

A Process Economic Approach to Develop a Dilute-Acid Cellulose Hydrolysis Process to Produce Ethanol from Biomass

NICK NAGLE,* KELLY IBSEN, AND EDWARD JENNINGS

*Center for Fuels and Chemicals,
National Renewable Energy Laboratory, 1617 Cole Blvd.,
Golden, CO 80401, E-mail: Nick_Nagle@NREL.gov*

Abstract

Successful deployment of a bioethanol process depends on the integration of technologies that can be economically commercialized. Pretreatment and fermentation operations of the traditional enzymatic bioethanol-production process constitute the largest portion of the capital and operating costs. Cost reduction in these areas, through improved reactions and reduced capital, will improve the economic feasibility of a large-scale plant.

A technoeconomic model was developed using the ASPEN Plus™ modeling software package. This model included a two-stage pretreatment operation with a co-current first stage and countercurrent second stage, a lignin adsorption unit, and a cofermentation unit. Data from kinetic modeling of the pretreatment reactions, verified by bench-scale experiments, were used to create the ASPEN Plus base model. Results from the initial pretreatment and fermentation yields of the two-stage system correlated well to the performance targets established by the model. The ASPEN Plus model determined mass and energy-balance information, which was supplied to an economic module to determine the required selling price of the ethanol. Several pretreatment process variables such as glucose yield, liquid: solid ratio, additional pretreatment stages, and lignin adsorption were varied to determine which parameters had the greatest effect on the process economics. Optimized values for these key variables became target values for the bench-scale research, either to achieve or identify as potential obstacles in the future commercialization process. Results from this modeling and experimentation sequence have led to the design of an advanced two-stage engineering-scale reactor for a dilute-acid hydrolysis process.

Index Entries: ASPEN Plus; pretreatment; bioethanol production; economic feasibility; *rZ. mobilis*.

*Author to whom all correspondence and reprint requests should be addressed.

Introduction

Recent advances in reactor design for the dilute-acid thermochemical treatment of biomass have resulted in the development of process alternatives in which high yields of soluble sugars from both cellulose and hemicellulose are obtained. A countercurrent process involving total hydrolysis of both cellulose and hemicellulose has been demonstrated at the bench scale using yellow poplar as a feedstock (1). Although kinetic modeling has shown that yields of 88% (2) can be achieved in a countercurrent configuration, previously reported studies indicated that total sugar yields of only 60% are achievable. The reasons for the disparity between modeling and experimental values have been linked to chromium leaching, which catalyzes sugar degradation reactions and nonideal flows in the reactor (owing to the collapsing biomass bed), which leads to increased residence time and additional sugar degradation. Modeling studies have shown that increasing the linear flow of the hydrolysis liquor relative to the biomass bed produces shorter retention times and higher sugar yields (2,3). The technical challenge is to balance the yield improvement from increasing the linear velocity with the increased energy demand to heat the liquor required for pretreatment.

During pretreatment, the biomass bed shrinks as sugar and lignin are released. A novel reactor design (4) was developed to capitalize on this phenomenon. The continual shrinking bed reactor (CSBR) uses an internal spring to continually shrink the biomass while keeping the liquid volume at an acceptable level (Fig. 1). Preliminary investigations used a series of percolation reactors equipped with internal springs (Fig. 2) to shrink the biomass bed. The reactors were configured to simulate a true countercurrent movement of liquid and solids and have achieved the yields of glucose and xylose suggested by modeling data (5). Preliminary economic analyses have shown that this total hydrolysis process could reduce the production cost of ethanol compared processes using enzymatic hydrolysis.

To exploit the total hydrolysis alternative, it must be integrated into a complete process that achieves a competitive production cost for ethanol. This requires an understanding of how the process steps interact and how they effect the production cost.

Process modeling of biomass to ethanol process has rapidly evolved since 1980 (6). As capabilities of software and microcomputers have dramatically increased, so has the ability to model the complex interactions of the process. The ASPEN Plus model is an advanced process simulator for process engineering that completes energy and mass balances around multiple-unit operations. Coupled with a spreadsheet model to determine production cost, it has the flexibility to identify variables having a major impact on the production cost and determine the magnitude of the impact. From process modeling of the biomass to ethanol process, it is apparent that the pretreatment, hydrolysis, and fermentation operations are complex and technically immature, as indicated by their contribution to the total

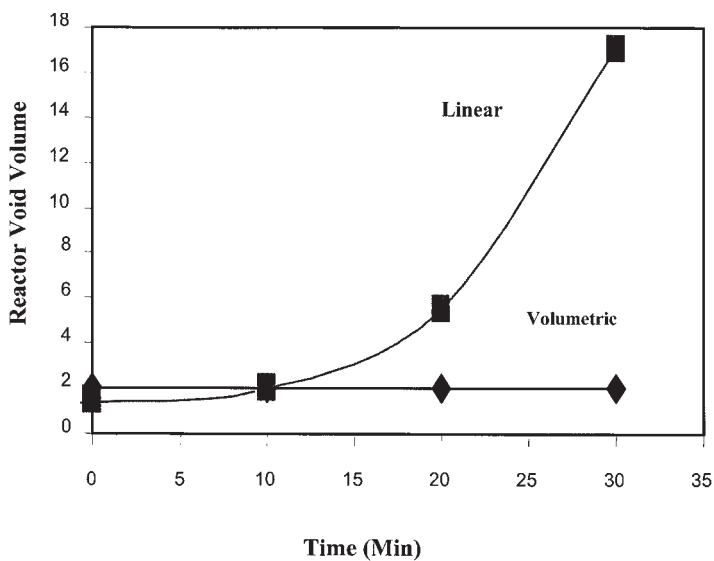


Fig. 1. Linear hydrolyzate velocity vs volumetric hydrolyzate velocity.

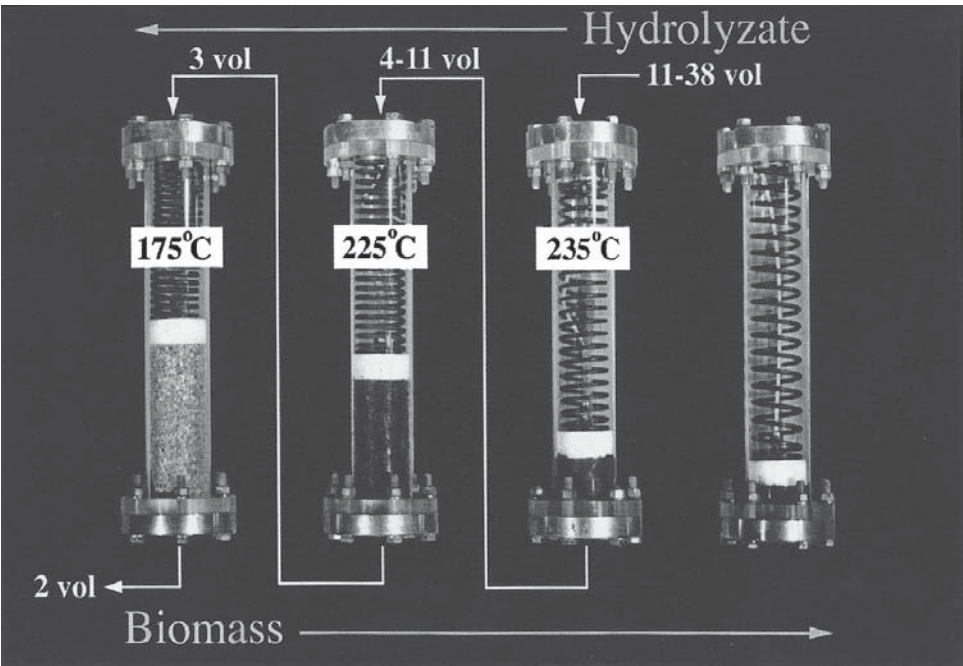


Fig. 2. Three-stage shrinking bed countercurrent reactor configuration.

product cost (7). Thus more information is needed in these areas to accelerate the design and costing of a total hydrolysis process.

Bench-scale integration of the unit operations coupled with a techno-economic model offer a flexible approach to determine the affect and eco-

conomic consequence that process conditions have on production cost (8). It has generally been recognized that pretreatment, hydrolysis, and fermentation represent the largest cost to a bioethanol process (7,9). Much of the research at the National Renewable Energy Laboratory has been directed toward lowering the cost for these processes.

Methods

Total Hydrolysis

The experimental protocols, analytical determinations, raw materials, and equipment specifications used in the countercurrent dilute-acid hydrolysis experiments using two-inch diameter percolation reactors have been presented in detail by Torget et al. (10). The major departure from the established protocols for this work was the inclusion of a spring-loaded mechanism to reduce the volume of the reactors as biomass is hydrolyzed, causing shrinkage of the bed. The spring is constructed of Hastaloy C-276 solid tubing, 8 inches long fully sprung, with 7 lbs of deflection/inch. The springs were manufactured by AAAA Specialties (Denver, CO). One eighth inch of Teflon tubing was threaded through the center of the spring and connected to the bottom of the headplate by a Swagelock fitting. The top of the tubing was connected to the bottom of a titanium plug using a national pipe thread (NPT) fitting. This allowed acid to be pumped through the spring and through the titanium plug, directly to the biomass. The titanium plug was manufactured by Falcon Fabrication (Golden, CO). The plug was machined to slide inside the reactor at pretreatment temperatures. Dispersion troughs were machined on the top of the plug along with a groove around the outside to secure a titanium dispersion frit. The reactor body, head plates, tubing, and valves were constructed out of Hastaloy C-276 material.

The reactors were loaded from the top with 92.0 g of yellow poplar sawdust. The spring mechanism was lowered into the top of the reactor and the headplate was bolted on the reactor body. The reactors were operated in a downflow mode with respect to acid flow. To demonstrate shrinkage at reaction temperatures Residence Time Distribution (RTD) studies were done to measure the void volume of the reactor under the shrinking-bed configuration. A densitometer was used to measure the density of the NaCl tracer as it flowed out of the reactor. The distribution studies were conducted at 175°C and 225°C, using an ice bath to maintain constant temperature for the densitometer.

The complete hydrolysis experiments were conducted using five CSBRs plumbed in series to simulate a countercurrent mode of operation, as previously described by Wright et al. (3). Three thermal stages were used, 175°C, 225°C, and 235°C for 10 min with a flow rate of 90 mL/min of 0.07% sulfuric acid. The system was over-pressurized using nitrogen gas to prevent flashing of product from the reaction. Mass balances, closures, and yield were calculated using an Excel spreadsheet (11).

Advanced Two-Stage Hydrolysis

Modeling targets were verified using an advanced two-stage process. This process is similar to the total hydrolysis yet has only two thermal stages, 180°C and 225°C. The first stage uses hot water (instead of acid) and 0.07% sulfuric acid is used as the catalyst for the second stage. The reaction time and pump rate have been modified to achieve the volume and hydrolysis targets necessary for the predicted two-stage system. Glucose was added to the hydrolyzate from the two-stage process to match the expected yield from a third stage based on the total hydrolysis results. After pretreatment, the hydrolyzate was placed in a Parr reactor and held for 3 h at 135°C to hydrolyze the oligomer xylan to monomeric xylose. The hydrolyzate was then split into two aliquots. The first was treated with potassium hydroxide to pH 9.0, then adjusted with sulfuric acid to pH 5.5 and treated with MR2000 (a proprietary lignin adsorbent) for 30 min. The second aliquot served as a control and was neutralized to pH 5.5 with potassium hydroxide with no further treatment. Both aliquots were then used for fermentation experiments.

Fermentation

All fermentations were performed with *rZymomonas mobilis* CP4 (pZB5). Inoculum was grown at 30°C, 150 rpm and at a pH of 5.5 in recombinant media (RM) (9) with a glucose-xylose ratio of 4:1. At 16 h the seed was centrifuged and resuspended in RM prior to inoculation of the fermentation vessels.

Owing to small volumes generated during the pretreatment stage, a unique fermentation system was designed to achieve fermentation targets. The system was set up in a small plexiglass tank fitted with an immersion circulator for temperature control (Cole Parmer, Vernon Hills, IL). Four bioreactors were constructed by fitting a 200-mL wide-mouth sampling jar with rubber stoppers. Holes were drilled in the stoppers for seed and base additions, a sample port, and a pH probe. The pH probes were attached to conductivity controllers and pumps (Cole-Parmer). Each reactor had a magnetic stir bar and an individual mini-stir plate for agitation. The fermentation vessels were loaded with 80% hydrolyzate (v/v), 10% RM media, 200 μ L tetracycline (conc) and water to achieve a working volume of 100 mL. A pure sugar control was included that had the identical acetic acid and hydroxymethyl-2-furfuraldehyde (HMF) concentration of the hydrolyzate. Each reactor was inoculated with seed to a final optical density (OD) of 2.0 at 600 nm. The pH was controlled between 5.8 and 6.0 using either 2 N potassium hydroxide or 2 N ammonium hydroxide. The temperature was controlled at 32°C, agitation of 250 rpm, and total run time was 96 h. Samples were taken every 2 h for the first 6 h, then once every 12 h. High-performance liquid chromatography (HPLC) analysis for glucose, xylose, acetic acid, lactic acid, furfural, hydroxymethyl-2-furfuraldehyde and ethanol were performed on all samples.

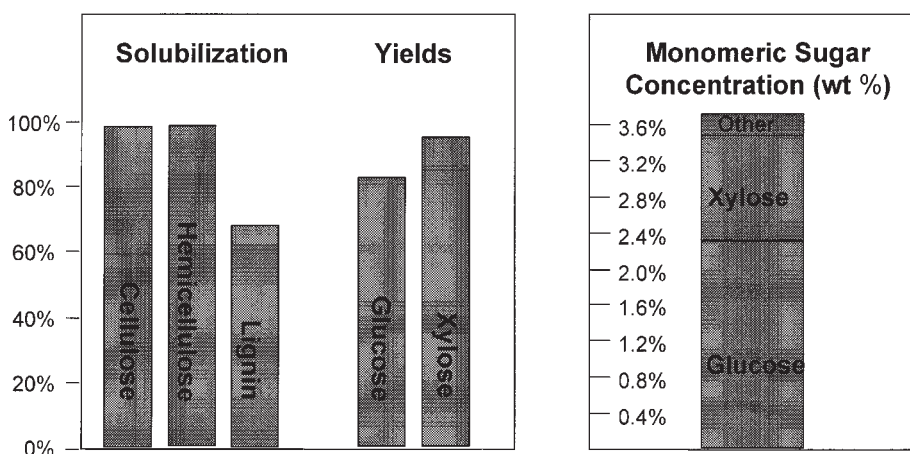


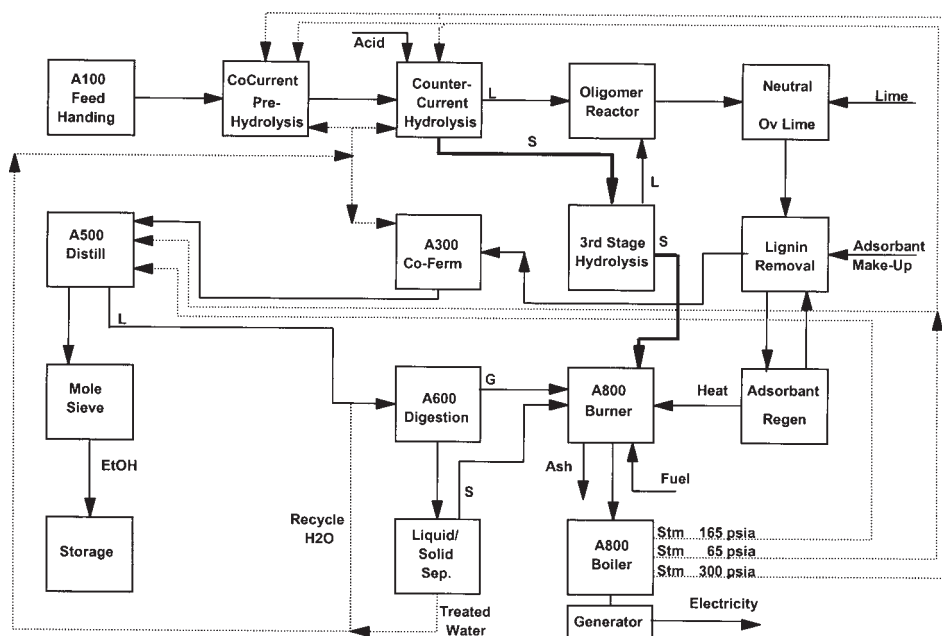
Fig. 3. Three-stage shrinking bed reactor performance using total hydrolysis.

Process Modeling

The process design was completed using procedures followed from bench-scale total hydrolysis pretreatment experiments (Fig. 3). Experimental conditions such as temperature, acid concentration, flowrate, and yield data for the incorporated into the design. The process design data were entered into the ASPEN Plus model (Aspen Tech Inc., Cambridge, MA). The ASPEN Plus biomass to ethanol model uses a properties database (12), created at NREL to supply data for the unique components found in the subroutine. This specific model included a two-stage pretreatment process consisting of cocurrent prehydrolysis steps using water and a countercurrent second stage using a dilute sulfuric-acid catalyst. The model calculates mass and energy balances and inputs the information into an Excel spreadsheet to determine ethanol production cost. A 2,000 dry ton/day plant with a 20-yr lifespan was sized and costed using ICARUSTM cost-estimation software or direct vendor quotes. Once a base case was established, key parameters were varied to determine the magnitude of the affect on the process economics. Several rounds of sensitivity analysis were performed using the two-stage base case. Targets for pretreatment sugar yields, liquor:solid ratio (void volume), concentration of sugar degradation products, fermentation targets, and options for processing the residual solids were identified and research efforts were focused on achieving those targets.

Results

Results from the total hydrolysis experiments (Fig. 4) indicated that more than 95% of the cellulose and xylan fractions can be hydrolyzed with recoveries of 83% glucose and 97% xylose. During the first stage at 175°C, more than 60% of the xylose and 10–15% of the glucan is hydrolyzed. During



the second stage at 225°C, the remaining 35–40% of the xylose and 50% of the glucose is released. Finally at 235°C, the remaining 40% of the cellulose is hydrolyzed. The monomeric sugar concentration was 3.6% (w/v). During the run, over 70% of the lignin was hydrolyzed, most of which was released during the second stage. The biomass plug was compressed to 12.5% of the original volume of the biomass. This continual shrinkage of the bed, as a function of hydrolysis, increases the linear velocity of the hydrolysis liquor while keeping the volumetric velocity constant. This “washing” of sugars out of the reaction zone reduces the degradation products while increasing the yield of sugars.

The data from these experiments was integrated into the techno-economic model to identify key variables and how changes in those variable affected the production cost. The first set of sensitivities (Fig. 5) was run using a two-stage pretreatment model with a co-current prehydrolysis first stage and a countercurrent second stage, with a detoxification step that included a overliming and soluble lignin removal as a base case. Results of the first round of sensitivities indicated that the addition of a third pretreatment stage to convert additional cellulose to glucose as opposed to burning the solids for boiler fuel or enzymatic hydrolysis could reduce the production cost of ethanol by \$0.41 (Fig. 5). Other significant improvements included increasing glucose yield, increasing the lifespan of the lignin adsorbent (MR 2000), and reducing the volume of acid and water (void volume) used in the process. Because of the major economic effect of adding a third stage pretreatment to the base case, a second set of sensitivities was

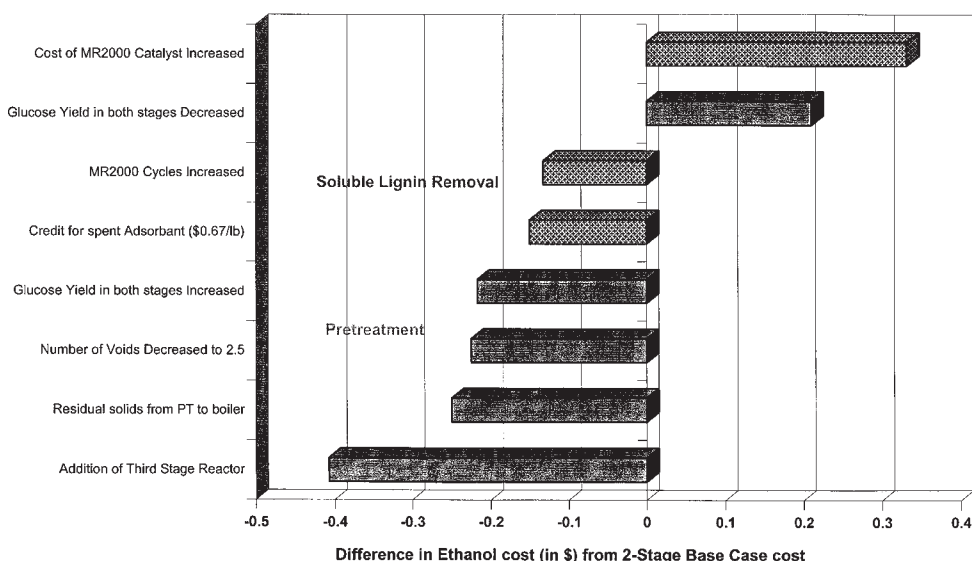


Fig. 5. Difference in cost between critical sensitivities in a countercurrent process and two-stage (enzymatic) base case.

run using this advanced pretreatment process as the new base case. During the next round of sensitivities variables that resulted in a difference of \$0.10 or greater were reported (Fig. 6). The model identified void volume, glucose and xylose yields from pretreatment, lignin recovery, cornstep liquor (CSL) usage and ancillary utility costs as the major cost variables. Reducing void volume (the amount of free liquid in packed reactor) was the largest single improvement in reducing production cost. Varying the number of void volumes from 2.5 to 2.0 would result in a cost reduction of \$0.17/gal cost for ethanol. Additionally, the sensitivities indicated that the use of corn steep liquor (CSL), increased glucose yield from the second and third stages, reducing the amount of degradation products and obtaining a credit for the recycling of the spent lignin adsorbent as areas for potential cost reduction in production cost.

Based on the results of the process sensitivities, the target values for void volume, sugar concentration, and sugar yields were combined to produce a research target case. Bench-scale research results to verify the optimized values for these variables (Table 1) correlated well with target values. Liquid to solid ratio (void volume), sugar concentration, and glucose and xylose yields were all met. The remaining mass of cellulose in the second stage as well as sugar degradation concentrations were all within predicted model ranges. Fermentation of the hydrolyzate (Fig. 7) met the targets for glucose utilization in 48 h; however, xylose utilization was less than predicted (39.2 vs 60%) in 48 h. Xylose utilization peaked at 48 h (Fig. 8) and extending the fermentation to 96 h did not significantly increase utilization or ethanol production. Comparison of the fermentation results between the pure sugar control, pH-adjusted hydrolyzate, and the hydrolyzate treated

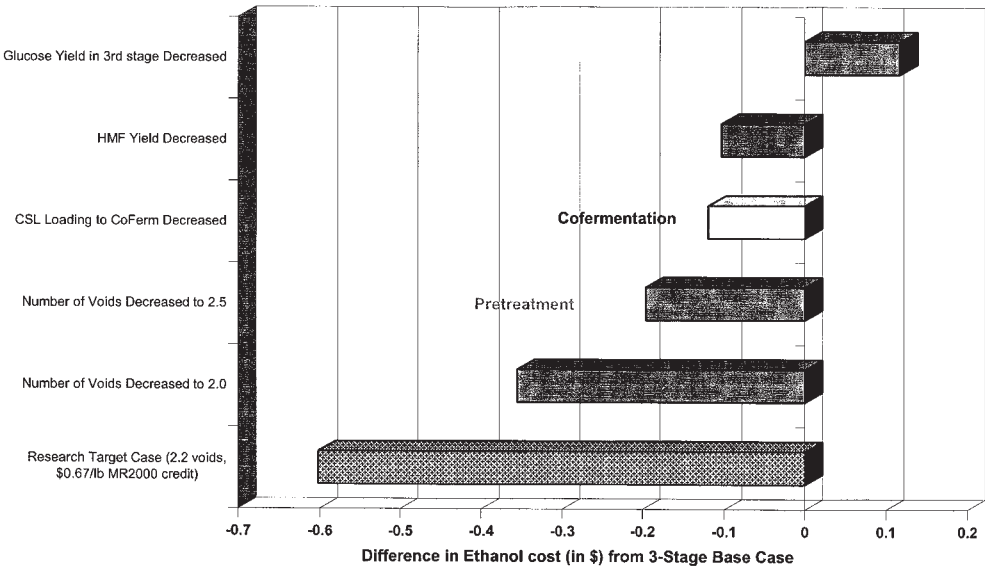


Fig. 6. Difference in cost between critical sensitivities and a three-stage (nonenzymatic) base case.

Table 1
Bench-Scale Verification of Target Values Predicated by ASPEN Plus Model

Parameter	Partial hydrolysis		Total hydrolysis	
	Target	Performance	Target	Performance
% Xylose solubilized	100.0	100.0	100.0	100.0
% Xylose recovered	95.0	97.0	95.0	97.0
% Glucose solubilized	55–60	57.3	100.0	100.0
% Glucose recovered	50–55	51.3	75–80	83.2
% Residual cellulose	35.0	35.2	0.0	0.0
Void volume	2.2	2.2	2.2	2.2

with MR2000 indicted that the pure sugar augmented with acetic acid and HMF had the highest conversion in the shortest time. No significant difference between the MR2000 treated and untreated hydrolyzate was observed, although greater than 90% of the soluble lignin was removed by the MR2000 adsorbent.

Discussion

A process model is created by developing engineering and research data that can be used to build a process design (Fig. 9). Integrating capital and operating cost with the process design results in a technoeconomic model that can be used as a tool to help to predict production cost. As different values for the variables are run, valuable information is gained on the

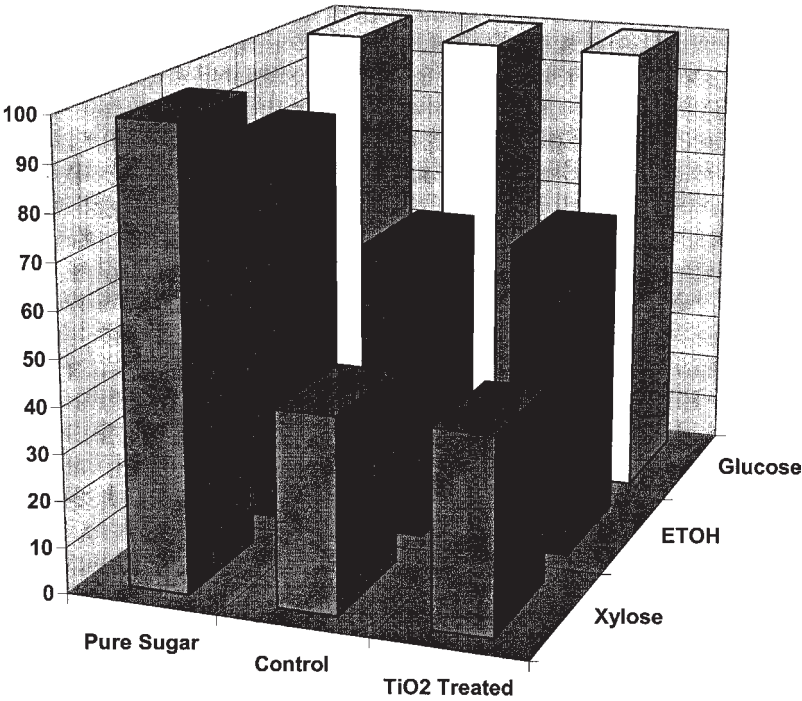


Fig. 7. Comparison of ethanol yields and sugar utilization in the fermentation of neutralized yellow poplar hydrolyzate vs pure sugar control spiked with acetic acid and hydroxymethyl furfural using *rZymomonas mobilis*.

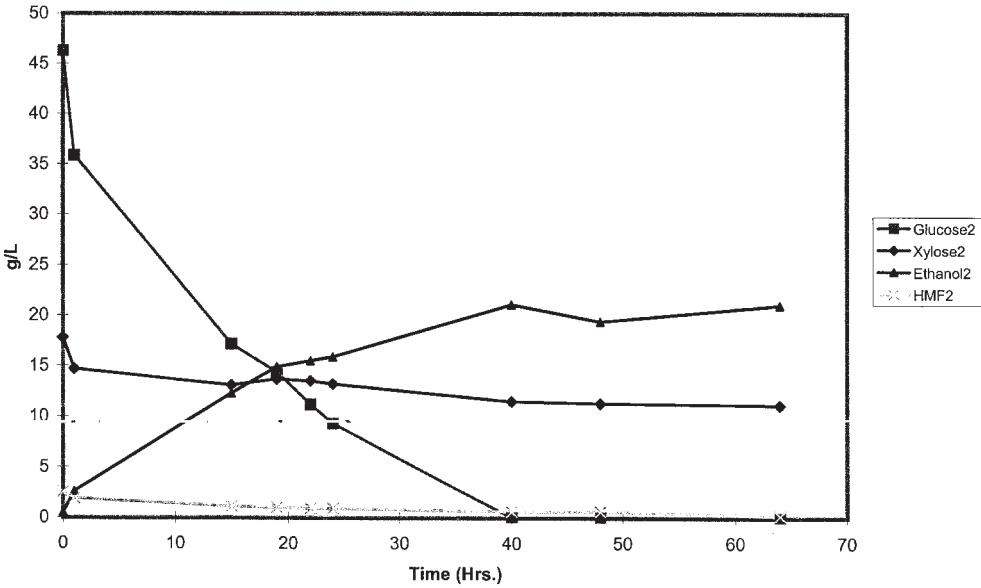


Fig. 8. Performance of *rZymomonas mobilis* in a batch fermentation using neutralized yellow poplar hydrolyzate.

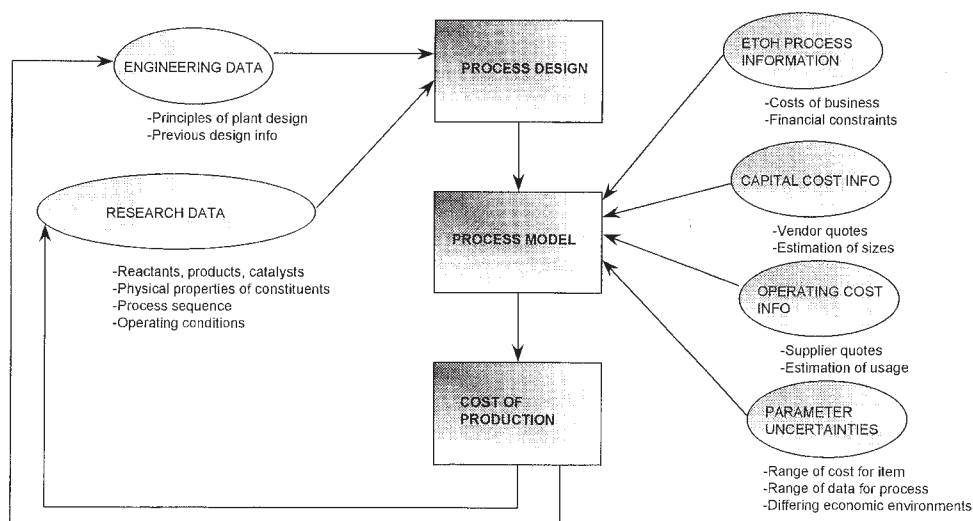


Fig. 9. How a process model is developed.

economic drivers and what target values are needed to achieve specific cost reductions. This iterative process helps select research direction and performance targets. The ASPEN Plus model discloses the interconnection between the process variables and the process operations. The liquid to solid ratio is the single largest variable affecting the total hydrolysis process economics. This interrelationship of the liquid-solid ratio can be seen throughout the entire process in terms of:

1. Increased steam consumption. Increasing the amount of liquor used during pretreatment correspondingly increases the amount of steam needed to bring the larger volume of material to reaction temperature, increasing energy costs.
2. Increase in the capital and operating cost for fermentation. Increasing the liquid solid ratio during pretreatment reduces the sugar concentration. This increases the volume of liquid sent to fermentation, requiring larger fermentors with additional operating and capital costs.
3. Reduced ethanol concentration resulting from reduced sugar concentration, as the ethanol concentration drops the energy requirements for the distillation unit increases.
4. Increase in the amount of spent beer that needs to be processed, increasing capital and operating cost for the waste-treatment unit operation.

The model indicates that reduced xylose yields from fermentation do not affect the process as greatly as pretreatment yields of sugars. This paradox is best explained in light of the energy requirements for the process. Unfermented carbon from fermentation has the potential to produce energy during anaerobic waste processing, which produces methane as an end

product. Although our xylose utilization was less than the target value, the overall affect was not as significant because of the additional methane produced for steam generation helped to offset the loss in ethanol yield from xylose. It is likely that more efficient heat integration and refinements in the shrinking-bed reactor concept will increase the overall benefit of higher fermentative ethanol yields.

Although the nutrient usage was found to impact the production cost, no optimization of the fermentation process was attempted. The primary focus was to demonstrate that *rZ. mobilis* could ferment the sugars in the hydrolyzate in 48 h without significant detoxification of the hydrolyzate. The ethanol yields from our pure sugar control, augmented with identical HMF and acetic-acid concentrations of the experimental hydrolyzate, were the highest. We have yet to explain the difference in ethanol yields of the pure sugar augmented with identical HMF and acetic-acid levels with the yields from the untreated hydrolyzate. Even when compared to the hydrolyzate treated with the lignin adsorbent, the pure sugar yields are still the highest. Although furfural is produced during the pretreatment, it is flashed off during the oligomer hold step, along with any other potential toxin having a high vapor pressure. A yet uncharacterized chemical or a secondary level of toxicity related to a combination of minor chemical constituents may be the cause for this affect. This may specifically target the pentose metabolism of *Zymomonas* (13), affecting the ethanol yield from xylose. Further research is directed to reducing nutrient usage, increasing xylose utilization, and developing alternative reactor configurations.

A dilute-acid total hydrolysis process has been developed at the bench-scale level that recovered over 83% of the potential glucose and 95% of the potential xylose from yellow poplar sawdust with reasonable sugar concentrations by employing the continual shrinking-bed reactor concept. The experimental conditions provided the basis for a process design that was modeled using ASPEN software coupled with an Excel spreadsheet to determine ethanol production cost. Several sensitivities were run that identified addition of a third stage, liquid to solids ratio (void volume), glucose yield from pretreatment, nutrient cost, and lignin adsorbent costs as major variables affecting the process economics. Target values were set for the variable and were verified in bench-scale research. The results of the bench-scale research and modeling efforts indicate that a total hydrolysis pretreatment is a viable process for bioethanol production. A two-stage engineering reactor using a co-current prehydrolysis as the first stage and a countercurrent shrinking bed as the second stage is currently under design.

Acknowledgments

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