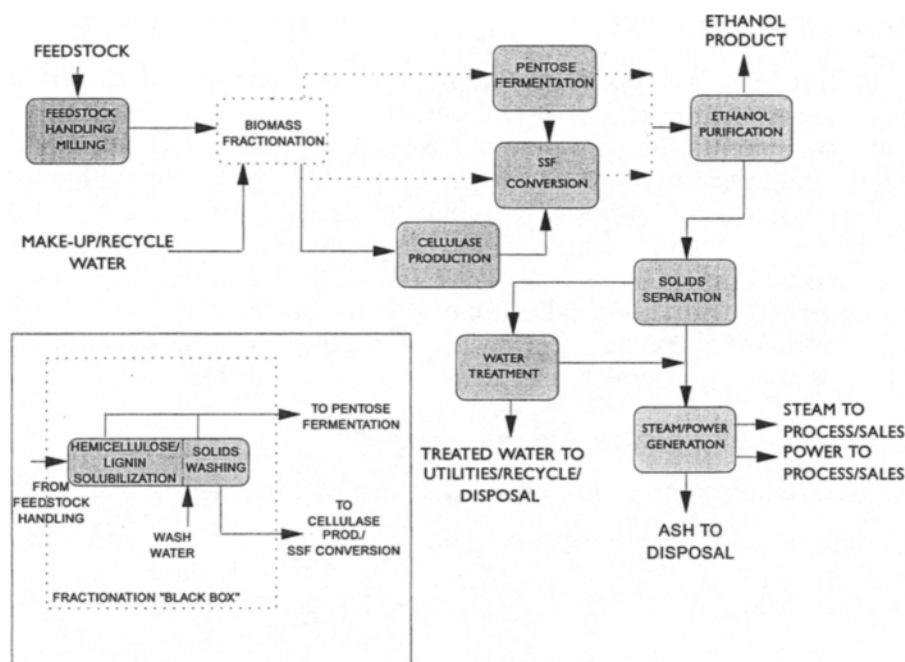
Fig. 3. Conceptual biomass-to-ethanol process utilizing biomass fractionation as an independent unit operation. Dashed arrows indicate possible process flow alternatives.

impact. This scenario also assumes hemicellulose solubilization with recovery of pentose sugars along with lignin solubilization, but does not specify any conversion technology. A flow diagram for such a process is presented in Fig. 3, including a conceptualization of the possible components of the fractionation "black box," as needed for the construction of material and energy balances. Again, it is assumed that hemicellulose and lignin are solubilized, leaving a relatively pure cellulose substrate, followed by a washing operation to displace pentose sugars from the cellulose.

In a manner similar to the biomass delignification analysis, a biomass fractionation base case and relevent sensitivity analyses were developed in order to evaluate its economic potential.

Material and Energy Balances

Material balances for the respective process alternatives were conducted using Microsoft Excel™ spreadsheet software. The flow rate and composition of each major stream throughout the process are calculated. The stream information is used in the calculation of raw materials, chemicals, and utilities requirements, allowing for the computation of a detailed energy balance.

Economic Evaluation

Pertinent information from the material and energy balance spread-sheet, along with process performance assumptions, is used to size capital equipment. Bare equipment costs, used in the computation of the total capital investment and the annual capital charge, along with operating costs associated with raw materials, chemicals, utilities, labor, maintenance, taxes, and insurance, are determined using the methods described by Hinman et al. (2). All costs are ultimately summarized on an annual basis. With the total annual ethanol production level available from the material balance, it is possible to determine the overall cost of ethanol production, which is reported on a per-unit basis.

Base Case Conversion Assumptions

Key assumptions used in base-case material balances are as follows:

Overall plant assumptions
- Plant type   Grass roots, N^{th} plant
- Cost basis   1990 US dollars, unspecified US location
- On-stream time   8000 h/yr (91.3%)
- Plant capacity   1745 dry t/d (1920 US t/d)
- Feedstock cost $46/dry t ($42/dry US t)

Dilute acid prehydrolysis assumptions
- Yield of xylose from xylan   80%
- Yield of glucose from cellulose   17%

Pentose fermentation assumptions
- Yield of ethanol from xylose   85.5%
- Fermentation time   2 d

SSF assumptions
- Yield of ethanol from cellulose   72%
- Fermentation time   7 d
- Cellulase enzyme requirement   7 FPU/g cellulose in SSF

Ethanol recovery assumptions
- Ethanol recovery yield   99.5%
- Product specification   Azeotropic ethanol denatured with 5% (wt) gasoline

RESULTS AND DISCUSSION

Standard Dilute-Acid Prehydrolysis

When switchgrass is substituted as the feedstock into the standard dilute-acid prehydrolysis process of Fig. 1, the resultant denatured ethanol

Table 1
Comparison of Feedstock Composition Used
in Material Balance for Hardwood and Switchgrass

	Chemical composition, % wt	
Component	Hardwood	Switchgrass
Cellulose	46.2	40.9
Xylan	24.0	19.8
Lignin	24.0	23.8
Soluble solids	5.6	9.6
Ash	0.2	6.0

production level drops to 198 million L/yr (52.4 million US gal/yr), as compared to the hardwood feedstock production level of 221 million L/yr (58.5 million US gal/yr). The cost per unit of denatured ethanol produced for the switchgrass-based feedstock is $0.0336/L ($1.272/US gal), as compared to $0.322/L ($1.217/US gal) for the hardwood-based process. The main reason for the lower ethanol production level is related to differences in the chemical composition of the feedstocks, as shown in Table 1 (2,26). For hardwood, the carbohydrate content (sum of cellulose and xylan) is about 70% of the total dry feedstock, whereas switchgrass has a total carbohydrate content of only 61%, resulting in lower ethanol production levels.

The cost per unit of ethanol produced from switchgrass is higher than for hardwood, but not as high as would be expected based on the decrease in ethanol production. Reasons for this include the fact that less intensive equipment and lower power requirements are needed to mill switchgrass as compared to hardwood chips. Modification of the cost estimate was made to reflect these differences. In addition, less entrained water in the switchgrass (12% moisture vs 50% moisture in hardwood) along with a higher bulk packing density for milled switchgrass result in smaller required volumes for the prehydrolysis reactors. This results in large savings in capital costs for the switchgrass process, which is compounded by the corrosion-resistant alloys used for this equipment. Also, smaller prehydrolysis reactors result in lower steam requirements, leading to a larger excess electricity credit.

Biomass Delignification Base Case

A base case for the biomass delignification process was analyzed. Key assumptions regarding conversion yields, rates, and so forth, are the same as listed previously. In addition, assumptions related specifically to the delignification operation are as follows:

- Degree of lignin solubilization   100%
- Fate of solubilized lignin   Unfermentable soluble organic
                                           solid, 0.8 kg methane/kg
                                           organic
- Insolubles captured in solids stream   90%
- Solids concentration in solids stream   25% (dry wt basis)
- Wash water usage rate   2.0 kg water/kg insolubles
                                           in solid stream
- Recovery of solubles in wash effluent   95%

Based on these assumptions, the projected ethanol production cost, without capital and operating costs associated with the delignification addition, is $0.335/L ($1.268/US gal), as compared to $0.336/L ($1.272/US gal) for the standard dilute-acid process. Reduction in required fermentation volumes and higher resultant ethanol concentrations are achieved owing to lignin solubilization, as well as a smaller boiler/turbogenerator unit, but any savings is largely offset by significant decreases in excess electricity credits. This difference in production economics, on an annualized revenue basis, is $0.197 million/yr. In effect, this value represents the total capital and operating expenditures, on an annualized basis, that can be allocated for the delignification process addition in order to break even with the production economics for the standard dilute-acid process. If 60% of this amount is allocated to operating costs and 40% to capital costs, which is representative of the allocation of costs to the entire process, the break-even operating expenditures are limited to $0.118 million/ yr, with an up-front total capital investment of $0.394 million (based on a 20% annual capital charge). Thus, without any improvements in conversion efficiency, only a trivial cost reduction results from the delignification process addition.

Biomass Fractionation Base Case

A similar base case for the biomass fractionation process was developed. Since a dilute-acid prehydrolysis is not specified for this alternative, all related capital and operating costs have been eliminated from this analysis. General conversion assumptions used in this case are unchanged.

The projected ethanol production cost, without capital and operating costs associated with the full fractionation process, is $0.300/L ($1.134/US gal), as compared to $0.336/L ($1.272/US gal) for the standard dilute-acid process. The difference in production economics is $7.208 million/yr. Most of this is directly attributable to the removal of costs associated with dilute-acid prehydrolysis, including capital costs and operating expenses related to steam, acid, and base use. Clearly, most if not all of these "cost savings" would ultimately be offset with the addition of a biomass fractionation step. If 60% of the annualized cost difference is allocated to operating costs and 40% to capital costs, the break-even operating expen-
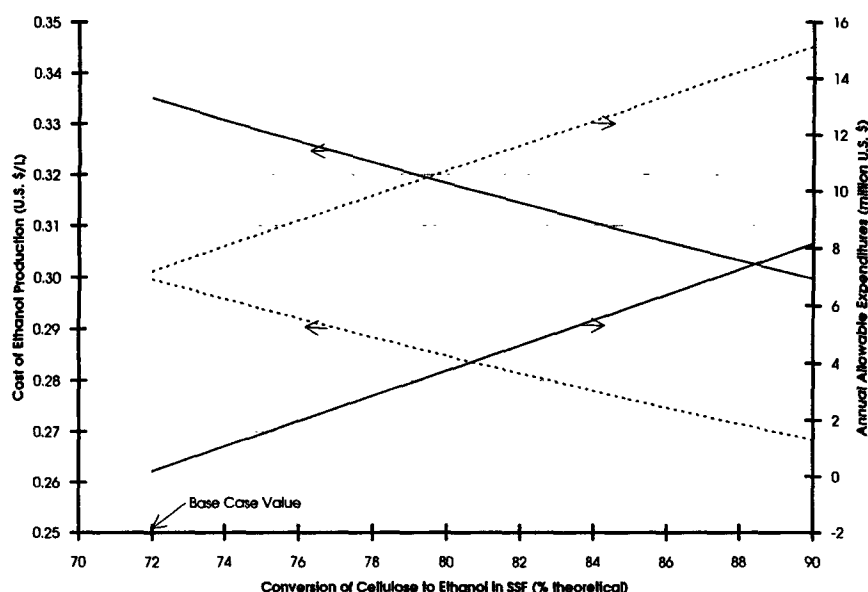
` Fig. 4. Impact of varying conversion of cellulose to ethanol in SSF on the overall cost of ethanol production and annual allowable expenditures to finance process addition for delignification (————) and fractionation (- - - - -) process scenarios.

ditures are limited to $4.325 million/yr, with an up-front capital investment of $14.416 million (bzsed on a 20% annual capital charge).

Sensitivity Analyses

Because little specific data is available regarding the various conversion performance assumptions made for the delignification and fractionation base cases, a series of sensitivity analyses, where several key performance parameters are varied individually over a range, was performed.

Process parameters that were found to have a significant impact on overall process economics include the yield of ethanol from cellulose in SSF conversion, the duration of the SSF conversion step, the required cellulase loading in SSF conversion, and the degree of lignin solubilization achieved in the delignification/fractionation operation. These impacts are presented graphically in Figs. 4-7. In Fig. 4, as the yield of ethanol from cellulose in SSF is increased to 90%, the cost of ethanol production drops to $0.300/L ($1.134/US gal) with a delignification process and to $0.268/L ($1.016/US gal) with a fractionation process. Again, these values do not include the capital and operating costs associated with these process additions. The level of allowable expenditures to finance the process additions so that they break even with their respective base cases rises to $8.151 million/yr for the delignification addition and to $15.143 MM/yr for the fractionation addition, both at 90% ethanol yield in SSF. In Figure 5, a
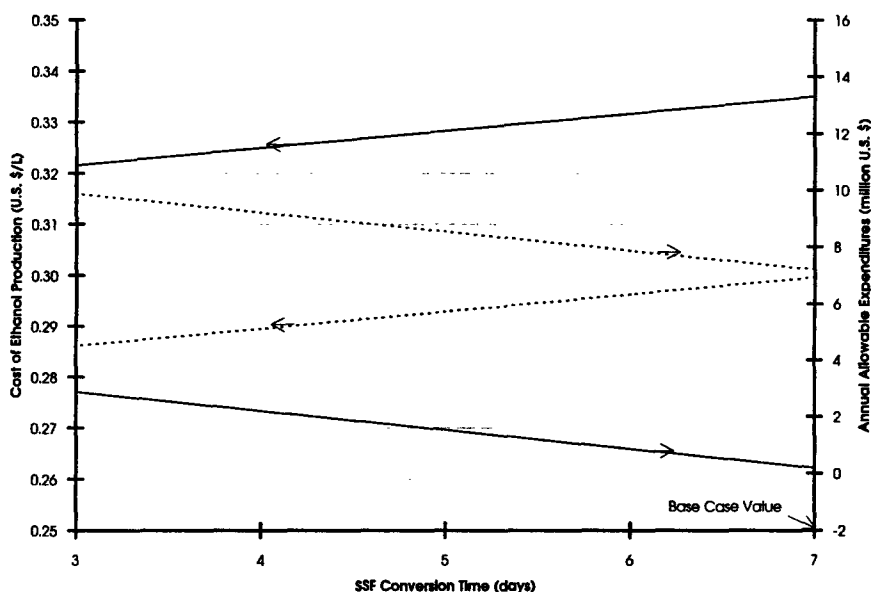
Fig. 5. Impact of varying SSF conversion time on the overall cost of ethanol production and annual allowable expenditures to finance process addition for delignification (————) and fractionation (- - - - -) process scenarios.
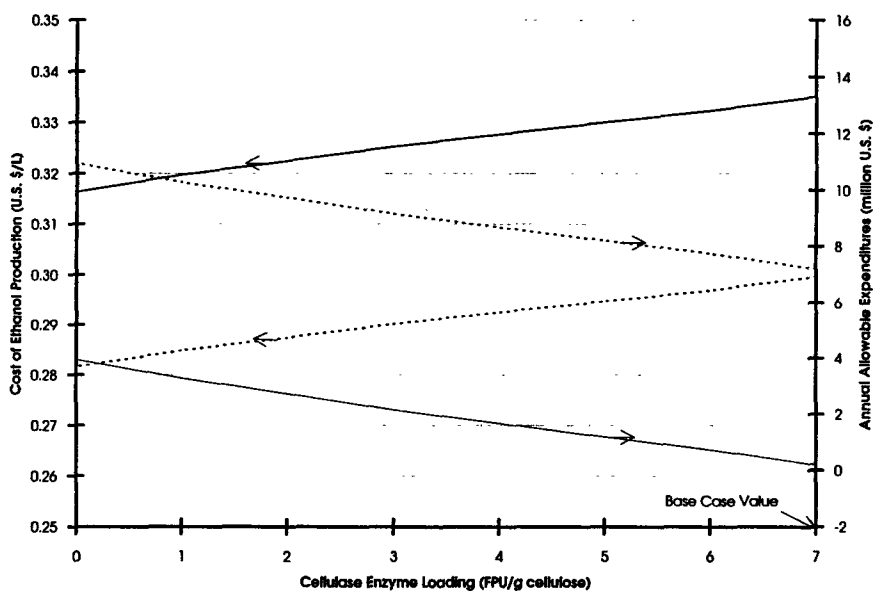

Fig. 6. Impact of varying cellulase enzyme loading in SSF on the overall cost of ethanol production and annual allowable expenditures to finance process addition for delignification (————) and fractionation (- - - - -) process scenarios.
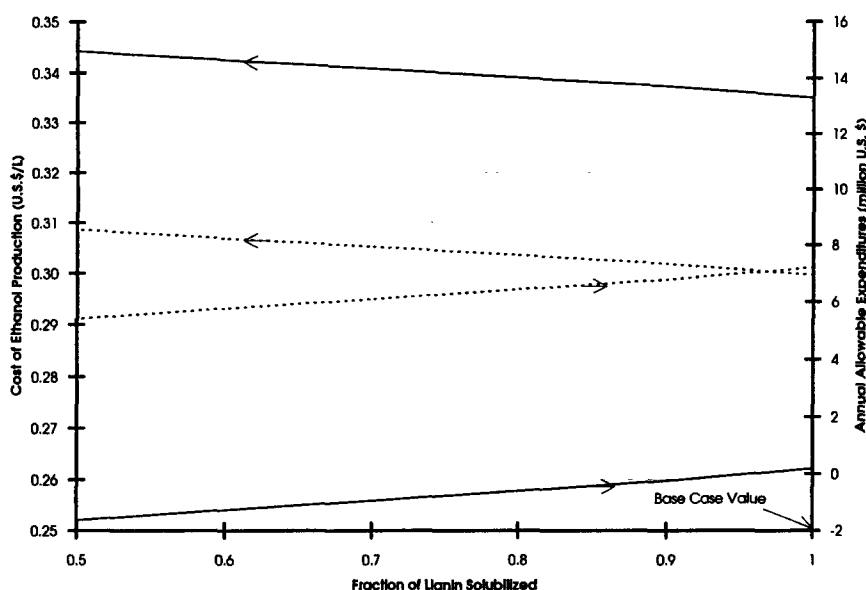
Fig. 7. Impact of varying fraction of lignin solubilized on the overall cost of ethanol production and annual allowable expenditures to finance process addition for delignification (————) and fractionation (- - - - - -) process scenarios.

similar analysis related to the SSF duration is presented. The slope of the curves is less steep than in Fig. 4, which is an indication that SSF duration is not as critical a parameter as yield of ethanol in SSF. Still, there is certainly a benefit in a shorter required SSF time. In Fig. 6, the impact of required cellulase loading in SSF is presented. Lower enzyme requirements can be achieved by solubilizing lignin, which has been shown to hinder the accessibility of enzyme to cellulose, as well as adsorb and inactivate cellulase (24,25). Also, the removal of lignin would allow for more efficient enzyme recycle options by providing a solid-free stream after SSF conversion, where the used cellulase would be free in solution rather than largely bound to an inert solid. The impact of reducing the cellulase requirement is fairly significant, as shown in Fig. 6. If an enzyme recycle scheme is used to reduce make-up cellulase requirements, then all capital and operating costs associated with enzyme recycle, in addition to the costs associated with the "black box," would have to be covered in the break-even allowable expenditures. Finally, in Fig. 7, the impact of lignin removal is examined. As less lignin is removed, the amount of inert solids in cellulase production and SSF conversion increases, increasing required reactor volumes in these steps. Also, increased levels of lignin lead to higher boiler and turbogenerator costs. This is partially offset by a higher electricity credit owing to a higher overall heating value in the boiler feed stream.

Table 2
Economic Impact of Performance Improvements Resulting
from Delignification/Fractionation Addition

Case	Overall allowable expenditures, million US $/yr	Allowable operating expenditures,[1] million US $/yr	Allowable total capital investment,[1] million US $
Delignification			
Delignification base	0.197	0.118	0.394
90% SSF yield	8.151	4.891	16.302
3 d SSF time	2.869	1.721	5.738
3 FPU/g cellulase use	2.168	1.301	4.336
Combined effect	12.890	7.734	25.780
Fractionation			
Fractionation base	7.208	4.325	14.416
90% SSF yield	15.143	9.086	30.286
3 d SSF time	9.880	5.928	19.760
3 FPU/g cellulase use	9.172	5.503	18.344
Combined effect	19.881	11.929	39.762

[1]Assumes 60% of overall expenditures to operating, 40% to capital (@20% annual capital charge).

In Table 2, potential available expenditures, as allocated to operating expenses and up-front total capital investment, based on varying conversion improvements in both the delignification and fractionation options, are presented. In addition, the cumulative impact of achieving all of these improvements is shown.

Other variables, including separator performance in the delignification/fractionation additions and lower required mixing power in cellulase production and SSF conversion, were analyzed, but were found to have limited impact on overall process economics.

CONCLUSIONS

Conceptual processes that include biomass delignification or fractionation options for the production of ethanol from switchgrass were evaluated. Since little data for this feedstock are available, the impact on overall ethanol production economics resulting from potential improvements that might be realized by including a delignification or fractionation step was evaluated. Although actual equipment and operating conditions for the delignification or fractionation step were not specified owing to limited data, it is possible to estimate the level of capital and operating expenses that would be available to finance these additions such that an overall economic benefit to the process is attained.

For the delignification option, which includes dilute-acid prehydrolysis as a component, improvements from assumed base-case values in ethanol

yield from cellulose, SSF conversion time, and cellulase requirements, along with full solubilization of lignin, lead to significant cost reductions to support this type of process addition. Even larger cost reductions are possible with similar improvements in these parameters for biomass fractionation, but this scenario must also include a hemicellulose hydrolysis step, since no dilute-acid prehydrolysis operation is included with this option.

ACKNOWLEDGMENTS

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