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High-Temperature Acid Hydrolysis of Cellulose for Alcohol Fuel Production

John D. Wright

Solar Energy Research Institute
A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

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PREFACE

This report describes the economics of fuel alcohol production by the high-temperature dilute acid hydrolysis of cellulosic materials. It is the first of a series of evaluations that will cover alternative acid hydrolysis processes (percolation and concentrated acid processes), enzymatic hydrolysis processes, ethanol-water separation methods, and by-product production and utilization. All reports will use similar assumptions, so that processes can be compared and important research areas identified.

The study was carried out by John Wright of the Solar Fuels and Chemicals Research Division's Technical Evaluation and Planning Group. The efforts of Matthew Yu, a summer intern, in modifying and running the simulation code, were critical to the completion of this project.

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SUMMARY

Objective

Parametric analyses of high-temperature, dilute-acid hydrolysis of cellulose were carried out to determine the effect of hydrolysis parameters and processing schemes on the selling price of ethanol, and to estimate the potential economics of such processes.

Discussion

Analyses were conducted using a simulation model that calculates mass and energy balances, estimates the capital cost of the plant, and determines the selling price of ethanol. All plants were designed to produce 50 million gallons per year from either a corn stover or aspen wood feedstock. The feedstock was subjected to prehydrolysis and hydrolysis to convert the cellulosic components to sugars. The sugars stream was neutralized and fermented, and the ethanol was purified by distillation. Approximately half of the selling price of ethanol is due to capital-related charges and half to operating costs (primarily feedstock costs.)

The solids concentration entering the reactors was the most important determinant of the cost of ethanol. Solids concentrations of approximately 30% by weight will need to be handled to make an attractive process. The cost of ethanol was affected very little by the use or exclusion of a prehydrolysis step, by the rate of recycling, and by small variations in the hydrolysis reactor parameters. Development of a yeast capable of fermenting xylose would decrease the product cost by approximately 30%. By-product credits for furfural could have a large impact if markets are available because furfural, a high-value product that can be produced as rapidly as ethanol, can be recovered and purified with little additional investment.

While the estimated uncertainty in the cost of ethanol is about ±30%, it should be noted that if a 30% solids feed stream can be handled, the predicted selling price of ethanol is about $1.50/gallon. This price, achieved with realistic feedstock costs ($20/ton for aspen wood and $30/ton for corn stover) and without by-product credits, is on the same order as the cost of ethanol from corn or chemical feedstocks.

Conclusions

The solids content of the processing streams is the most important processing parameter. Xylose fermentation has the potential to further reduce the cost of ethanol by 30%. Sales of furfural and lignin by-products could significantly reduce the selling price of ethanol if markets are available. The price of ethanol was not greatly affected by prehydrolysis, unreacted solids recycle, or small changes in hydrolysis conditions. The predicted selling price of $1.50/gallon, while subject to an uncertainty of approximately ±30%, is of the same magnitude as that for ethanol produced from corn or petrochemical feedstocks.

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SECTION 1.0

INTRODUCTION

In the past decade, a concerted effort has been made to develop renewable alcohol fuels (primarily methanol and ethanol) as substitutes for gasoline. Ethanol may be used as an octane enhancer, as a fuel extender when blended with unleaded gasoline, or burned as a neat fuel.

The technology for the combustion of ethanol in automobile engines is well developed. Gasohol, a 10% ethanol-90% gasoline mixture may be burned in automobile engines that have not been adjusted or retuned. In Brazil, a large percentage of the new cars sold are designed to burn ethanol. The primary reason for the low consumption of ethanol as a fuel in the United States is its price. In mid-1982, the average bulk price of unleaded gasoline was \$1.00/gal, while that of ethanol made from corn was approximately \$1.60/gal at the production plant gate. Additionally, gasoline has a gross heating value of 32,990 kJ/L (124,800 Btu/gal), compared to ethanol's 22,204 kJ/L (84,000 Btu/gal).

Mankind has known how to produce ethanol (grain alcohol) for at least 4000 years. All that is required is for yeast to be added to a solution of sugar (glucose) and water. Because of the inhibitory effect of ethanol on yeast, glucose-water solutions can be fermented to a maximum concentration of approximately 10%-15% ethanol by weight. In order to concentrate the ethanol to a point where it can be burned, it is necessary to remove the water by distillation or one of the newer alternate technologies (solvent extraction, supercritical extraction, adsorption, absorption, membrane separation, etc.).

The simplest way to produce ethanol is to use sugar cane or sugar beets as a feedstock and to wash them in hot water to extract the sugar. Yeast is added to ferment the glucose/water solution, and the ethanol is purified by distillation. The process is a large energy consumer but makes almost complete use of the sugar. With sugar costs of approximately \$0.22/kg (\$0.10/lb) and 100% of the theoretical conversion efficiency, the sugar contributes \$0.34/L of ethanol (\$1.29/gal). The costs for return on investment, depreciation, operating costs, overhead, etc. must be added to this cost. The resulting ethanol selling price is approximately \$0.66/L of ethanol (\$2.50/gal) (Weiss and Mednick 1982). Therefore, research will not lower the cost of ethanol from sugar crops significantly.

Fermentation alcohol is presently made from corn. Corn is approximately 80% starch (carbohydrate), which is a polymer of glucose. With corn costs on the order of \$0.11/kg, the cost of raw materials is \$0.81/gal of ethanol. The final selling price of ethanol is approximately \$0.42/L (\$1.60/gal). Because the process is highly refined and largely dependent on the cost and availability of corn and on credits for coproducts such as distillers' dried grains, additional research will only slightly reduce the selling price of ethanol from corn.

Cellulose (from wood or crop residues) is also a polymer of glucose. However, its cost is much lower than feedstocks from food crops such as sugar cane, sugar beets, and corn. For example, aspen wood chips are available at a cost of approximately $0.022/kg ($20/ton). This is equivalent to $0.076/kg of glucose or, at 100% of theoretical conversion efficiency, $0.12/L of ethanol ($0.45/gal). Thus, utilization of cellulosic feedstocks offers the potential for reducing the cost of ethanol to a competitive level. Additionally, because cellulosic feedstocks do not have a food value, the potential for competition between food and fuel uses is reduced.

The structure of cellulose is more resistant to degradation than that of starch, and the breakdown (hydrolysis) of cellulose to sugar can be a difficult and expensive process. It is primarily this step that requires research if the production of ethanol from wood or crop residues is to compete successfully with fossil fuels or with more expensive starch or sugar feedstocks that are easier to process.

The hydrolysis of cellulose may be accomplished by either acid or enzymatic processes. Acid processes are relatively fast, requiring residence times in the hydrolysis reactor from 6 seconds to a few hours. However, the advantage of rapid acid hydrolysis is somewhat offset by its low yields (50%-75% of theoretical), expensive materials of construction, and the high temperatures and pressures required in some systems. Enzymatic processes are considerably slower, requiring reaction times of a day or more, but potentially offer yields approaching theoretical, and can be carried out at atmospheric pressure and low temperature in inexpensive vessels.

This report provides a parametric analysis of acid hydrolysis processes that use dilute acids, high temperatures, and short residence times. The analyses examine the effect of processing variations on yield, capital cost, and overall process economics.

SECTION 2.0

OBJECTIVES AND SCOPE

The primary objective of this report is to describe the effect of various acid hydrolysis processing configurations on the selling price of ethanol. The report covers processes that can be described by the kinetic models derived by Saeman (1945) and Grethlein (1980, 1981). These processes operate at high temperature (140°-240°C) and high pressure (1.4-4.1 MPa or 200-600 psia), with dilute acid concentrations (0.5%-1.5% by weight) and short residence times (6-60 s). The emphasis is on determining how hydrolysis configurations and conditions affect the overall economics of ethanol production. The effects of variations in reactor temperature and pressure, residence time, and acid concentration are illustrated, and the effect of using prehydrolysis and recycling unreacted solids is presented. Solids concentration entering the prehydrolysis and hydrolysis reactors is varied. These studies are conducted with both aspen wood (typical of many woods) and corn stover (typical of crop residues) as feedstocks. Finally, the effect on hydrolysis of using the five-carbon sugar (xylan) fraction is studied. The selling price of ethanol is used to compare the relative merits of the different processing options.

A secondary objective of this report is to estimate the ultimate potential of the acid hydrolysis process for the production of ethanol from cellulose. To this end, preliminary estimates are made of the impact of xylose utilization, lignin extraction, and furfural recovery.

The primary tool in the analysis is an acid hydrolysis simulation model developed by Chem Systems Inc. (1981a and 1981b). This computer model performs material and energy balances on user-defined acid hydrolysis systems and computes the capital investment, operating costs, and the selling price of ethanol.

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SECTION 3.0

FEEDSTOCK CHARACTERISTICS

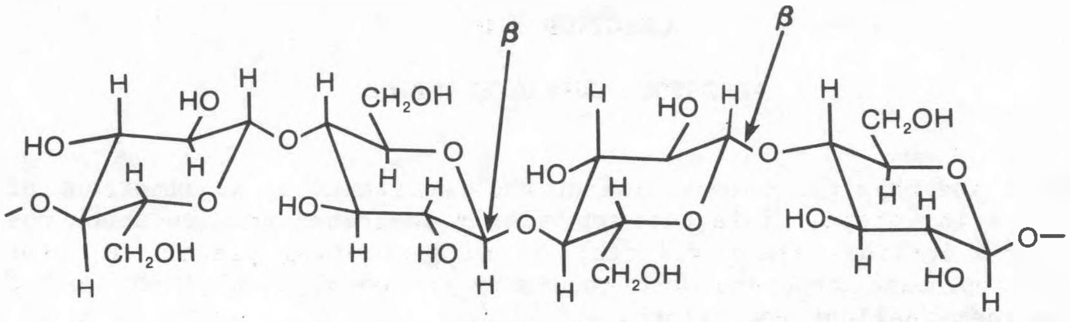
The chemical and physical composition of the feedstock has an important effect on the processing steps. This section briefly describes the feedstock characteristics and outlines their effects on the processing plant. For further information on the structure and chemistry of wood, Fan (1980) and Wenzl (1970) provide excellent references.

The compositions of corn stover and aspen wood are shown in Table 3-1. The single largest component of any biomass feedstock is water. Water adds to the weight of the biomass that must be collected and shipped to the processing plant. Because water is inert, it lowers the value of a feedstock sold by weight.

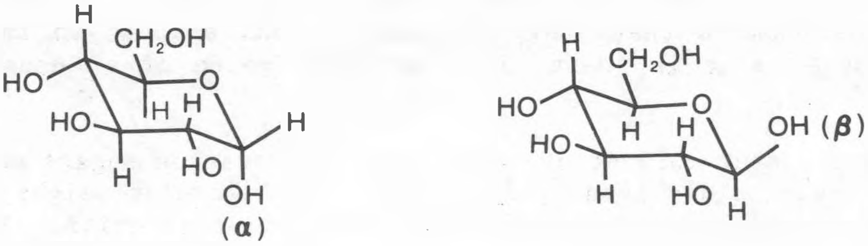
Cellulose is a linear polymer of D-glucose (a six-carbon sugar) molecules held together by β-glycosidic bonds (Fig. 3-1). The molecular weight of cellulose is approximately 400,000, corresponding to 2800 glucose units. The cellulose fibers are arranged in bundles of parallel chains in which adjacent chains are bound together by hydrogen bonding between hydroxyl groups. This large-scale structure results in a crystalline material with great mechanical strength and high chemical stability. Because the C-O glycosidic bond is the weakest in the chain, it is possible to break (hydrolyze) the polymer into its component sugars. However, the hydrolysis of crystalline cellulose requires high temperatures and strong acids in order for the reaction to proceed at an appreciable rate. The harsh reaction conditions also degrade the desired product (glucose). Therefore the hydrolysis of cellulose involves a search for the optimum conditions in which the ratio of glucose formation rate to glucose degradation rate is maximized.

Table 3-1. Feedstock Composition

Component	Field Dry Corn Stover (wt %)	Aspen Wood (wt %)	Molecular Weight
Water	30.7	50.0	18
Crystalline cellulose	22.5	20.7	n x 162
Amorphous cellulose	3.9	3.7	n x 162
Pentosan } Hemicellulose	16.1	10.9	n x 132
Hexosan } Hemicellulose	6.5	4.4	n x 162
Carbohydrates	5.3	0.0	n x 342
Insoluble lignin	7.0	8.3	
Insoluble protein	3.0	0.0	
Ash	3.9	0.1	
Extractives	1.1	1.9	
Total	100.0	100.0	



Cellulose Chain



α-D-Glucose β-D-Glucose

Figure 3-1. Chemical Structure of a Cellulose Chain, α-D-glucose, and β-D-glucose

Because polymers inevitably have chain ends and occasional bends or kinks in the chain, the crystal lattice is disrupted in some regions. These amorphous regions comprise approximately 15% of the cellulosic structure and are more open and therefore more susceptible to attack than the densely packed crystal structure. The rate of hydrolysis is much greater in the amorphous cellulose than in the crystalline cellulose.

Hemicellulose is a polymer made up mainly of D-xylose (a five-carbon sugar) and D-glucose, with lesser amounts of D-manose, D-galactose, l-arabinose, and organic acids. For the purpose of the simulation model, hemicellulose is considered to consist solely of hexosans (glucose) and pentosans (xylose). Unlike cellulose, which always has the same structure and composition, hemicellulose has a structure and composition that can vary widely from species to species. Individual polymer chains contain from 50 to 100 simple sugar units. Because the individual chains of hemicellulose are branched and have no regular long-term structure, hemicellulose is not crystalline in structure like cellulose. Therefore, the hemicellulose is readily hydrolyzed.

Carbohydrates (starch) are also polymers of glucose. However, in carbohydrates the glucose molecules are held together by α-glycosidic bonds (Fig. 3-2). Starch consists of both linear polymers (amylose) and branched polymers (amylopectin). Amylose has a molecular weight of 10,000-50,000 (60-300 glucose units) and amylopectin has a molecular weight of 50,000-1,000,000 (300-6,000 glucose units). Because the shape of the α-glycosidic bond does not allow for packing that is as close as in the β-bond, and because of the branched structure of amylopectin, starch is amorphous and may be rapidly hydrolyzed.

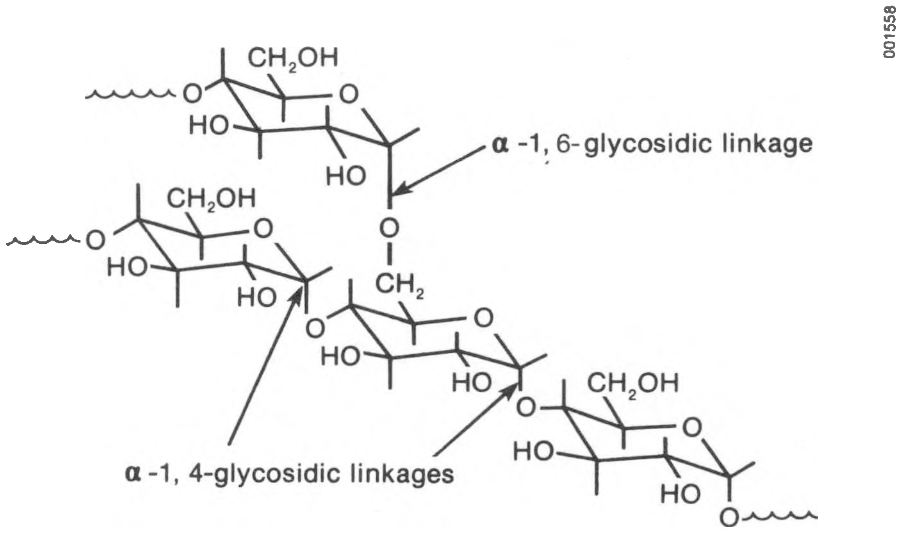


Figure 3-2. Chemical Structure of Amylopectin, a Component of Starch (Carbohydrate)

Because of the nature of glycosidic bonds (α and β), man is able to digest starch but not cellulose, even though both are glucose polymers. Man and other carnivorous animals do not produce the enzymes (β-amylases) necessary to hydrolyze the β-glycosidic bond. This is the reason for the high value of starch crops (such as corn and wheat) and the low value of cellulosic materials.

Lignin is a branched polymer based mainly on the phenylpropane unit. It occurs in an amorphous state mixed with hemicellulose in a layer surrounding the cellulose (cell wall). The exact structure of lignin is not known, but it serves to protect the cellulose from attack, both in nature and in fuel conversion processing. Lignin passes through the hydrolysis reactor essentially unchanged, as do insoluble protein, extractives, and ash.

The physical structure of a softwood is shown in Fig. 3-3. The tracheids contain the fibers of cellulose and are separated from each other by mixed layers of hemicellulose and lignin. The cells of wood are separated by middle lamella, where the bulk of the lignin is located.

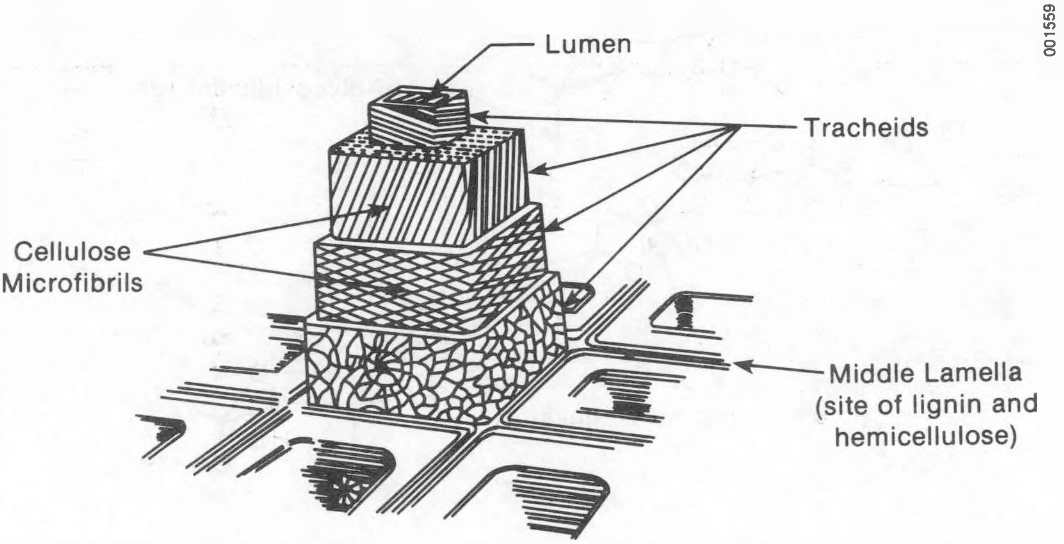


Figure 3-3. Cross-Section Showing Structure of a Softwood

SECTION 4.0

PROCESS DESIGN

In this section an overview of the entire cellulose-to-ethanol process is presented. Next, a more detailed description is provided of each of the major processing steps. This base case design for a plant producing 50 million gallons of ethanol per year is described in a report by Chem Systems Inc. (1981a).

4.1 OVERALL PROCESS DESCRIPTION

The overall processing schematic for the conversion of cellulosic feedstocks to ethanol is shown in Fig. 4-1. While the sizes of equipment and actual processing conditions will vary slightly with the feedstock processed, the layout of the facility will remain unchanged.

The feedstock, whether wood chips, corn stover, or other cellulosic feedstock, is shredded to approximately 1.6 mm in diameter (10 mesh) to make handling easier and to increase the surface area. The shredded particles are mixed with water and sent to the prehydrolysis unit.

The prehydrolysis reactor operates at 140°C (284°F) and 0.5 wt % sulfuric acid. These conditions are sufficient to hydrolyze almost all of the amorphous cellulose and hemicellulose (pentosans and hexosans) yet are mild enough that the sugars produced are not degraded into furfural and hydroxy methyl furaldehyde (HMF). The stream leaving the reactor consists of water, the sugars (glucose and xylose) produced from the hydrolysis of the amorphous fractions of the feed, and unreacted crystalline cellulose and lignin. This stream is washed and centrifuged to remove the sugars. The sugars are soluble and leave with the wash water, while the unreacted solids are sent on to the hydrolysis unit.

The hydrolysis reactor operates at the more severe conditions of 235°C (455°F) and 1.0 wt % acid with a residence time of approximately 12 seconds. These conditions are severe enough to hydrolyze approximately 75% of the crystalline cellulose to glucose. However, the conditions are so severe that they further degrade a third of the glucose produced to 2-hydroxy methyl 5-furaldehyde. Therefore, a typical conversion of crystalline cellulose to glucose in a single pass through the hydrolysis reactor is approximately 50%. The product stream from the reactor is flashed to quickly reduce its temperature and then washed, centrifuged, and filtered to remove the soluble sugars from the unreacted solids. The unreacted solids are used as feed for a 4-MPa (600-psia) steam boiler to provide heat for the process.

The sugar-water solutions from prehydrolysis and hydrolysis are neutralized. The prehydrolysis step contributes approximately 45% of the glucose, and the hydrolysis step contributes 55%. The solution is neutralized by the addition of calcium hydroxide, which reacts with the sulfuric acid to produce calcium sulfate and water. The calcium sulfate sludge is removed by filtration and sent to waste disposal. The neutralized sugar solution moves to the fermenter.

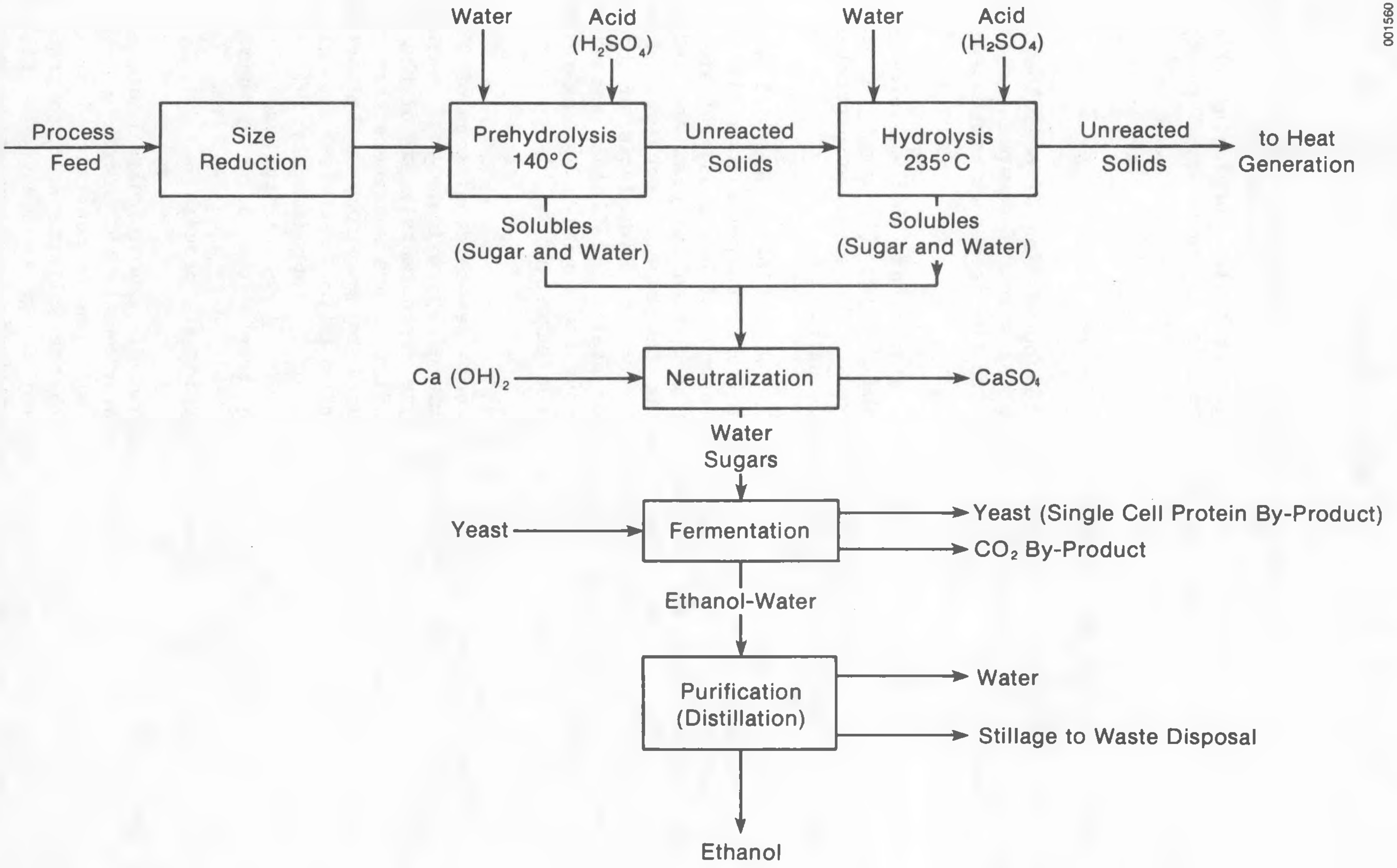


Figure 4-1. Cellulose-to-Ethanol Overall Processing Plan

The neutralized sugar solution is passed through columns of activated carbon to remove any toxic materials. The treated solution is then sent to the continuous fermentation trains, where yeast converts the glucose into ethanol and carbon dioxide. The carbon dioxide is recovered, cleaned, liquefied, and sold as a by-product. Spent yeast is recovered and sold as a single cell protein animal feed. The liquid stream containing mainly water, ethanol, and unconverted five-carbon sugars is sent to the purification section.

The ethanol is concentrated to 94 wt % in the overheads of a distillation column. The bulk of the water and stillage (five-carbon sugars and other compounds) is removed at the bottom of the column, and sent to waste disposal. The overheads are sent to a dehydration column, which uses a benzene azeotropic distillation column to remove the water and produce an anhydrous (100%) ethanol product.

4.2 DETAILED PROCESS DESCRIPTIONS

4.2.1 Prehydrolysis

The cellulosic feedstock from raw material storage is fed to a shredder that reduces the feed to approximately 1.6-mm-diameter particles (10 mesh) to increase the surface area and allow for easier handling. The shredded feed is then sent to the prehydrolysis section where the amorphous cellulose and the hemicellulose (pentosans and hexosans) are hydrolyzed under mild conditions.

Because the crystalline cellulose is highly resistant to chemical attack, severe conditions are needed to hydrolyze it. At the temperatures in the hydrolysis reactor, the glucose and xylose form almost instantly from the hemicellulose and amorphous cellulose, which are largely destroyed by the time the crystalline cellulose is converted. The prehydrolysis reactor uses relatively mild conditions, which are strong enough to hydrolyze the amorphous components but are still benign enough that the resultant sugars undergo only slight degradation. The kinetic expressions that describe these reactions are the same as those that govern the hydrolysis reactor and are described in detail in Sec. 5.0.

The prehydrolysis step is shown in Fig. 4-2. The ground solids are diluted to a specified concentration in a mixing tank. Acid is added to the solids and allowed to soak into the particles. By allowing the acid to permeate the particles before they are heated to reaction temperature, diffusion of acid into the particles will not limit the initial rate of the prehydrolysis reaction. The solids proceed into the plug-flow reactor, where they are rapidly heated to 140°C by the injection of 1.3-MPa (200-psia) steam. The solids remain in the reactor for one minute and are flashed to atmospheric pressure through an orifice. Control of the flow rate, rapid heating with steam, and virtually instantaneous quenching of the reaction with the flash allow precise control of the reaction time.

The flash drum effluent is sent to the first centrifuge, where solubles (water, glucose, and xylose) are removed. The solids from the first centrifuge are diluted (repulped) and centrifuged again to remove a greater percent-

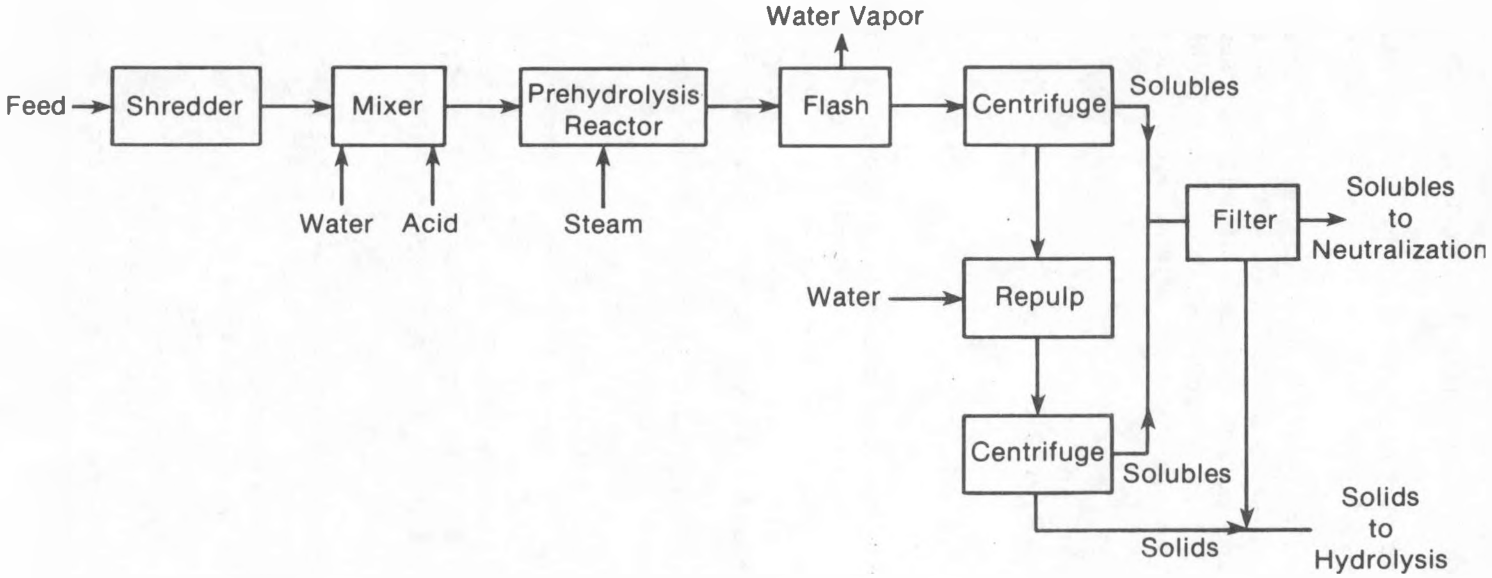


Figure 4-2. Size Reduction and Prehydrolysis Sections

age of the solubles. They are filtered to remove carried-over solids and are sent to neutralization. The solids (primarily lignin and crystalline cellulose) from the filter and the second centrifuge are sent to the acid hydrolysis section.

4.2.2 Hydrolysis

The hydrolysis process (Fig. 4-3) converts crystalline cellulose to glucose and HMF and separates the soluble sugars from the lignin and remaining unreacted crystalline cellulose. The glucose/water stream is sent to neutralization, and the unreacted solids are used as boiler fuel or recycled. The hydrolysis kinetics are discussed in detail in Sec. 5.0.

The hydrolysis process is identical to the prehydrolysis process except for the more severe conditions and the provision for solids recycling. The solids are mixed with acid and water, heated with 4.04-MPa (600-psia) steam to 235°C (455°F), and held for 12 s. The products are flashed and the solubles separated in the centrifuge/filter. The unreacted solids are split: part are mixed with the reactor feed, and part are used as boiler fuel. Recycling increases the overall conversion efficiency of the hydrolysis section. The hydrolysis and prehydrolysis sections are the primary energy consumers at the plant. Direct condensation and flash cooling are not energy-efficient processes, but they are necessary for the good control over the reaction time necessary to produce high yields.

4.2.3 Neutralization

In the neutralization step (Fig. 4-4) the sugar solutions from the prehydrolysis and hydrolysis processes are neutralized with calcium hydroxide [$Ca(OH)_2$] to the proper pH for fermentation. Neutralization is exothermic and takes place at 120°C (248°F). The resultant solution has a pH of 4.0 (the pH preferred by the fermentation yeasts). The product stream is flashed to atmospheric pressure, filtered to remove the calcium sulfate ($CaSO_4$) sludge formed during the neutralization reaction, and sent to fermentation.

4.2.4 Fermentation and Carbon Dioxide Recovery

The fermentation step (Fig. 4-5) has three parts: detoxification, fermentation, and carbon dioxide (CO_2) recovery. The ethanol stream produced in the continuous cascade fermenters is sent to purification. CO_2 is recovered, liquefied, and sold as a by-product. A yeast purge stream is sold as single-cell protein (SCP) animal feed.

The neutralized sugar solution is passed through columns of activiated carbon to remove HMF, furfural, and any other trace degradation products that may be toxic to the yeast. The furfural assumed to be removed in the carbon beds could be removed in an earlier step and profitably sold as a by-product.

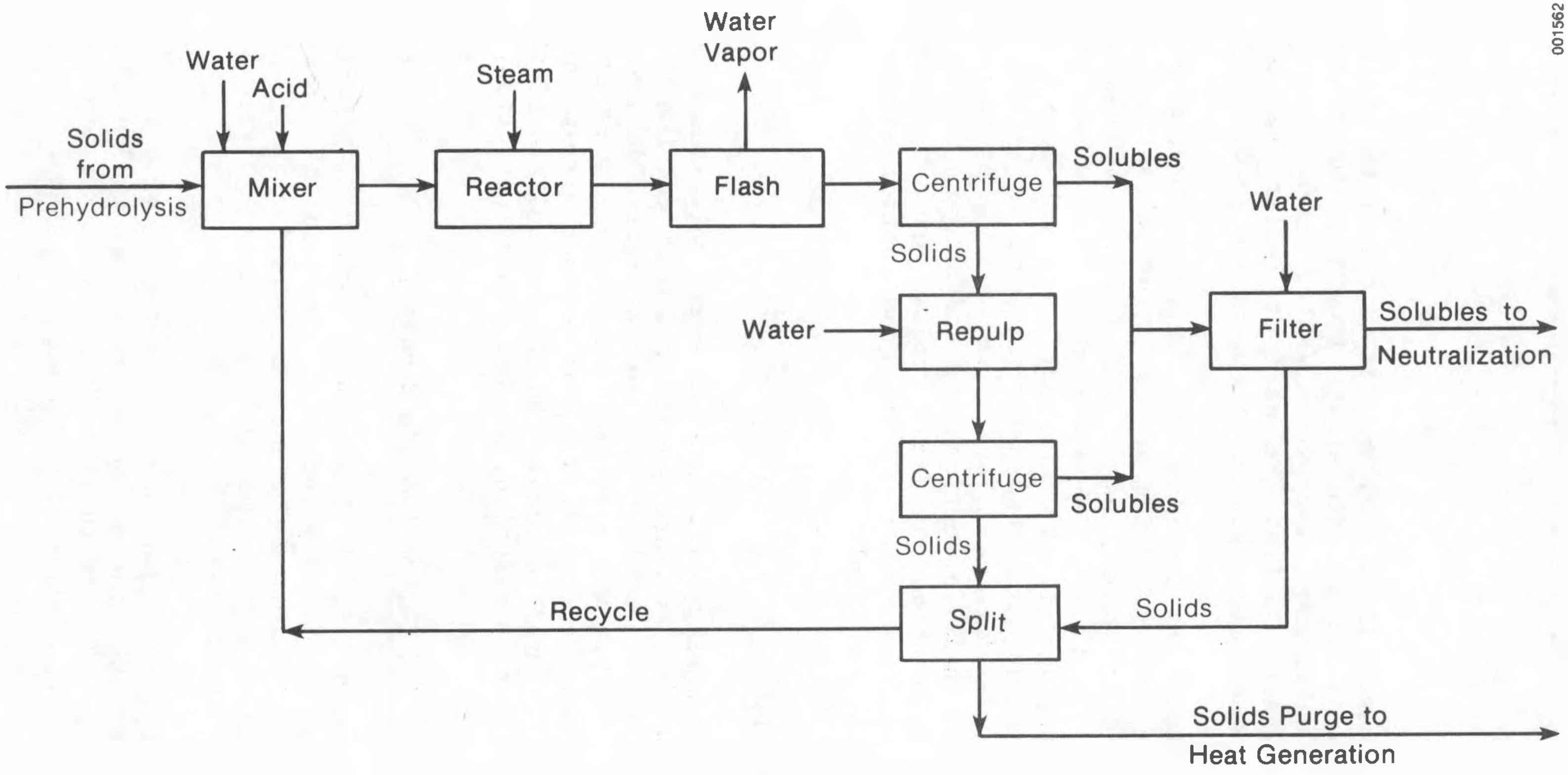


Figure 4-3. Hydrolysis Section

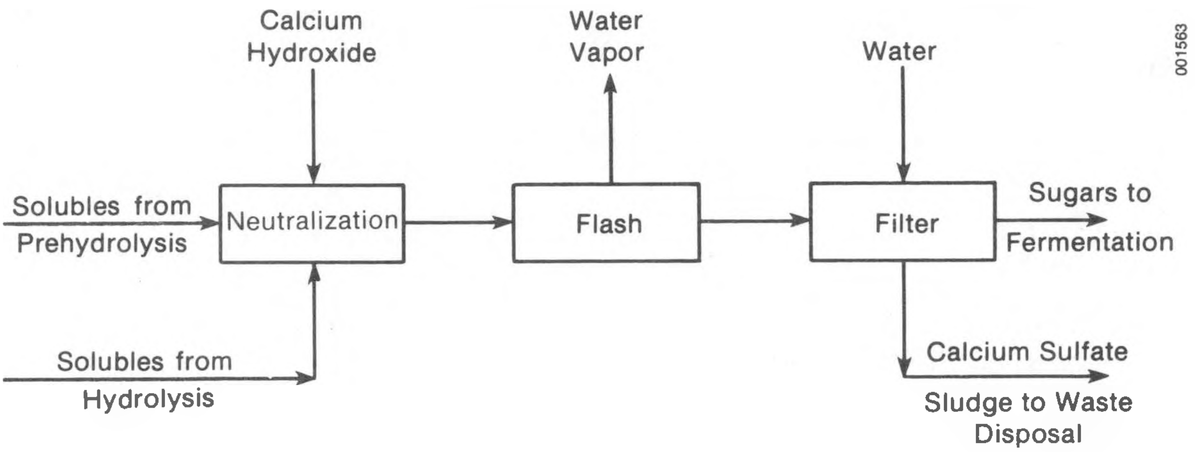


Figure 4-4. Neutralization Section

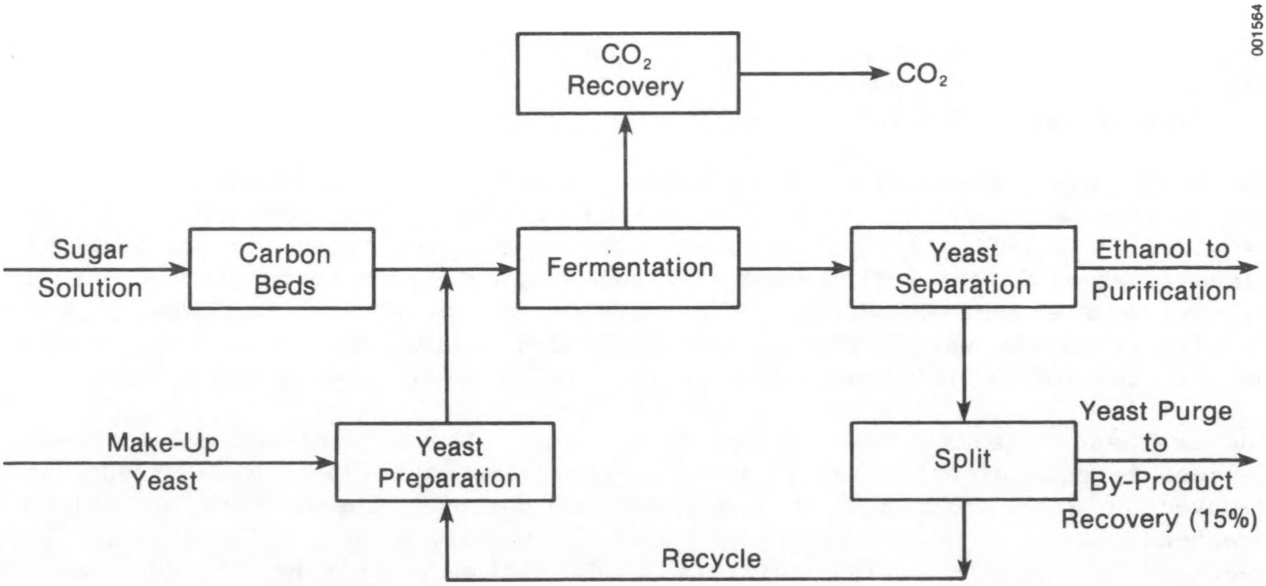


Figure 4-5. Fermentation Section

Fermentation is carried out at 30°C (85°F) in a continuous cascade scheme. The fermentation time is 24 hours. Ninety-five percent of the glucose is converted by the yeast to ethanol and carbon dioxide as shown in the following reaction:

$$\underset{(180)}{C_6H_{12}O_6} \rightarrow \underset{(46)}{2C_2H_5OH} + \underset{(44)}{2CO_2} \quad .$$

In this reaction, 51 wt % of the glucose is converted to ethanol and 49 wt % to CO_2. Three percent of the glucose is converted to glycerol, and 2% is converted to yeast. The yeast grows 10% during the cycle. Eighty-five percent of the yeast is recycled to the reactor, and the remainder is sold as a single-cell protein by-product. The concentration of yeast in the fermenter is augmented with fresh yeast to 9 wt % of the total glucose input. The xylose passes through the fermenter unchanged. The xylose is not fermentable with existing yeasts and passes through the fermenter unaffected.

The fermenters used are closed vessels. The CO_2 is scrubbed with water to remove soluble impurities and then compressed to 2.02 MPa (300 psia). The compressed gas is passed through beds of activated carbon to remove any remaining impurities. The gas is chilled, dried on a dessicant bed, liquefied, and then sold as a by-product.

4.2.5 Ethanol Purification

The ethanol-water stream from the fermenter is concentrated to the 94 wt % ethanol/6% water azeotrope in a beer still and then dehydrated to produce anhydrous ethanol by a ternary benzene distillation (Fig. 4-6). The aqueous stillage (mainly water and xylose) is sent to the waste ponds. Steam usage is minimized by heat integration.

The beer from fermentation is preheated with various processing streams and enters the rectification column (beer still). Heat to run the beer still is provided by 1.3-MPa (200-psia) steam. The upper part of the column utilizes sieve trays while the bottom uses disk and doughnut trays to handle the water, xylose, and suspended solids. The aqueous bottom stream (stillage), containing primarily water, xylose, and suspended solids, is sent to waste disposal. The column overhead stream is the binary water-ethanol azeotrope.

The overhead streams from the beer still enter the dehydration column where benzene ternary distillation is used to break the azeotrope. Pure ethanol is removed from the bottom of the dehydration column. The dehydration column overhead stream is a tertiary azeotrope of ethanol, water, and benzene. The overhead streams from the dehydration and stripping columns are condensed. Upon condensation the stream separates into aqueous and organic components. The stream goes to a decanter from which the organic component (containing benzene, ethanol, and a small amount of water) is returned to the dehydration column, and the aqueous component (primarily water with small amounts of benzene and ethanol) is returned to the stripping column. The remaining water is separated from the benzene and ethanol in a stripper column. The aqueous bottoms from the stripping column are sent to waste-water treatment. The heat required for the dehydration and stripper columns is cascaded from the beer still, and the azeotropic distillation therefore does not require additional energy.

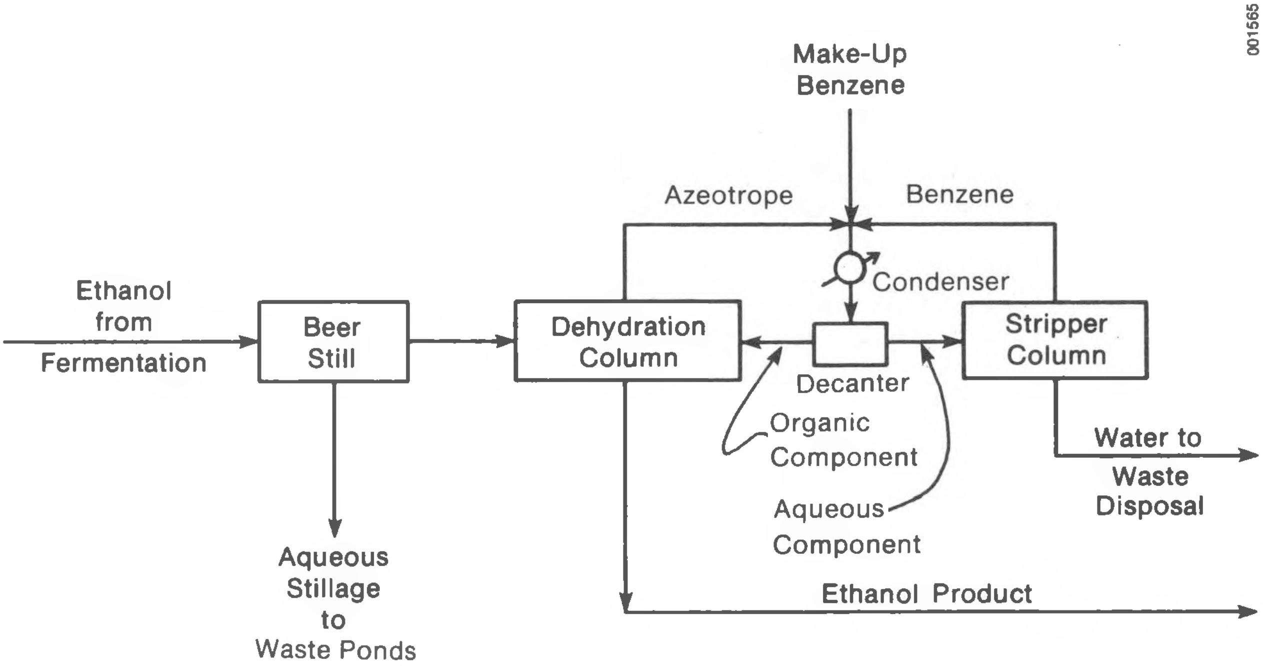


Figure 4-6. Purification Section

4.2.6 Offsite Facilities

Offsite facilities are those required to operate a plant, but they are not directly involved in the chemical processing. They include heat generation, waste disposal, storage for raw materials and products, and the various utilities.

In the heat generation block the unreacted solids from the hydrolysis reactor (mainly lignin and unreacted crystalline cellulose) are neutralized, dried to 50% solids, and burned in the lignin boiler to produce 4.04-MPa (600-psia) steam. The lignin boiler is sized to dispose of the entire hydrolysis purge stream. The high-pressure steam provides heat for the hydrolysis reactor. Excess steam is throttled to 1.35 MPa and used to heat the prehydrolysis reactor and distillation section and to dry the boiler feed. If excess steam is available after the plant load is met, it is sold as a by-product at a price competitive with steam generated by a coal boiler, or at a lower price based on the value of the unreacted solid feed. If the lignin boiler is not large enough to supply the plant demand, a coal boiler with flue gas desulfurization is added to supply the necessary stream. The boilers comprise the single largest capital investment in the plant.

The aqueous stillage and various condensed flash vapors are collected and sent to a waste treatment pond. Electrical and cooling water systems are sized to meet the plant load. Storage of ethanol, sulfuric acid, feedstock, and by-products is sized for two weeks' operation. Calcium hydroxide is stored in one-week quantities.

4.2.7 Other Options

Several possible options for pretreatment and processing that could be used with acid hydrolysis were not included in this analysis. These options include steam explosion and solvent delignification with ethanol, other pretreatments to remove lignin and further reduce the size of the particles entering the reactors, and combustion of the unfermented solubles.

Steam explosion and solvent delignification are feedstock pretreatments (before hydrolysis) that serve to reduce the size of the cellulosic feed and to recover a lignin stream that can be sold as a by-product. The size reduction function is not important in acid hydrolysis, where the rate of the hydrolysis reactions is not governed by the surface area available. However, in enzymatic hydrolysis, the reaction occurs at the particle surface, and such a pretreatment is essential. Delignification is also a useful pretreatment for enzymatic hydrolysis, because the presence of lignin also retards the hydrolysis rate. However, lignin has no adverse effect on acid hydrolysis. Therefore, the usefulness of solvent delignification depends on whether lignin can be produced as a by-product at a competitive price. Lignin has a fuel value of \$0.04/kg (\$0.02/lb), based on its energy content as a boiler fuel. The use of steam explosion and ethanol solvent extraction would set the breakeven lignin selling price at \$1.14/kg (\$0.52/lb) (Chem Systems Inc. 1981c). In this study, the value of lignin is set by its fuel value, and delignification is clearly uneconomic. However, if higher value markets exist, lignin may be a high value by-product.

An alternate process configuration would use the stillage (primarily xylose) from the bottom of the beer still as a fuel. However, this requires large and expensive multiple-effect evaporators to raise the solids concentration in this dilute stream to a level that will support combustion. However, it would also reduce the cost of waste treatment.

Another processing option would be to remove much of the excess water prior to the fermentation step. This process would reduce capital costs of the fermenter and the purifier as well as the energy required in purification. However, removal of excess water requires large, expensive, multiple-effect evaporators, which are also large energy users. Analyses by Chem Systems Inc. (1981c) suggest that it is more cost-effective to remove the water in the purification section after fermentation. Final resolution of this question must include the increased cost of waste treatment when additional large volumes of high biological oxygen demand (BOD) waste water must be processed.

SECTION 5.0

HYDROLYSIS OF CELLULOSE

The hydrolysis of cellulose in aqueous solution is a two-step heterogeneous reaction. Rapid protonation of the glucosidic bond is followed by the slow scission of the bond (McBurney 1954). Under different conditions the reaction appears to occur by different mechanisms.

Although the actual reaction is heterogeneous, Saeman (1945) showed that it could be modeled as a first-order homogeneous reaction where the cellulose concentration is expressed as a concentration of potential glucose. After the glucose is formed, the glucose is then degraded to HMF in a first-order homogeneous reaction. The reactions of xylose can be expressed in a similar manner.

The following expressions describe the hydrolysis and degradation reactions:

$$\text{crystalline cellulose} \xrightarrow{K_1} \text{glucose} \xrightarrow{K_2} \text{HMF}$$

$$\text{amorphous cellulose} \xrightarrow{K \simeq \infty} \text{glucose} \xrightarrow{K_2} \text{HMF}$$

$$\text{xylans} \xrightarrow{K \simeq \infty} \text{xylose} \xrightarrow{K_3} \text{furfural} \longrightarrow \text{tars}$$

where K_1, K_2, and K_3 are rate constants in units of min^{-1}.

The rate equations for the crystalline cellulose reactions are

$$\frac{dC_c}{dt} = -K_1C_c \tag{5-1}$$

and

$$\frac{dC_g}{dt} = K_1C_c - K_2C_g \ , \tag{5-2}$$

where

C_c = crystalline cellulose concentration expressed as a fraction of the potential glucose

C_g = glucose concentration expressed as a fraction of the potential glucose.

The conversion of amorphous cellulose and hexosans to glucose appears to proceed essentially instantaneously at high temperature. The potential glucose in the amorphous cellulose and hemicellulose can be assumed to be present at the beginning of the reaction. The rate equations can then be integrated to give the fraction of the potential glucose available at any time as

$$C_g(t) = C_c(0)\left(\frac{K_1}{K_1 - K_2}\right)\left[\exp(-K_2t) - \exp(-K_1t)\right] + C_g(0)\exp(-K_2t)\ , \qquad (5\text{-}3)$$

and the amount of crystalline cellulose remaining unreacted at any time as

$$C_c(t) = C_c(0)\exp(-K_1t)\ , \qquad (5\text{-}4)$$

where (0) is the fraction present at time = 0. A similar integrated kinetic expression can be written to give the amount of xylose remaining at any time:

$$C_x(t) = C_x(0)\exp(-K_3t)\ , \qquad (5\text{-}5)$$

where C_x is the fraction of potential xylan available as xylose.

The rate constants K_1, K_2, and K_3 are of the Arrhenius form:

$$K_1 = k_1A^m\exp(-E_1/RT)\ , \qquad (5\text{-}6)$$

$$K_2 = k_2A^n\exp(-E_2/RT)\ , \qquad (5\text{-}7)$$

and

$$K_3 = k_3A^p\exp(-E_3/RT)\ . \qquad (5\text{-}8)$$

The preexponential factors k_1, k_2, and k_3 have units of min^{-1}. The preexponential factors are multiplied by the acid weight fraction (A) raised to a power (m, n, p) to account for the effect of acid concentration on rate. E_1, E_2, and E_3 are activation energies expressed in cal/g mol, R is the gas constant, and T is temperature in K.

The parameters for these equations were evaluated for several different feedstocks by Grethlein (1981) and are presented in Table 5-1.

Because the reactions in Table 5-1 are all first-order reactions, they comprise a linear system and their responses can be added. For example, in Eq. 5-3 the first term is the contribution of the crystalline cellulose (including the degradation of the product sugars), while the second term represents the contribution of the amorphous cellulose (which is completely available initially and degrades with time).

Table 5-1. Kinetic Model Parameters

Parameter	Crystalline Cellulose Hydrolysis	Glucose Degradation	Xylose Degradation
k_1, k_2, k_3 (min^{-1})	5.33×10^{16}	3.84×10^{9}	8.78×10^{15}
m, n, p	1.14	0.57	1.00
E_1, E_2, E_3 (cal/g mol)	-36,955	-20,988	-33,560

It is instructive to look at the individual reaction curves as a function of time. The fraction of the initial glucose remaining is shown in Fig. 5-1 as a function of reaction time for 1% H_2SO_4 at different temperatures. This corresponds to the fraction of glucose from the amorphous components remaining after a given time. Even at 1% acid, the degradation is minimal at 140°C (the conditions in the prehydrolysis reactor). However, at 240°C, conditions similar to those in the hydrolysis reactor, 60% of the initial sugar is lost after the 12-s residence time.

Figure 5-2 shows the degradation of xylose as a function of time and temperature. The pattern is the same as for glucose, but the temperature dependence is more pronounced. At 140°C the degradation in 1 min is negligible, while at 240°C all of the xylose is degraded within 8 s.

The simulation program assumes that all the degraded xylose reacts to form furfural. In reality, the xylose degrades to form an intermediate product. The intermediate product degrades to furfural and tars, and the furfural reacts further to form additional tars.

The furfural degrades into two tars by polymerization and resinification. High yields of furfural are favored by higher temperatures and higher acid concentrations (Root, Saeman, and Harris 1959; Wenzl 1970).

The assumption that all degraded xylose is converted to furfural is acceptable if we are interested only in the amount of xylose produced in the hydrolysis. However, furfural can be a valuable by-product. If we are also interested in the yield of furfural, a better understanding of the kinetics is required. As a rough approximation, 70% or less of the xylose which is degraded is converted to furfural.

Because the hydrolysis of crystalline cellulose can be approximated as a first-order reaction, it can be presented in the same manner as the degradation of glucose and xylose (Fig. 5-3). Note that at 140°C, 1 min residence time, and 1% acid (conditions more severe than in the prehydrolysis reactor [140°C, 1 min, 0.5% acid]), the crystalline cellulose is essentially unaffected. Under the same conditions, the amorphous cellulose and hemicellulose are rapidly converted to their component sugars. However, at 235°C and 12 s residence time (hydrolysis reactor conditions), only 28% of the crystalline cellulose remains unhydrolyzed.

The glucose formed upon hydrolysis of crystalline cellulose is simultaneously being degraded to HMF, but we intend to maximize the yield of the intermediate glucose produced. As is shown in Eq. 5-3, the intermediate yield depends on the relative magnitude of K_1 and K_2, and we want K_1/K_2 to be as large as possible. Both K_1 and K_2 increase with increasing temperature and acid concentration. However, K_1 increases more quickly than K_2. Figure 5-4 shows K_1 and K_2 as a function of temperature for fixed acid concentration. The effect of raising the acid concentration is similar but less pronounced. The dependence

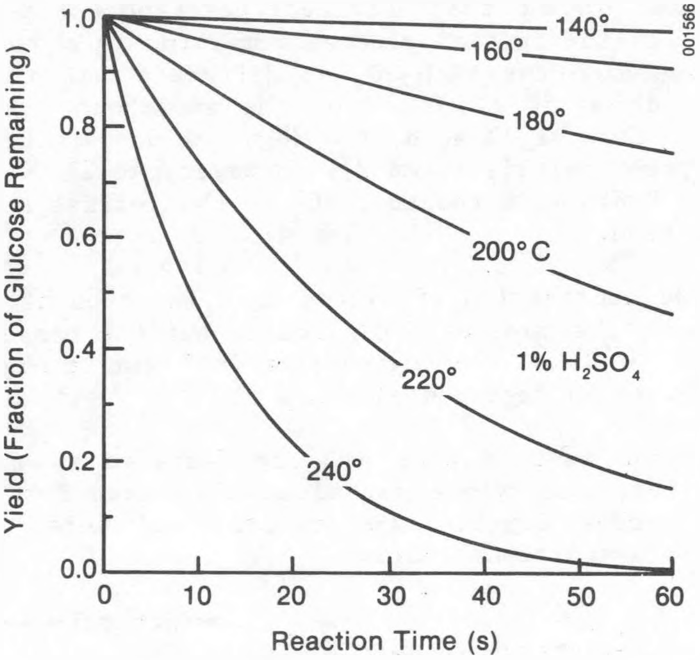


Figure 5-1. Degradation of Glucose: Fraction of Initial Glucose Remaining as a Function of Time and Temperature

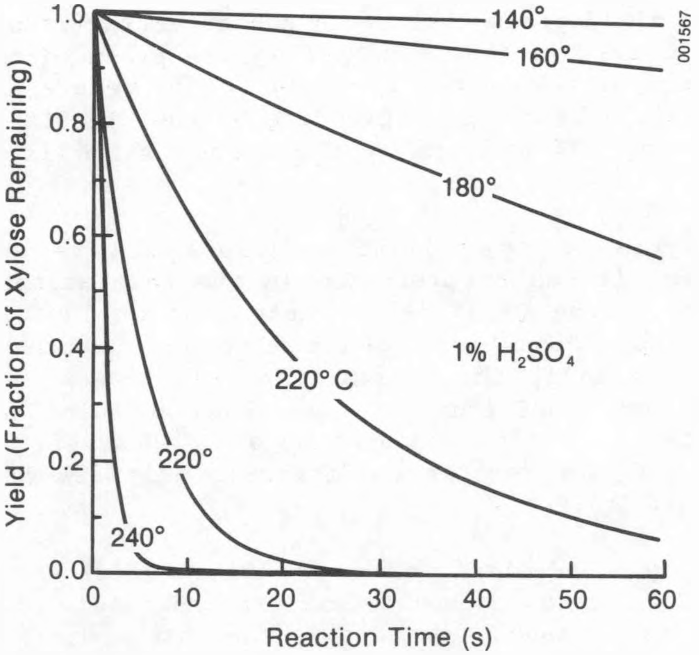


Figure 5-2. Degradation of Xylose: Fraction of Initial Xylose Remaining as a Function of Time and Temperature

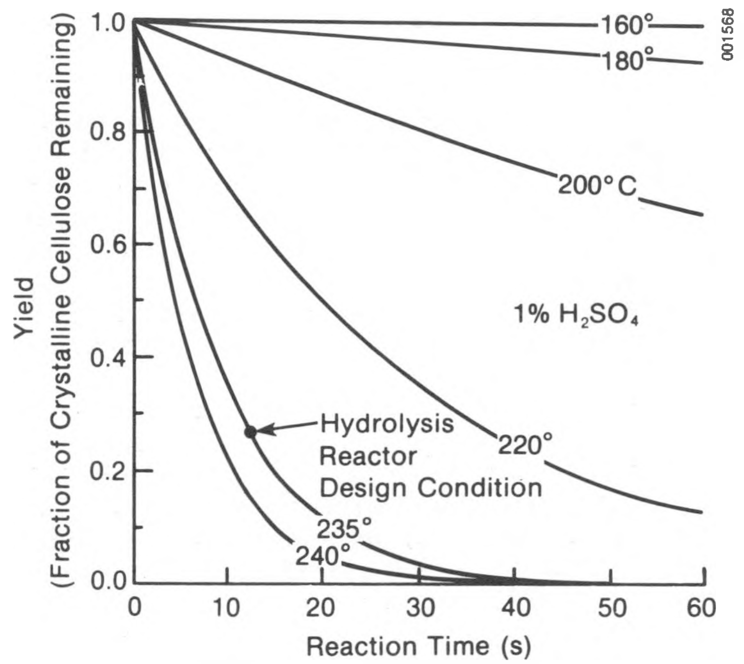


Figure 5-3. Hydrolysis of Cellulose to Glucose as a Function of Reaction Time and Temperature

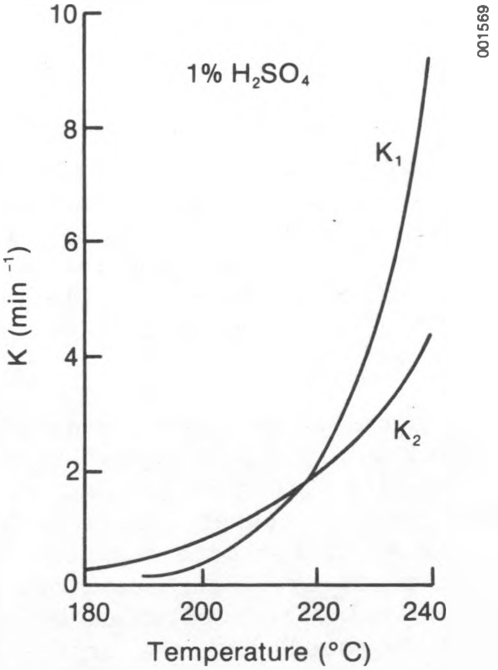


Figure 5-4. Rate Constants for the Degradation of Crystalline Cellulose and Glucose as a Function of Temperature

of K_1/K_2 on acid concentration and temperature is shown in Fig. 5-5. All combinations of acid concentrations and temperatures that give the same ratio of K_1/K_2 produce the same yield.

Figure 5-6 shows the yield (glucose produced/potential glucose from crystalline cellulose) for the combined hydrolysis of crystalline cellulose and the degradation of glucose as a function of time and temperature (at fixed acid concentration). As the temperature increases, the reaction proceeds more quickly (because both K_1 and K_2 have increased), and the yield improves because K_1/K_2 increases. Similar families of curves can be plotted for different acid concentrations. For higher acid concentrations, high yields and short optimum reaction times would be achieved at lower temperatures.

If a prehydrolysis reactor is used, the amorphous cellulose and the hexosans and xylans from the hemicellulose are hydrolyzed immediately. The degradation of the sugars (negligible at 140°C) is described by Fig. 5-1 and 5-2. If the prehydrolysis step is bypassed, the glucose yield can be thought of as a linear combination (weighted average) of the crystalline and amorphous yields (fraction crystalline multiplied by crystalline yield, plus amorphous fraction multiplied by amorphous yield). Equation 5-3 shows this correlation, and Fig. 5-7 shows the result for aspen wood (28% of the potential glucose is present as hexosans and 72% as crystalline cellulose). The greatest yields are still found at high temperatures and short residence times, but now we must trade the amorphous yield, which is maximized almost instantly, against the crystalline yield, which is maximized at longer residence times. In this situation, the greater the amorphous fraction, the shorter will be the optimum residence time (for a fixed reactor temperature and acid concentration). This is illustrated in Fig. 5-8.

The kinetic parameters derived by Grethlein et al. (1980) appear to be valid over a wide range of conditions, including those used in this study. The kinetic parameters are also in good agreement with those reported by Saeman (1945) and those occurring in the NYU extruder reactor. Saeman's experiments were carried out using glass ampule reactors, low solids contents, and reaction times of several minutes. Dartmouth has conducted experiments over the range of 5-420 s, in both glass ampules and flow reactors, with solids loadings of up to 23%. Chem Systems Inc. (1981d) compared Grethlein's kinetics with the results of the NYU flow reactor operating at 29% solids and found good agreement.

In summary, because all the reactions are first order, the total yield is the sum of the yields of the individual constituents. The rates of all the reactions (degradation of crystalline cellulose, glucose, and xylose) increase with increasing temperature and acid concentration. The amorphous components hydrolyze instantly upon exposure to hot acid and begin degrading immediately. Therefore, the most efficient recovery of the amorphous components is achieved by a mild hydrolysis (prehydrolysis) at conditions where the amorphous components are hydrolyzed but not degraded, and the crystalline cellulose remains unchanged. Because the rate of cellulose degradation increases more quickly with increased temperature and acid concentration than does the rate of glucose degradation, high yields are achieved at high temperatures and acid concentrations and short reaction times. The maximum practical yields from crystalline cellulose are about 50%-60%. If both the amorphous and crystal-

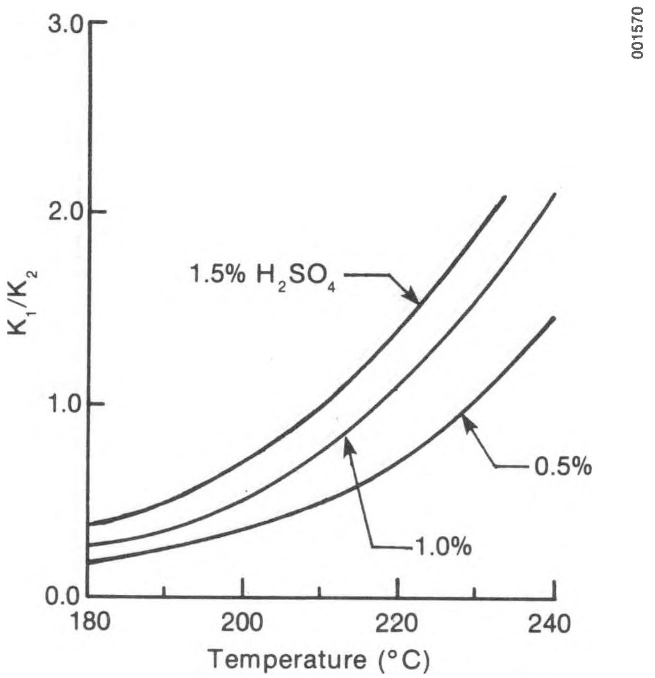


Figure 5-5. Ratio of Crystalline Cellulose Hydrolysis to Glucose Decomposition as a Function of Temperature and Acid Concentration

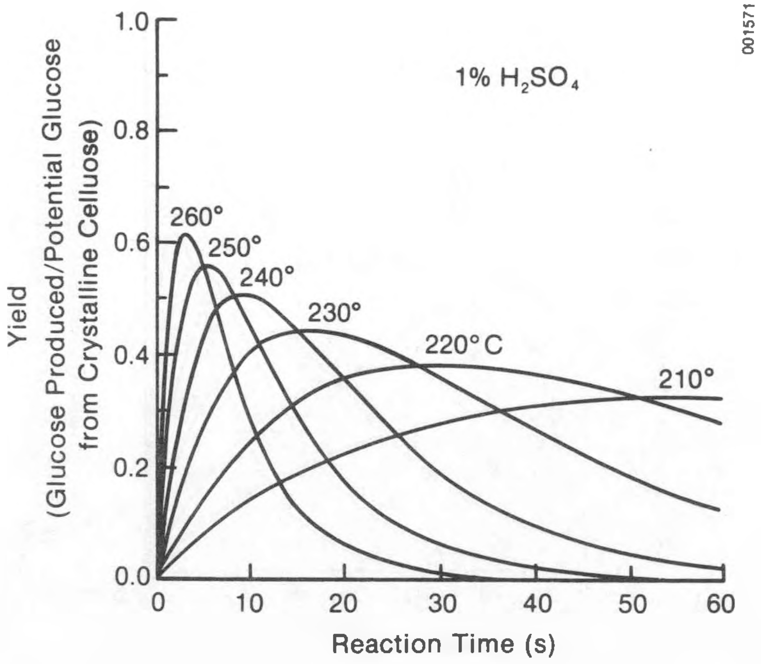


Figure 5-6. Glucose Yield from the Hydrolysis of Crystalline Cellulose as a Function of Reaction Time and Temperature

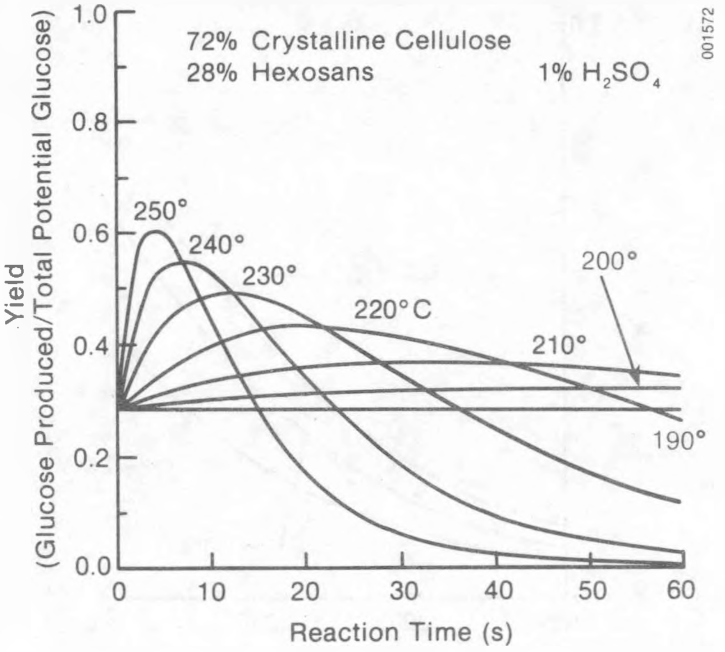


Figure 5-7. Hydrolysis of Aspen Wood to Glucose as a Function of Reaction Time and Temperature

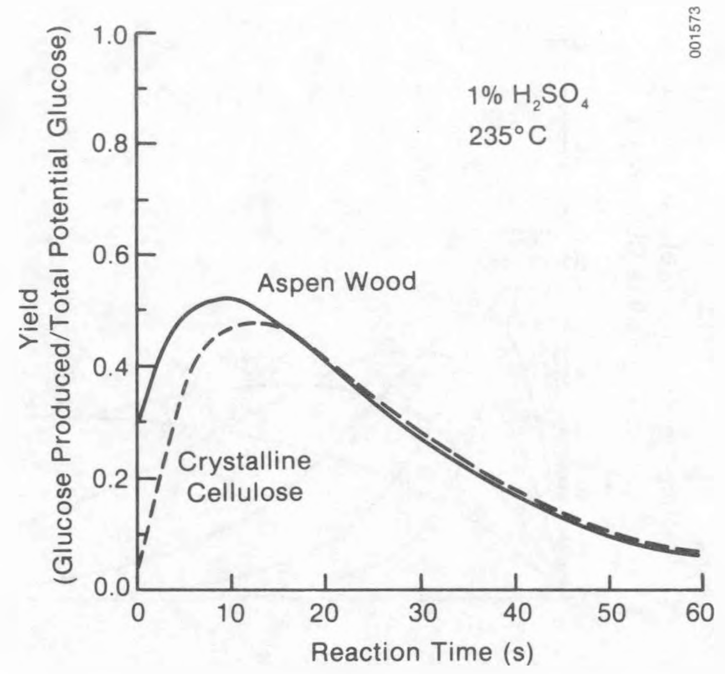


Figure 5-8. Hydrolysis of Aspen Wood and Crystalline Cellulose as a Function of Reaction Time

line fractions are hydrolyzed in the same reactor, the optimal reaction time is shorter than if only the crystalline fraction were being hydrolyzed. As the amorphous fraction is increased, the optimal time is further decreased.

With an understanding of the kinetics of acid hydrolysis, we now have a tool that allows us to determine an optimum reactor residence time for any given feedstock and processing configuration. This knowledge is useful in understanding the parametric analyses presented in the following section.

SECTION 6.0

SIMULATION MODEL

To determine the effect of different hydrolysis conditions and configurations on the economics of ethanol production, it is necessary to model the operation of the entire facility, to calculate capital and operating costs, and to calculate selling price. These calculations are executed by a computer simulation model developed by Chem Systems Inc., under subcontract to SERI. This section briefly describes the model. Chem Systems Inc. provides detailed documentation of the basic design and operation in other reports (1981a and 1981b).

The purpose of the model is to provide a tool for comparing various process alternatives and configurations. The figure used to compare the merit of the various schemes is the selling price of ethanol. Effort was made to develop a simulation model and economic assumptions that provide realistic estimates of the cost of ethanol. However, the large potential for variations in economic assumptions and feedstock costs, as well as the many simplifications necessary to make a model that did not use excessive computational time, inevitably results in large uncertainties in the final cost. Since all cases studied employ the same set of assumptions, the trends, cost differences, and relative comparisons between process configurations shown in the parametric analyses can be presented with confidence. However, the absolute selling price has a much larger uncertainty.

The simulation model was developed for implementation on an IBM 5120 computer using the APL language. The model uses a detailed simulation of the kinetics of prehydrolysis and hydrolysis. The fermentation and purification sections contain less programming detail, since the program is not designed to optimize them. Because of the size limitations of the IBM 5120 and the length and complexity of the program, the program is divided into the following five blocks:

EDITOR - Creates input and storage data files and prints a summary of the input data

SYM1 - Calculates the material balance and stores the results

SYM2 - Adjusts the material balance to the required plant size, calculates the utility balance, and prints the material and utility balance summaries

SYM3 - Calculates and prints the plant capital cost.

SYM4 - Computes the selling price of ethanol and prints an economic summary.

SYM1 calculates the material balance for the processing scheme described in Sec. 4.0. The assumptions described in that section are included in the computer code. SYM2 calculates the steam balance described in Sec. 4.2.6. The electrical and cooling water requirements are calculated from the stream flow rates.

SYM3 calculates the capital cost of the plant. The cost of each major piece of process equipment in a 50 million-gal/yr base case plant was estimated using the ICARUS COST program developed by the Icarus Corp. of Rockville, Md. The cost of equipment in other cases is determined by appropriate scaling laws of the form

$$\mathrm{cost}_2 = \mathrm{cost}_1 \left(\frac{\mathrm{size}_2}{\mathrm{size}_1}\right)^{\alpha}.$$

where α is an empirically derived exponent that describes the economies of scale for each piece of equipment.

Costs are scaled with significant flows and parameters such as the total flow rate for pumps, solids loading for filters, and flow rate and residence time for tanks. Different scaling exponents are used as appropriate. If necessary, multiple pieces of equipment are used where a single unit can not be built in a large enough size.

SYM4 computes the cost of ethanol based on the simulation results. The costs are based on first quarter 1982 dollars, and the plant is located on the U.S. Gulf Coast. The discounted cash flow (DCF) analysis used to calculate the selling cost contains the following assumptions:

- Time of construction--2 years with uniform expenditure of capital throughout this period.
- Working capital
  - The sum of

    Feedstock inventory--0.5 month of raw materials at delivered price

    Finished product inventory--0.5 month of products and by-products

    Accounts receivable--1 month's gross cost of production

    Cash--1 week's expenses (gross cost of production less depreciation)

    Warehouse/spare parts inventory--3% of ISBL* capital cost
  - Less

    Accounts payable--one month of raw materials at delivered prices
- Total federal and local taxes at 50%.
- Straight-line depreciation over a 5-year period for ISBL facilities and a 10-year period for off-site facilities, with no salvage value for the plant.
- Cost of sales at 6% of the product selling price.
- A gradual sales buildup of 60% of capacity in the first year, 80% in the second, and 100% from the third year on.

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*ISBL stands for "inside battery limits" and refers to that part of the plant directly involved in the processing scheme.

Because of the treatment of working capital in the DCF calculations, the interest rate on working capital does not appear as a separate item in the cost of production analysis.

SERI

SECTION 7.0

PARAMETRIC ANALYSES

Parametric analyses were conducted to determine the effect of variations in process conditions and changes in plant configuration. Section 7.1 describes the base case--the process that represents an initial projection of an optimum plant built with current technology. Section 7.2 describes the effect of changing the operating parameters and processing scheme within the prehydrolysis and hydrolysis sections. Issues addressed include solids concentration in the reactor feed, recycling of unreacted solids, and the effects of prehydrolysis, two-stage hydrolysis, acid concentration, and temperature. Section 7.3 presents preliminary estimates of the effect of some of the major downstream changes that are possible (furfural and lignin by-product credits, xylose fermentation, and reductions in product purity).

7.1 BASE CASE

This section describes the rationale for the 50-million-gal/yr plant size, the feedstock costs, and the processing conditions.* The overall layout of the base case is illustrated in Fig. 4-1, including size reduction, prehydrolysis, hydrolysis, neutralization, fermentation, and purification. This section deals with the specific assumptions used in the prehydrolysis and hydrolysis blocks.

The base case plant was sized to produce 50 million gal/yr of ethanol from either corn stover or aspen wood. For the purpose of cost estimating, a U.S. Gulf Coast location was assumed.

For a fixed feedstock cost, increasing the capacity of the ethanol plant reduces the price of ethanol. Because the capital investment per unit of capacity becomes smaller as plant size is increased, the contribution of capital charges to the cost of ethanol are decreased, and larger plants are preferred. However, the feedstock cost slowly increases with plant size because the collection radius required to obtain the necessary feedstock and the costs of transporting the feedstock both increase. At some plant size, the decrease in capital investment per unit of output is counterbalanced by the increase in feedstock costs. A production level of 50 million gal/yr would require a collection radius of approximately 30 miles (assuming a yield of 30.75 gal of ethanol per ton of corn stover, a crop residue yield of 2 tons per acre, and a concentration of 50% corn on the area around the plant). These conditions are typical for Iowa farmland. At such conditions, a 50 million gal/yr plant is probably the largest that could reasonably be built (Neenan, Parker, and Hoagland 1982; Dauve and Flaim 1979).

The cost of the corn stover consumed by the plant was assumed to be \$30/ton (\$0.015/lb) and the cost of aspen wood \$20/ton (\$0.01/lb). These costs are consistent with the ranges quoted by Neenan and Dauve and are conservative estimates when compared to those used in earlier ethanol fuels studies. Con-

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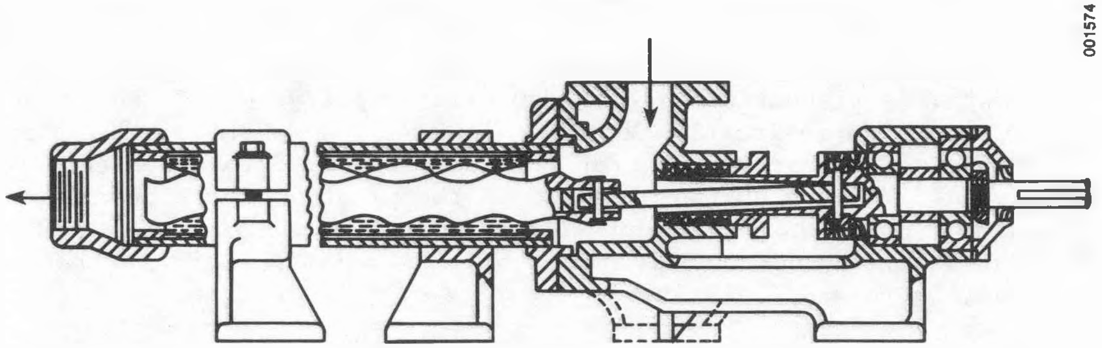
*1 gallon = 3.78 liters.

verting the feedstock to glucose with 100% efficiency would correspond to sugar costs of \$0.039/lb for corn stover and \$0.034/lb of glucose for aspen wood.

The solids concentration in the feed to the reactor was set at 15 wt %. This concentration is well within the range that can be moved by a positive displacement screw pump such as a Moyno pump (Fig. 7-1). The prehydrolysis reactor conditions were 140°C, 0.5 wt % sulfuric acid concentration in the soluble part of the feed, and 1 min residence time. In the hydrolysis reactor, the temperature was 235°C, the residence time 12 s, and the acid concentration 1.0 wt %. Forty percent of the unreacted solids from the outlet of the hydrolysis reactor are recycled and mixed with the fresh feed.

The detailed material balance for the base case simulation is shown in Appendix A. Several broad conclusions can be drawn by studying the printout. The solids entering the prehydrolysis and hydrolysis reactors are diluted to 15% to facilitate pumping. Next, additional large quantities of water are used to wash the solids and remove the soluble sugars. By the time the sugar streams reach the fermenters, the glucose concentration is only 4%. The water used throughout the process is continually heated and cooled, consuming large quantities of energy. Furthermore, the size and cost of the processing equipment are proportional to the flow rate. Therefore, a subject of prime interest is the effect of increasing the solids content (decreasing the water content) of the processing streams.

The utilities summary (Table 7-1) shows that purification, prehydrolysis, and hydrolysis are all large consumers of energy (the hydrolysis reactions are carried out at high temperature while purification essentially requires the evaporation of water). The total capital investment is \$122 million, or \$2.44/gal per year of capacity. The capital cost estimate (Table 7-2) shows that the major cost items in the processing plant are fermentation (36%), prehydrolysis (21%), hydrolysis (17%), and purfication (13%). Surprisingly, the



SOURCE: Perry and Chilton 1973.

Figure 7-1. Moyno Single-Rotor Screw Pump with Elastomeric Lining

Table 7-1. Utilities Summary for Base Case[a]

Treatment	Steam (10^3/h) 15 psia	30 psia	55 psia	200 psia	600 psia	Power (hp)	Cooling Water (gal/min)	Process Water (gal/min)
Prehydrolysis	0	-44.5	0	244.8	0	1984.7	0	2548.3
Hydrolysis	0	-218.1	0	0	192.9	1970.3	0	1398.0
Neutralization	-24.1	0	0	0	0	1068.1	0	88.4
Fermentation	0	0	0	0	0	8119.7	11557.9	0
Purification	0	0	0	385.6	0	124.7	4027.6	0
Heat generation	0	0	8.9	-130.4	-192.9	47.9	1082.9	0
Waste treatment	0	0	0	0	0	0.8	1867.1	0
TOTAL	-24.1	-262.6	8.9	500.0	0	13316.1	18535.5	4034.7

[a] Total boiler feedwater required: 385.3 gal/min.

Table 7-2. Base Case Capital Cost Summary (1st Quarter 1982, in K$)

Purchased equipment costs		
Raw material handling	257	
Prehydrolysis	3,505	
Hydrolysis	2,859	
Neutralization	1,638	
Fermentation	5,998	
Purification	2,127	
Heat generation	357	
Waste treatment	31	
Total purchased equipment cost	16,772	
Installation	21,497	
Total installed equipment cost		38,269
Engineering and construction overhead		5,769
Engineering fee and contingency		6,239
CO_2 recovery system package		8,372
Total plant ISBL cost		58,649
Offsites capital costs		
Ethanol storage (14 days)		835
Calcium hydroxide storage (7 days)		407
Sulfuric acid storage (14 days)		227
Feedstock storage (14 days)		2,852
By-product storage (14 days)		192
Yeast storage (14 days)		68
600 psia lignin steam boiler		21,725
600 psia steam boiler		23,302
Cooling water system		1,762
Electricity		2,571
Buildings (3% ISBL)		1,759
General utilities (5% ISBL)		2,932
Site development (3% ISBL)		1,759
Piping (3% ISBL)		1,759
Pollution control (2% ISBL)		1,173
Total offsite facilities cost		63,325
Total plant capital cost		121,974

capital costs of offsite facilities account for \$63.3 million or 52% of the total investment. The largest individual cost items are the lignin boiler (\$21.7 million) and the supplemental coal boiler (\$23.3 million). The magnitude of these numbers shows that reducing energy usage can greatly reduce the capital costs.

Table 7-3 shows the contributions to the selling price of ethanol. Of the total cost of \$2.15/gal, almost half (\$0.89/gal) is the cost of feedstock (primarily the cost of aspen wood). Utilities cost \$0.29/gal, and labor and overhead expenses total \$0.22/gal. By-product credits (for CO_2 and single-cell protein) reduce the production costs by \$0.21/gal. The cash cost of production (raw materials, utilities, labor, and overhead minus by-product credits) is \$1.18/gal, or 55% of the selling price. The cash cost of production may be thought of as those costs that are incurred only when the plant is in operation. The charges proportional to the capital cost of the plant (depreciation and return on investment) account for 45% of the cost of ethanol (\$0.97/gal).

Therefore, the most effective ways to lower the selling price are to improve the yield (raw materials are 41% of the selling price), and to reduce the capital investment (45% of the selling price).

7.2 HYDROLYSIS MODIFICATIONS

This section describes the effects of changing the operating parameters and processing scheme within the prehydrolysis and hydrolysis sections.

7.2.1 Solids Concentration

Both plant capital cost and energy usage are proportional to the processing stream flow rates, which are inversely proportional to the solids concentration. The base case assumes a solids concentration of 15%, a mixture with the consistency of paste or sludge. (For comparison, 30% solids are essentially dry to the touch, 8% solids resemble thick molasses, and 4% solids appear as a very dirty liquid.)

The base case assumes that the prehydrolysis and hydrolysis reactors utilize the design employed by Grethlein (1980) at Dartmouth. In this reactor, a Moyno single screw pump (Fig. 7-1) pushes the acid-soaked cellulosic feed into a heat exchanger and then into the tubes (Fig. 7-2). The shell side of the heat exchanger is filled with high-pressure (4 MPa [600 psia]) steam. A section of the tubes is perforated for steam injection. The steam condenses on the feed, heating it to the final reaction temperature in approximately 1 s. The slurry flows through the reactor and is flashed through an orifice to quench the reaction.

Figure 7-3 shows the effect of changes in the solids concentration at the reactor inlet on the selling price and cash cost of production of ethanol. The difference between the selling price and production price are the capital-related charges. We see that the capital and production costs are both inversely proportional to the solids concentration. Solids concentrations of

Table 7-3. Base Case Economic Summary (Estimate of Cost of Production of Ethanol Acid Hydrolysis)

Capital Summary

Basis		Capital Cost	M$
Location:	U.S. Gulf Coast	ISBL	58.6
	First quarter, 1982	Offsite facilities	63.4
Capacity:	50.0 million gal/yr		
	149,335 metric tons/yr	Total fixed investment	122.0
Operating Time:	8000 h/yr (91% capacity)	Working capital	11.8

Production Cost Summary

Item	Units/gal	Price (¢/unit)	Annual Cost (K$)	¢/gal	$/metric ton
Raw Materials					
Aspen wood (lb)	68.9660	1.0	34,483		
Sulfuric acid (lb)	2.3225	4.3	4,993		
Calcium hydroxide (lb)	1.7510	2.0	1,751		
Catalysts and chemicals			3,188		
Total raw materials			44,416	88.8	297.4
Utilities					
Power (kWh)	1.58238	4.6	3,639		
Cooling water (10^3 gal)	0.17794	7.3	649		
Process water (10^3 gal)	0.03873	65.0	1,259		
Boiler feedwater (10^3 gal)	0.00370	113.0	209		
Steam, 200 psia (10^3 lb)	0.08000	480.0	19,201		
Steam, 55 psia (10^3 lb)	-0.04445	470.0	-10,447[a]		
Total utilities			14,511	29.0	97.2
Operating Costs					
Labor, 46 workers @ $26,000[b]			1,196		
Foremen, 9 workers @ $29,600[c]			266		
Supervision, 1 @ $35,600			36		
Maintenance, materials, and labor[d]			3,519		
Total operating cost			5,017	10.0	33.6
Overhead Expenses					
Direct Overhead[e]			674		
General plant overhead[f]			3,261		
Insurance and property tax[g]			1,830		
Total overhead expenses		5,765	11.5	38.6	
By-Product Credit					
Carbon dioxide, (lb)	6.51707	2.8	-9,124		
Single-cell protein feed (lb)	0.19357	15.0	-1,452		
Total by-product credit			-10,576	-21.2	-70.8
Cash cost of production			59,133	118.2	395.9
Depreciation[h]			18,062		
Net cost of production			77,195	154.3	516.9
Selling price at 15% discounted cash flow			215.3	635.2	

[a] Indicates credit for excess steam sold.

[b] 10 workers per shift

[c] 1 foreman per shift

[d] 5% of ISBL

[e] 45% of labor and supervision costs

[f] 65% of operating costs

[g] 1.5% of total fixed investment

[h] 20% ISBL + 10% OSBL

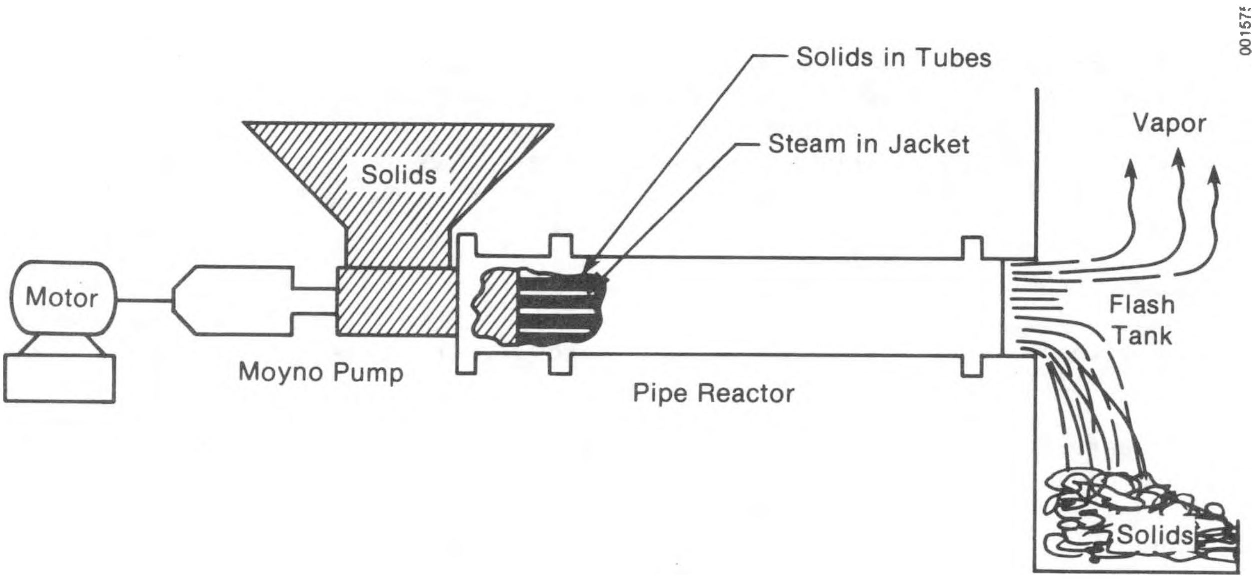


Figure 7-2. Pipe Reactor Based on Dartmouth Design

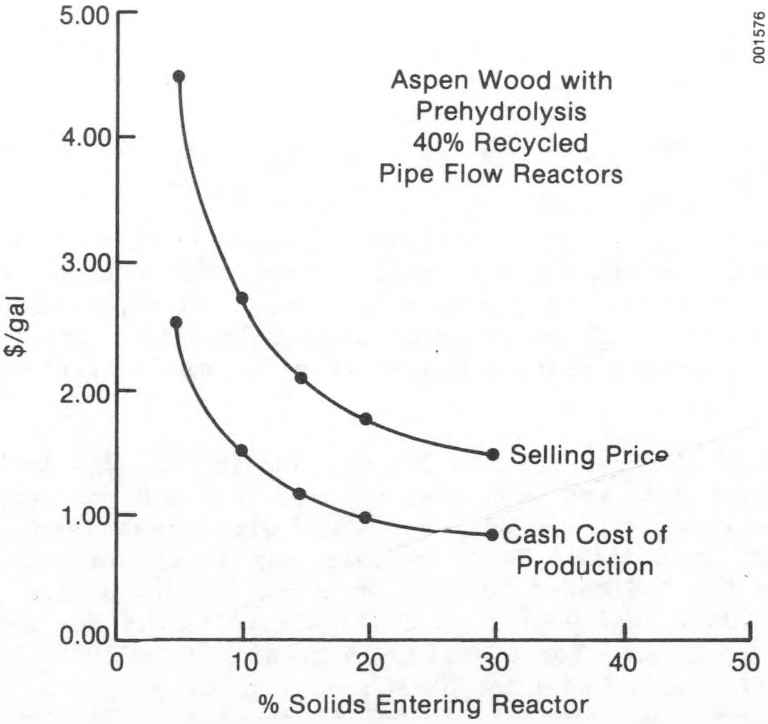


Figure 7-3. Effect of Solids Concentration on the Selling Price of Ethanol

20%-30% are necessary to produce competitively priced ethanol. A comparison of costs at 15% and 30% solids is instructive in understanding the trend.

Solids concentration has a minimal effect on the process yield; reaction kinetics and reactor yield are independent of concentration. However, the centrifuges and filters are slightly less efficient at removing soluble sugars from high solids streams. Therefore, the process uses 5.6% more aspen feed materials at 30% solids than at 15%. This amounts to an increase of $0.05/gal of ethanol.

Because the amount of acid added to the stream is a set fraction of the water and solubles feed rate, the cost of acid decreases with increased solids concentration. This effect is of the same magnitude as the increase in wood costs, and the two cancel each other.

The energy usage is proportional to the flow rate, which in turn is inversely proportional to the solids concentration. Increasing solids from 15% to 30%, which roughly halves the flow rates throughout the system, reduces the steam consumption in the prehydrolysis and hydrolysis reactors by 54%, and reduces steam usage in the purification section by 40%. This cuts the steam consumption so that the entire plant requirements can be met by the lignin steam boiler. Eliminating the coal boiler reduces the offsites capital cost 40%. The reduction in steam usage is large enough that excess steam can be sold, and the utility contribution to production costs drops from $0.29 to $0.03/gal.

In addition, by eliminating the coal boiler, the ISBL costs are reduced by 23%. The decrease is not linear with flow rate because many equipment items have economies of scale and some systems (CO_2 recovery) are unaffected. The offsites costs are reduced 40%, and the total capital investment 31%. The net effect is to decrease the calculated selling price of ethanol by 30% from $2.15 to $1.51/gal.

Solids concentrations of up to 30% can be pumped with a Moyno pump. Pumping of higher solids concentrations may require other types of pumps. For example, use of alternating piston-type pumps could provide near pulse-free pumping of feed with high solids content. Only slight gains can be achieved by operating at a solids content higher than 30% since little additional water is removed.

The portions of the curves between 30% and 50% in Fig. 7-4 include the assumption that whatever pump was used cost no more than a Moyno pump. Because very high solids loadings can be achieved only with fresh feed, a prehydrolysis section was not included. This decision has little effect on the outcome. The decrease in the indicated selling price beyond 30% solids is an indication of the maximum additional amount we could afford to pay for a system operating at high solids content. For example, increasing from 30% to 50% solids could decrease the price of ethanol by $0.04/gal. Considering the effect of capital charges on the selling price of ethanol (through depreciation and cash flow), it is calculated that an ISBL cost increase of up to $4.5 million would be justifiable. This corresponds to a $1.5 million allowable increase in the cost of purchased equipment in the hydrolysis and prehydrolysis section.

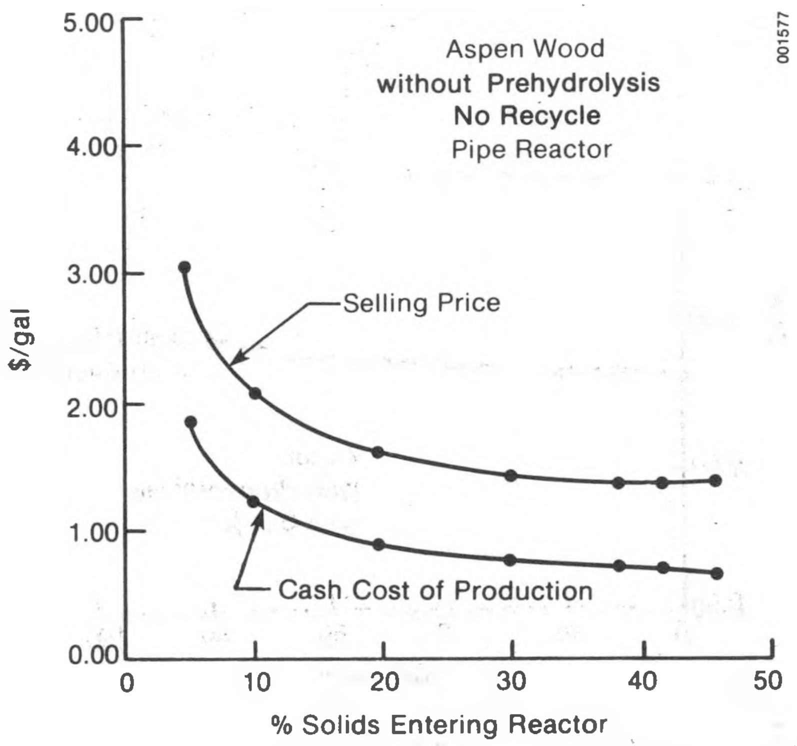


Figure 7-4. Cost of Ethanol at High Solids Content

7.2.2 Recycling Unreacted Solids

Because the cost of feedstock is important, recycling unreacted solids into the hydrolysis reactor feed is studied. Because unreacted crystalline cellulose behaves the same in the reactor as fresh cellulose, some of the unreacted solids are recycled. This does not affect either the kinetics (Grethlein 1982) or the yield per pass, but because the amount of crystalline cellulose entering the reactor is greater than would be the case without recycle, the total amount of glucose produced is increased.

Figure 7-5 shows the effect of recycling on a system operating with a 30% solids concentration entering the reactor and an aspen wood feedstock. If 0% to 40% of the unreacted solids from hydrolysis is recycled, the selling price is essentially unaffected. Recycling raises the glucose yield for the entire process (ratio of the glucose sent to fermentation to the potential glucose in the feed) from 56% to 60%. The effect of recycling is small because prehydrolysis (which produces approximately 40% of the glucose from 28% of the feed) is not affected and because the increase in feed to the hydrolysis reactor is not significant. To a first approximation, 28% of the crystalline cellulose feed remains after one pass through the hydrolysis reactor. If 40% of the remainder is recycled, the cellulosic feed to the hydrolysis reactor is increased 11%. (The actual amounts must be calculated iteratively and are slightly higher.) This increased feed is then converted to glucose with approximately 50% yield.

Recycling 40% of the unreacted solids reduces the cost of aspen feed by 6.5% from the no-recycling case. Partially offsetting this is increased use of

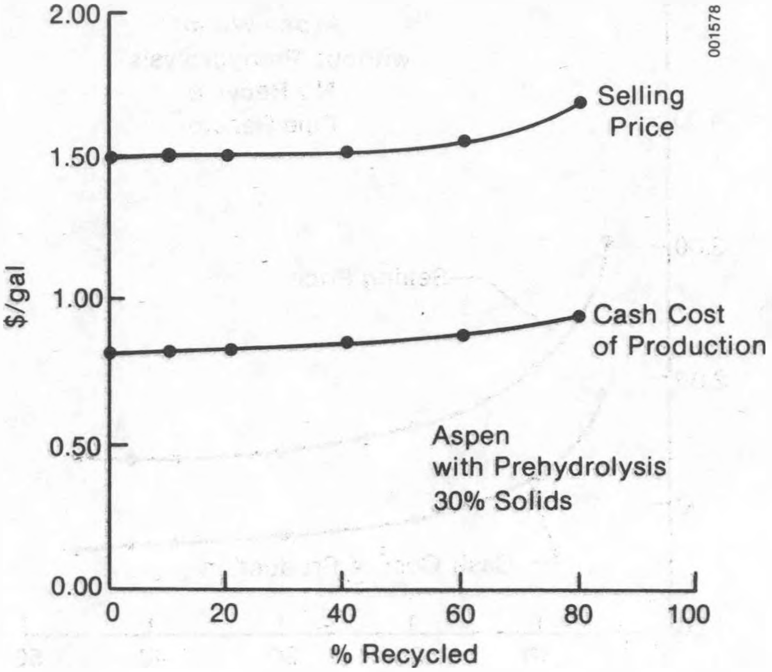


Figure 7-5. Effect of Unreacted Solids Recycle on Selling Price of Ethanol

acids and bases and more importantly, an increased use of steam. Use of recycling also increases the amount of solids that must be handled by the centrifuges, raising the capital-related costs in the process plant. However, because less unreacted solids remain to be burned, increasing the recycling rate decreases the size and cost of the lignin boiler. All of these perturbations are small, and thus the cost of ethanol is essentially unchanged.

If the amount recycled is greater than 40%, the cost of ethanol begins to rise. This is best illustrated by the case in which all the unreacted solids are recycled. In this case, all the nonreactive substances accumulate in the hydrolysis system, and the reactor and associated equipment are of infinite size and cost. For example, the concentration of inerts in the reactor feed (excluding water) is 36.3% at 0% recycle, 48% at 40% recycle, and 60.4% at 80% recycle. Therefore, as the solids recycle rate is increased, we see a buildup of inert materials in the system that increases the capital cost and steam usage but does not increase the yield.

Table 7-4 presents the components of selling price at 0%, 40%, and 80% recycle. It is important to note that yield and recycling are more important in cases where feedstock is more expensive. Recycling also compares more favorably where the feed is delignified prior to the hydrolysis reactor, and the buildup of inerts is less (Chem Systems Inc. 1981b).

Table 7-4. Effect of Solids Recycling on Selling Price of Ethanol ($/gal, 30% solids)

Cost Item	Solids Recycled		
	0%	40%	80%
Aspen wood	0.78	0.73	0.68
Chemicals	0.12	0.12	0.14
Utilities (cost-credit)	-0.05	0.03	0.15
Operaton and overhead	0.18	0.18	0.19
By-product credits	-0.21	-0.21	-0.21
Subtotal	0.82	0.85	0.95
Capital charges	0.69	0.66	0.75
Total	1.51	1.51	1.70
Yield (%)	56	60	65

7.2.3 Two-Stage Hydrolysis

A second method of improving the yield is to conduct a prehydrolysis and a two-stage hydrolysis. In the two-stage hydrolysis, the washed unreacted solids from the hydrolysis reactor are used as the feed for a second hydrolysis section. This processing scheme reduces the cost of ethanol slightly in some cases and increases it in others (Table 7-5). If no prehydrolysis is used, the added expense of the second stage is justified by the relatively large increase in yield. If prehydrolysis is used, the potential increase in yield is smaller, and therefore the added investment in recycling or a second stage is not justified. However, a two-stage hydrolysis is a better method of obtaining high yields than is a high recycle rate. Such a step would be more cost-effective if the feedstock costs were greater.

Table 7-5a. Effects on Selling Price of Two-Stage Hydrolysis or Recycling, with No Prehydrolysis ($/gal, 30% solids)

Cost Component	0% Recycle	80% Recycle	2-Stage Hydrolysis
Corn stover	1.04	0.78	0.82
Chemical	0.12	0.15	0.13
Utilities	-0.25	0.11	-0.01
Operation and overhead	0.16	0.18	0.17
By-product credits	-0.21	-0.21	-0.21
Subtotal	0.85	1.01	0.90
Capital charges	0.69	0.68	0.62
Total	1.54	1.69	1.52

Table 7-5b. Effects on Selling Price of Two-Stage Hydrolysis or Recycling, with Prehydrolysis ($/gal, 30% solids)

Cost Component	0% Recycle	80% Recycle	2-Stage Hydrolysis
Corn stover	0.79	0.70	0.70
Chemicals	0.11	0.13	0.11
Utilities	0.03	0.23	0.15
Operation and overhead	0.17	0.18	0.18
By-product credits	-0.21	-0.21	-0.21
Subtotal	0.89	1.03	0.93
Capital charges	0.63	0.78	0.70
Total	1.52	1.81	1.63

The usefulness of the second hydrolysis step is best understood by comparing it with a hydrolysis reactor that recycles a fraction of the unreacted solids. A recycle reactor does not get a second chance to convert all the unreacted cellulose, but has to accept an increased fraction of inerts in the feed, which raises the capital and utility costs. On the other hand, a two-stage system has a second chance at all of the unreacted crystalline cellulose (with a greater potential for increased yield and decreased feedstock costs) but does not incur a buildup of inert materials. Therefore, to achieve the same glucose output, the two-stage hydrolysis unit handles a smaller volume of material than a single-stage unit, thus reducing the capital and utility costs. However, because the processing equipment is smaller, there are no economies of scale for this operation.

7.2.4 Prehydrolysis

The purpose of prehydrolysis is to make the most efficient use of the amorphous components of the cellulosic feedstock. However, the increased yield comes at the cost of increased capital expense and energy usage. Figure 7-6 shows that for aspen wood costing 1.0¢ per delivered pound, processes that omit prehydrolysis have a slight advantage. However, in Fig. 7-7 we see that with a corn stover feedstock at 1.5¢ per delivered pound, the process with prehydrolysis is marginally better. This is because corn stover contains a higher percentage of amorphous six-carbon sugars, and because the cost of potential glucose is $0.045/lb from corn stover and $0.035/lb from aspen wood. Therefore, a decision as to whether prehydrolysis is a useful step must be made for each different feedstock and feedstock cost.

The costs and benefits of adding prehydrolysis are of the same magnitude and are illustrated here for the case of an aspen wood feedstock and no recycling. Prehydrolysis increases the glucose yield; it also allows efficient (97%) recovery of the amorphous six-carbon sugars (28% of total), while hydrolysis converts an additional 48% of the crystalline fraction (72% of the total). Thus the total theoretical yield should be 61.7%. The actual yield is 56% because of inefficiencies in separation. Without prehydrolysis both the amorphous and crystalline fractions are fed directly to the hydrolysis reactor,

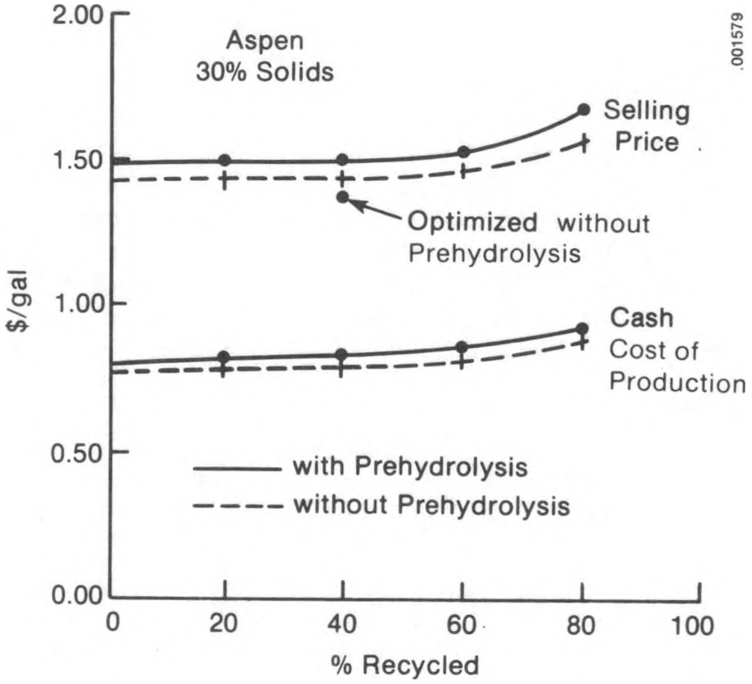


Figure 7-6. Effect of Prehydrolysis of Aspen Wood on Selling Price and Cash Cost of Production

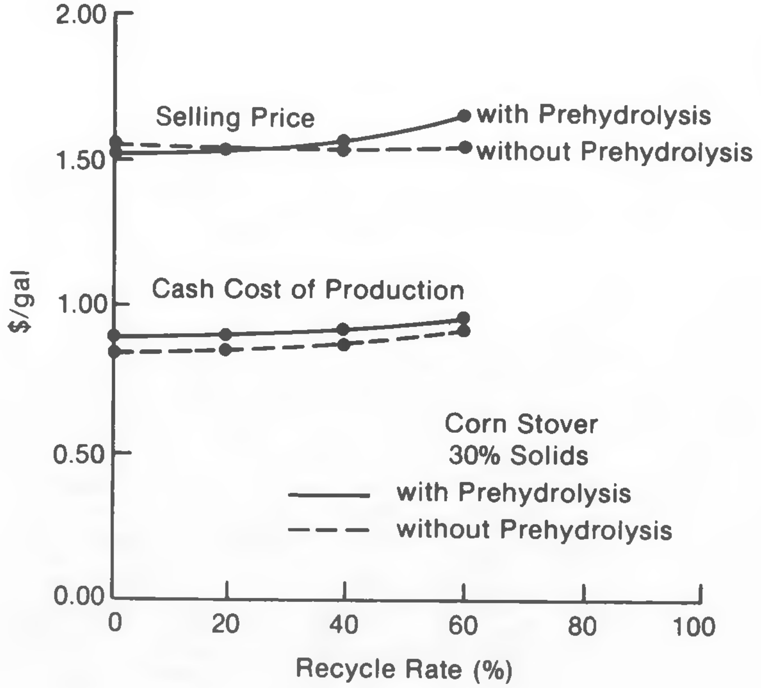


Figure 7-7. Effect of Prehydrolysis of Corn Stover on Selling Price and Cash Cost of Production

which is reconfigured to operate at a shorter residence time (as explained in Sec. 5.0) to decrease degradation of the amorphous fraction. In this case the yield is 68% of the amorphous six-carbon fraction and 41% of the crystalline fraction, for a combined reactor yield of 48%. Because of separation conditions, the process yield (the ratio of glucose sent to neutralization to potential glucose) is 45%. Therefore, with prehydrolysis the yield increases from 45% to 56%, and the aspen costs are reduced by 20% or $0.19/gal. However, eliminating prehydrolysis allows a greater steam utility credit, which is somewhat offset by the larger lignin boiler required to handle the larger solids stream. Furthermore, the elimination of prehydrolysis lowers the ISBL costs by 15%. Taken together, the effects give the plant with an aspen feed without prehydrolysis an advantage of $0.10/gal the more efficient but more complex process with prehydrolysis.

Table 7-6 shows the effect of prehydrolysis on the capital cost, while Table 7-7 shows the difference in contributions to the selling price.

7.2.5 Reactor Temperature and Acid Concentration

In Sec. 5.0 we showed that higher reactor temperatures and acid concentrations increase the potential yield and decrease the optimal reaction time. Fig. 7-8 shows the maximum obtainable yield and optimum reactor time for different acid concentrations and reaction temperatures. This plot is created by connecting the maxima in plots such as Fig. 5-7. It shows, for example, that with an aspen feed, no prehydrolysis, no recycling, and a 1% acid concentration, increasing the reactor temperature from 235° to 240°C increases the theoretical hydrolysis yield from 48.5% to 52%. Also, increasing the acid concentration from 1.0% to 1.5% while holding the reaction temperature constant at 235°C raises the yield from 47.7% to 54%. To study the effect of changes in temperature and acid concentration, we take a base case of aspen feed, no prehydrolysis, 40% recycling, 235°C, and 30% solids concentration. We first increase temperature while holding the acid concentration constant, and then change acid concentration at a constant temperature.

Increasing the temperature 5°C results in an 8% reduction in the price of ethanol. This comes mainly from the reduced cost of raw materials (aspen and acid), and secondarily from the slightly smaller capital charges made possible by the lower flow rates. For this decrease in price, we assume that higher temperatures in the reactor can be achieved with 600 psia steam. Grethlein et al. (1980) state that the reactor pressure must be maintained at 0.7 MPa (100 psia) above saturation to achieve complete steam condensation and stable operation. This would mean 240°C is the maximum reactor temperature possible with 600 psia steam. Use of higher-pressure steam would require a more expensive utility system. It is not known whether this would be cost-effective or not. A second limitation is that of residence time. Figure. 5-7, shows that as the optimum residence time decreases, the yield curve also falls much more steeply as we move away from the maxima. This means that the reaction time must be carefully controlled. The finite heat-up time (1 s) and inevitable variations in the flow rate set the minimum practical residence time at approximately 6 s.

Table 7-6. Effect of Prehydrolysis on Capital Cost (1st Quarter 1982,K$)

Costs	Without Prehydrolysis	With Prehydrolysis
Purchased equipment costs		
Raw material handling	317	277
Prehydrolysis	0	2,458
Hydrolysis	2,869	1,614
Neutralization	880	1,026
Fermentation	3,344	4,207
Purification	1,701	1,808
Heat generation	423	368
Waste treatment	31	31
Total purchased equipment cost	9,564	11,789
Installation	13,753	16,131
Total installed equipment cost	23,317	27,920
Engineering and construction overhead	3,290	4,055
Engineering fee and contingency	3,558	4,385
CO_2 recovery system package	8,407	8,387
Total plant ISBL cost	38,572	44,747
Offsites capital costs		
Ethanol storage (14 days)	835	835
Calcium hydroxide storage (7 days)	224	145
Sulfuric acid storage (14 days)	157	143
Feedstock storage (14 days)	3,389	3,032
By-product storage (14 days)	193	192
Yeast storage (14 days)	68	68
600 psia lignin steam boiler	34,542	28,608
600 psia steam boiler	0	0
Cooling water system	1,025	1,217
Electrical	1,560	1,786
Buildings (3% ISBL)	1,157	1,342
General utilities (5% ISBL)	1,929	2,237
Site development (3% ISBL)	1,157	1,342
Piping (3% ISBL)	1,157	1,342
Pollution control (2% ISBL)	771	895
Total offsite facilities cost	48,164	43,185
Total plant capital cost	86,736	87,933

Table 7-7. Effect of Prehydrolysis on Selling Price (0% recycle, 30% solids, optimized hydrolysis conditions, in $/gal)

Cost Component	Without Prehydrolysis	With Prehydrolysis
Aspen wood	0.97	0.78
Chemicals	0.13	0.12
Utilities (credit)	-0.28	-0.04
Operation and overhead	0.17	0.18
By-product credits	-0.21	-0.21
Subtotal	0.78	0.83
Capital Charges	0.68	0.68
Total	1.46	1.51

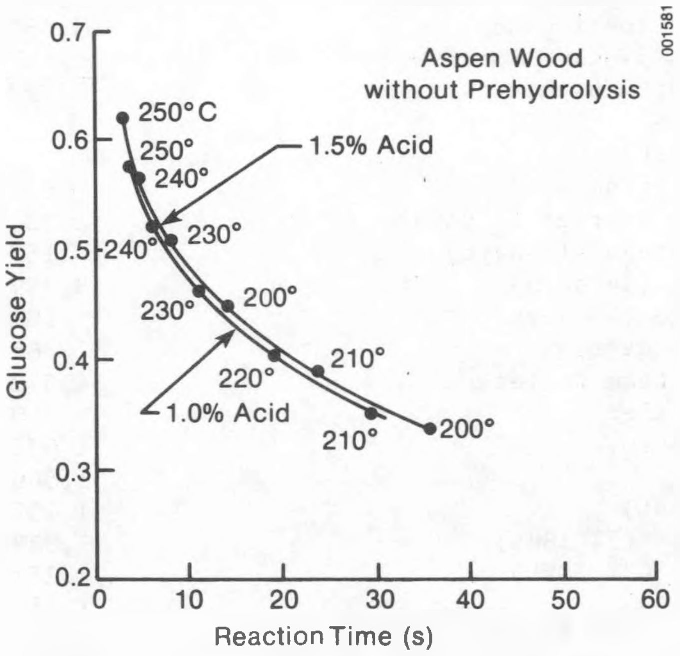


Figure 7-8. Maximum Yield and Optimal Reaction Time for Crystalline Cellulose as a Function of Reactor Temperature (^oC) and Acid Concentration

Increasing the acid concentration to 1.5% gives a larger increase in yield than does raising the reaction temperature, but increasing acid costs reduces the selling price slightly less than does increasing temperature (Table 7-8). Raising the acid concentration by 0.5% decreases the selling price from $1.45 to $1.36/gal. Again, potential increases in yield are limited by residence time considerations.

Table 7-8. **Effect of Temperature and Acid Concentration on Selling Price** (in $/gal)

Cost Component	Base Case 1.0% Acid, 235°C	Elevated Temperature 1.0% Acid, 240°C	Extra Acid 1.5% Acid, 235°C
Aspen	0.88	0.82	0.80
Chemicals	0.15	0.12	0.15
Utilities	-0.17	-0.17	-0.16
Operation and overhead	0.16	0.16	0.16
By-product credits	-0.21	-0.21	-0.21
Subtotal	0.81	0.72	0.74
Capital charges	0.64	0.62	0.62
Total	1.45	1.34	1.36
Yield (%)	49.19	54.0	55.4

7.3 DOWNSTREAM MODIFICATIONS

This section describes briefly some of the downstream changes (in fermentation, purification, and by-products) that could significantly affect the selling price of ethanol so that we can make estimates of the ultimate potential of acid hydrolysis processes and identify important areas for research. Topics include fermentation of xylose, furfural as a by-product, and a decrease in the required ethanol concentration. Recovery of lignin as a by-product could also have a large effect on the economics, but because of the complexity of lignin recovery, it is not covered in this report.

7.3.1 Xylose Fermentation

Xylose from the hemicellulose fraction of the feedstock may account for up to 30% of the potential sugar and 50% of the recoverable sugar, but xylose can not be fermented to ethanol with present industrial yeasts. Researchers at SERI and other institutions are working to develop yeasts capable of fermenting five-carbon sugars (xylose) to ethanol (LORRE 1982). The reaction would proceed according to the equation

$$\underset{(150)}{6\ C_5H_{10}O_5} \rightarrow \underset{(46)}{10\ C_2H_5OH} + \underset{(44)}{10\ CO_2}\ . \tag{7-1}$$

In the ideal case, the yeast that fermented the xylose would live in the tank as a coculture with the conventional fermentation yeast. In this manner, the yield would be increased without affecting the cost of fermentation. The effect of xylose fermentation was determined using the stoichiometry of Eq. 7-1 and the same assumptions on fermentation efficiency and products for the five-carbon fermentation as for six-carbon fermentation. This sets an upper limit on the improvement that could be obtained with xylose fermentation.

Figure 7-9 shows the effect of solids recycling in a system with xylose fermentation. The most important point is that the selling price is 20%-25% lower than without xylose fermentation. Because xylose conversion increases the yield, it lowers the feedstock costs by 25%. Increasing the yield also means that less material needs to be handled to achieve the same output. Therefore, smaller equipment is needed throughout the plant, with a corresponding decrease in the capital charges.

Table 7-9 presents a comparison of the economics of the conversion of corn stover with and without xylose fermentation. We assumed a capacity of 50 million gal/yr for both plants.

Utilization of xylose affects hydrolysis in the same manner as increasing the amount of amorphous cellulose (where 1 mole of xylose is equivalent to 5/6 mole of glucose). Therefore, if we were to use a single-step prehydrolysis/hydrolysis, the yield of the amorphous fraction would be much more important than if xylose were not fermentable. When the yield of a combined prehydrolysis/hydrolysis reactor is plotted versus reaction time for different temperatures, we find that the maximum yield occurs at the conditions corresponding to prehydrolysis (Fig. 7-10). The initial yield of the amorphous components declines faster than the crystalline cellulose yield increases. Therefore, the majority (58%) of the sugars may be recovered by prehydrolysis, and the total yield can be increased only 50% to approximately 80% by further expensive processing. In this case, it is advantagous to use only prehydrolysis, and leave out the hydrolysis step. This case is illustrated in Fig. 7-11, where the cost of ethanol is shown in a system with xylose fermentation as a function of the percentage of solids.

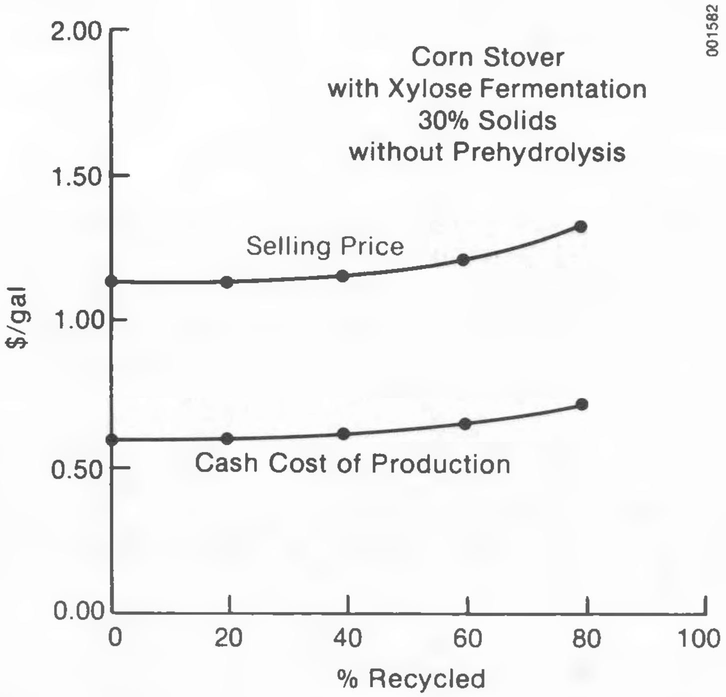


Figure 7-9. Price of Ethanol vs. Percentage of Unreacted Solids Recycled with Xylose Fermentation

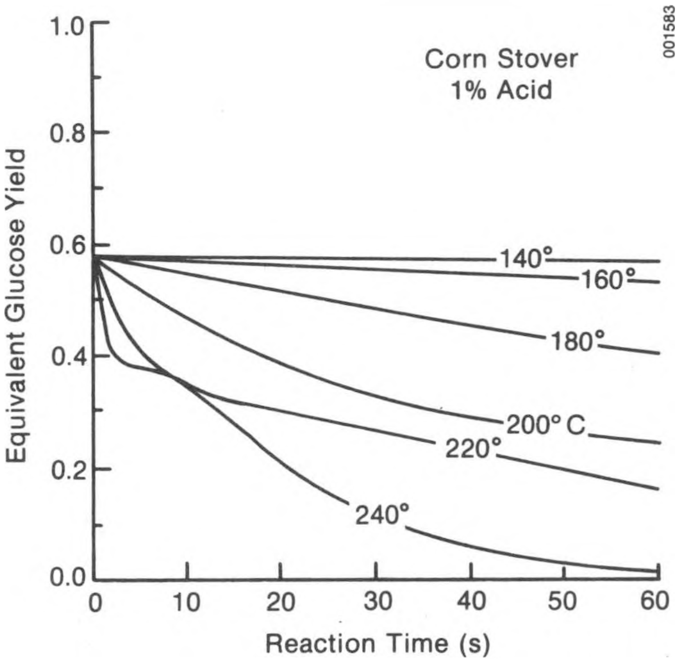


Figure 7-10. Yield of Combined Prehydrolysis and Hydrolysis in a System with Xylose Fermentation

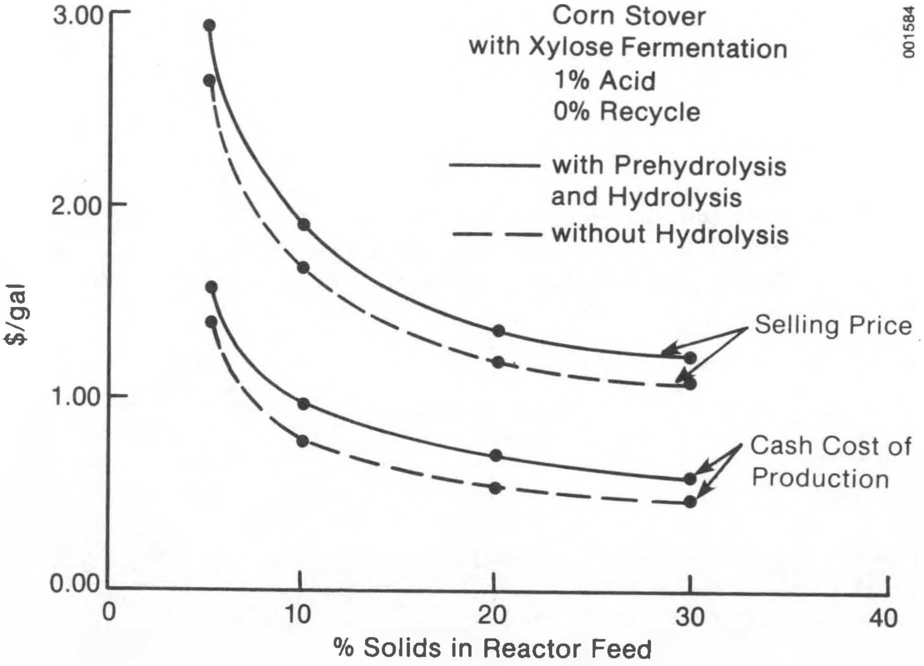


Figure 7-11. Cost of Ethanol vs. Percentage of Solids in the Reactor Feed for Systems Using Xylose Fermentation with Prehydrolysis and Hydrolysis and with Prehydrolysis Only

Table 7-9. **Effect of Xylose Conversions on Selling Price** (0% recycle, 30% solids concentration entering the reactor, prehydrolysis, in \$/gal)

Cost Component	Without Xylose Fermentation	With Xylose Fermentation
Corn stover	0.79	0.49
Chemicals	0.11	0.09
Utilities	0.04	0.08
Operation and overhead	0.17	0.15
By-product credits	-0.21	-0.21
Subtotal	0.90	0.60
Capital charges	0.63	0.54
Total	1.53	1.14

The system without hydrolysis produces lower-cost ethanol. Table 7-10 presents a comparison of the costs and yields of the two types of systems.

7.3.2 Furfural By-Product Credit

If a prehydrolysis step is not incorporated into the acid hydrolysis process, the pentosans in the hemicellulose are degraded to furfural and tars. In the base case, furfural is considered a waste product and is removed in carbon bed purifiers. In actual practice, furfural is a chemical intermediate with a mid-1982 selling price of \$0.66/lb. While the production of furfural in large quantities would depress prices, it appears that furfural can provide valuable

Table 7-10. **Effects on Selling Price and Yield of Prehydrolysis Only vs. Prehydrolysis and Hydrolysis for a System Using Xylose Fermentation** (0% recycle, 30% solids in \$/gal)

Cost Component	Prehydrolysis Only	Prehydrolysis and Hydrolysis
Corn stover	0.67	0.49
Chemicals	0.08	0.09
Utilities	-0.22	0.08
Operation and overhead	0.15	0.15
By-product credits	-0.21	-0.21
Subtotal	0.47	0.60
Capital charges	0.61	0.56
Total	1.08	1.14
Yield (%)	57%	79%

by-product credits at much lower prices. Furthermore, the incremental cost of removing furfural should be fairly low.

Taking a by-product credit for furfural dramatically reduces the selling price of ethanol (Fig. 7-12). The processes for which we define the economics used a corn stover feedstock, no prehydrolysis, a 30% solid feed to the reactor, no recycling, and a 6.5-s residence time at 1% acid and 235°C. The value of the furfural sold is directly deducted from the operating cost of the plant. Note that the cost of furfural is low because this analysis shows only the incremental costs of furfural production rather than total costs. (Production of furfural alone would not be as financially attractive, because there would be no ethanol by-product credit.)

The ratio of six-carbon to five-carbon sugars in corn stover is approximately 2 to 1. However, because of the inefficiencies in the conversion of cellulose to glucose, and because only 51% of the glucose is converted to ethanol (the remainder is converted to carbon dioxide) while up to 70% of the xylose may be converted to furfural, the ratio of furfural product to ethanol product is only slightly less than one. We assume that the maximum amount (70%) of the xylose is degraded to form furfural. More detailed kinetic data on the reaction of xylose and furfural are needed to make an accurate estimate of the furfural yield.

Availability of furfural markets will have a large effect on the type of processing selected. If a net return (selling price minus incremental production costs) of greater than $0.05/lb can be obtained, it will be advantageous to produce furfural instead of using prehydrolysis and converting the five-carbon

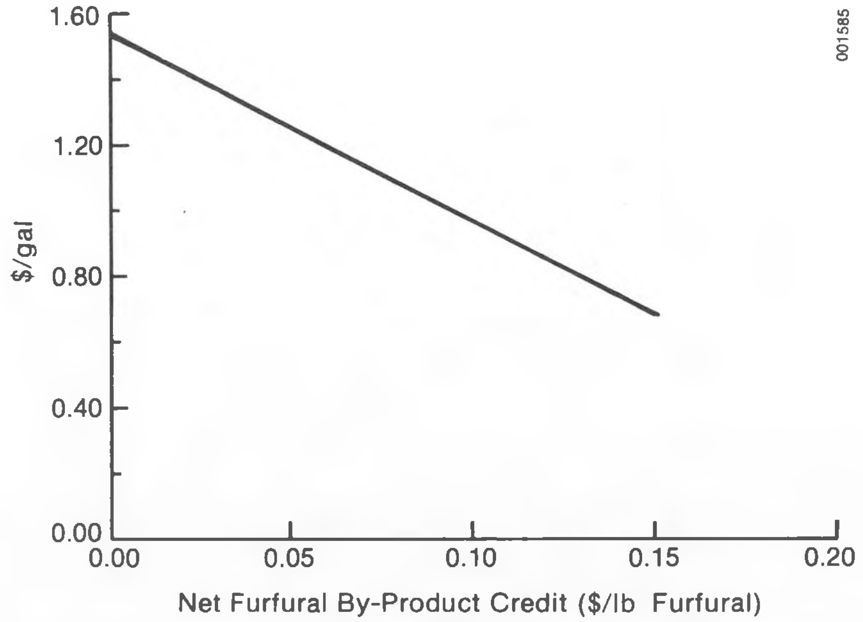


Figure 7-12. Selling Price of Ethanol as a Function of the Net Furfural By-Product Credit

sugars to ethanol (when such technology becomes available). However, large furfural markets will be available to the first plants built, and additional plants will tend to saturate the market, because the chemical market is limited.

7.3.3 Product Purity

By reducing the purity of the ethanol product, we can reduce the energy usage in purification, the capital cost of purification, and therefore the selling price of ethanol.

Figure 7-13 shows the effect of reductions in product purity on the selling price of ethanol and ethanol solutions. As is shown by the top curve, reductions in product purity cause only a small reduction in the selling price of a gallon of ethanol. Reducing the purity to 85% reduces the cost of a gallon of ethanol by $0.09, while reducing the purity to 50% lowers the price $0.12 to $1.42/gal. Since most of the benefit of reduction in purity is achieved by the 85% level, this would probably be the preferred concentration, because further decreases in ethanol concentration would add greatly to storage and transportation costs.

The base case for the calculations uses a corn stover feed, no prehydrolysis, no solids recycling, and 30% solids concentration entering the reactor. The effect of purity on the cost components is shown in Table 7-11. If the product is less than 94% pure, the capital charges are reduced because the two columns to perform the extractive distillation are not needed. However,

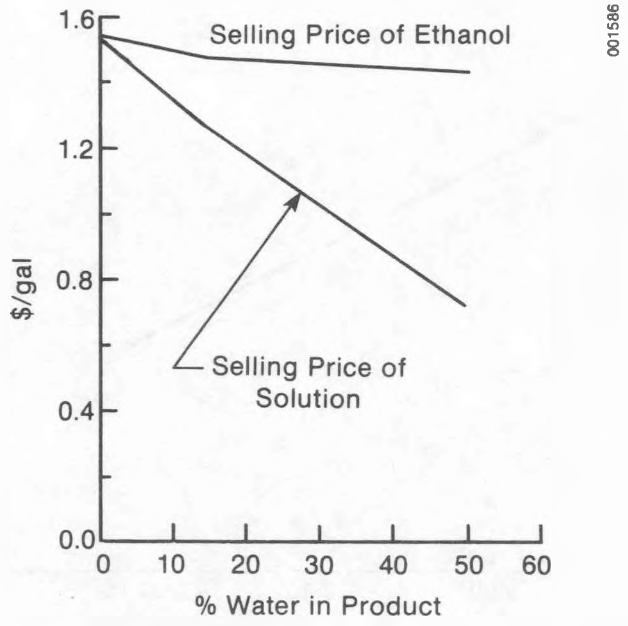


Figure 7-13. Effect of Product Purity on Selling Price

Table 7-11. Effect of Product Purity on Selling Price of Ethanol (Normalized to $/gal of Ethanol, in $/gal)

Cost Component	100%	85%	50%
Corn stover	1.04	1.04	1.04
Chemicals	0.12	0.12	0.12
Utilities	-0.26	-0.30	-0.33
Operation and overhead	0.16	0.15	0.15
By-product credits	-0.21	-0.21	-0.21
Subtotal	0.85	0.80	0.77
Capital charges	0.69	0.65	0.65
Total	1.54	1.45	1.42

lowering the purity to 94% does not save any energy, because the entire heat requirements of the extractive distillation are met by waste heat from the beer still. Decreasing product purity further saves very little on capital cost but cuts the energy usage in the beer still. For example, the energy required to distill 6.5 wt % ethanol to 94% is 25,700 Btu/gal, while the energy needed to concentrate to 75% is 10,800 Btu/gal.

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SECTION 8.0

CONCLUSIONS

The parametric analyses of high-temperature acid hydrolysis of cellulose for fuel alcohol production indicate the potential for significant reductions in the selling price of ethanol. The acid hydrolysis model utilized in this study is best suited for comparisons of processes and not for its ability to predict absolute costs. However, results are reported and compared in dollars per gallon to provide a common measure of the economics of the process. Changes in the hydrolysis conditions lowered the cost 32% from the base condition from $2.15/gal to $1.45/gal of ethanol for a 50 million-gal/yr plant using aspen wood at $20/delivered ton. While the uncertainty of these figures is about 30%, it is important to note that the ethanol selling prices predicted are competitive with those for ethanol produced from corn, and that these figures were derived with conservative feedstock costs and no large by-product credits. By-product credits could reduce this figure considerably.

The amount of water in the process flows has the largest effect on process economics. The presence of large amounts of water raises the steam usage and increases the equipment size and capital cost of the plant. Increasing the solids concentration in the reactor feed from 15% to 20%-30% accounted for most of the reduction in the price of ethanol. However, little improvement can be gained by operating at greater than 30% solids. Other changes in the processing configuration and conditions have a smaller impact on process economics. Use of prehydrolysis is beneficial in some cases and not others. Its use is favored by high feedstock costs and high ratios of amorphous to crystalline six-carbon sugars. In any case, the effect of prehydrolysis is small.

Increasing both the acid concentration and temperature in the hydrolysis reactor improves the economics by increasing the yield with little increase in utility or chemical costs. The improvement possible by these techniques is limited by practical lower bounds, beneath which the residence time in the reactor cannot be controlled and the heat-up and quenching time become significant. Increasing the yield by recycling unreacted solids from the hydrolysis reactor or by employing a two-stage hydrolysis reactor has little or no economic benefit. The highest yield, expressed in terms of the ratio of glucose sent to fermentation to potential glucose in the feed, is about 68%.

By-product credits and downstream process changes can greatly reduce ethanol's selling price. Development of a yeast coculture that could ferment xylose to ethanol in the existing fermenter would lower the ethanol selling price to the range of $1.10/gal. This might also mean that the preferred processing for a feedstock such as corn stover that has a high amorphous fraction would be only prehydrolysis. Addition of hydrolysis is of marginal value because the percentage increase in the yield is relatively small. Recovery of furfural as a by-product from a system without prehydrolysis is more beneficial than xylose fermentation if the net profit (selling price minus incremental cost of production) is greater than $0.05/lb of furfural. In such a plant the weight of furfural produced would slightly exceed that of the ethanol. Net furfural credits of $0.10/lb would reduce the selling price of ethanol by $0.85/gal.

Decreasing the product purity decreases the cost of ethanol, but the maximum gain is approximately $0.12/gal. The effect is small because energy and capital costs in the purification section are not a large part of the total cost of production.

In summary, increasing the solids concentration in the reactor feed, by-product credits for furfural, and xylose fermentation offer the largest potential reductions in the selling price of ethanol. Increasing the reactor temperature and acid concentration result in smaller price reductions, as does decreasing product purity. Inclusion or exclusion of prehydrolysis has little effect, as does unreacted solids recycling and two-stage hydrolysis. The value of running the reactors with a feedstock that contains more than 30% solids is slight.

SECTION 9.0

RECOMMENDATIONS

This section presents recommendations for further research that would be beneficial to acid hydrolysis processes and for improvements to the flow sheet. Improvements to the flow sheet involve substitution or alteration of the steps within the overall process that would be economically beneficial but would require little or no research to implement.

The most important process parameter is the concentration of solids that can be pumped into the prehydrolysis and hydrolysis reactors. Concentrations of 20%-30% are necessary if acid hydrolysis for fuel alcohol production is to be economical. The ability to pump such slurries to high pressures while accurately controlling the flow rate needs to be demonstrated.

The cost of the hydrolysis reactors was estimated for 316 stainless steel pipe reactors. If exotic materials of construction are required, the cost of the reactor may become significant. A detailed design study should be carried out to identify a specific design and accurately estimate its cost.

An important assumption in the kinetic analysis is that in both the hydrolysis and prehydrolysis reactors, the amorphous cellulose and hemicellulose are instantly converted to simple sugars. This conversion undoubtedly occurs in the hydrolysis reactor, but may not occur in the milder conditions of the prehydrolysis reactor. If prehydrolysis of the amorphous fraction is not instantaneous, prehydrolysis conditons may need to be more severe or the residence time increased. Furthermore, the optimum residence time for a one-step hydrolysis may be somewhat longer if degradation of the sugars from the amorphous fraction does not begin immediately. Research is necessary to determine the actual kinetics of hemicellulose hydrolysis in the temperature range of 100°-180°C.

The second major improvement is the development of yeasts or bacteria capable of fermenting five-carbon sugars to ethanol. This improvement could reduce the cost of ethanol by 30% because it lowers both the feedstock costs and the total capital investment.

Furfural has the potential to be a valuable by-product. Its current markets are limited and would be quickly saturated. However, a guaranteed supply of relatively low cost furfural could stimulate new markets. Determination of the kinetics of xylose degradation can identify the conditions that maximize the value of the hydrolysis products (sugar and furfural). Engineering is required to define the processing steps and the costs of furfural recovery. Also, research is recommended to identify new uses and processes for furfural to expand its market and enhance its value.

Lignin also has the potential to be a high value by-product. Research is required to identify the best way to recover the lignin and to better define its uses.

Hydroxymethyl furaldehyde (HMF) is produced in large quantities by the hydrolysis reactor and is very toxic to fermentation yeasts. Adsorption of such large amounts of HMF by carbon beds may not be practical. The costs of carbon adsorption should be carefully evaluated, and alternate methods of HMF separation should be investigated if necessary. The chemistry of HMF should be investigated to determine if it may be utilized in such a way that its value as a byproduct is greater than its fuel value.

A key unknown is the ease with which the hydrolysis solids and liquids can be separated by centrifugation. Our simulation assumes that the solids are concentrated to 40%, repulped to 20%, and recentrifuged to 40%. If this solids content cannot be achieved in the centrifuge, more water will be carried through the process, and more wash water will be required. This would increase the energy and equipment usage. The separation properties of the hydrolysis solids and water need to be determined to better define the effects of this key process parameter.

The centrifuges that remove the sugars and water from the reactor products are expensive and use large amounts of water. The water content of the process streams might be reduced by replacing some or all of the centrifuges with countercurrent, screw-type extractors.

The stillage rejected from the bottom of the beer still is rich in organics. It may be possible to send these streams to a digester to produce methane instead of simply allowing them to be consumed in the waste ponds.

A simple improvement in the energy balance of the plant would be to produce higher pressure steam in the lignin or coal boilers or both, and to cogenerate electricity and 600-psi saturated steam. This would increase the capital investment but further reduce the utility costs.

More energy could be saved in short-residence-time acid hydrolysis processes if the highly irreversible quench/flash at the end of the reactor could be avoided, possibly by using a multistage flash. The hydrolysis reactor products would first be flashed to approximately 140^{o}-150^{o}C (55-70 psia) and then to 120^{o}C (30 psia). The flash vapors would then be used to preheat the reactor feed. In the prehydrolysis reactor, a similar use could be made of the flash vapors. Alternatively, because close control of reaction time is less important in the prehydrolysis reactor, countercurrent heat exchange with the feed could be used to preheat the feed and cool the products.

A second method of quenching the reaction would be to inject the calcium hydroxide into the end of the reactor. In this manner the reaction would be chemically quenched and the products cooled by countercurrent heat exchange. However, experiments would be necessary to determine whether this quenching process allows close enough control of the reaction time. The optimum process may be a combination of chemical and flash quenching.

SECTION 10.0

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APPENDIX A

This section presents a printout of the input parameters, material balance, capital cost estimate, and economic summary for the base case.

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                                          SUMMARY OF INPUT DATA
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                                      SOLAR ENERGY RESEARCH INSTITUTE
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RAW MATERIALS HANDLING BLOCK

                ETHANOL PRODUCTION RATE (MM GAL/YR):          50.0
                ESTIMATED TOTAL PROCESS FEED (LBS/HR):     326600.0
                PROCESS FEED IS Aspen Wood
                FEED MILLING IS BYPASSED
                STEAM EXPLOSION IS BYPASSED
                STEAM EXPLOSION WASH IS BYPASSED

DELIGNIFICATION BLOCK

                SOLVENT DELIGNIFICATION IS BYPASSED

PREHYDROLYSIS BLOCK

                PREHYDROLYSIS IS INCLUDED
                SOLIDS CONCENTRATION ENTERING REACTOR (PERCENT):          15.0
                ACID CONCENTRATION IN SOLUBLES ENTERING REACTOR (PERCENT):              .5
                REACTOR TEMPERATURE (DEG. C):         140.0
                REACTION TIME (SECONDS):         60.0
                SOLIDS FROM CENTRIFUGE FEED IN EFFLUENT SOLIDS (PERCENT):          95.0
                CENTRIFUGED SOLIDS CONCENTRATION (PERCENT):          40.0
                SOLIDS CONCENTRATION FOLLOWING REPULPING (PERCENT):          20.0
                WATER WASH FACTOR ON WATER AND SOLUBLES IN POLISH FILTER SOLIDS:          1.5
                SOLUBLES ON FILTERED SOLIDS REMOVED BY WASH (PERCENT):          93.8
                GLUCOSE FORMATION KINETICS:       5.331E16  (A)*1.14 EXP(-36995/RT)
                GLUCOSE DECOMPOSITION KINETICS:   3.841E09  (A)* .57 EXP(-20988/RT)
                XYLOSE DECOMPOSITION KINETICS:    8.780E15  (A)*1.00 EXP(-33560/RT)

ACID HYDROLYSIS BLOCK

                SOLIDS CONCENTRATION ENTERING REACTOR (PERCENT):          15.0
                ACID CONCENTRATION IN SOLUBLES ENTERING REACTOR (PERCENT):             1.0
                REACTOR TEMPERATURE (DEG. C):         235.0
                REACTION TIME (SECONDS):         12.0
                SOLIDS FROM CENTRIFUGE FEED IN EFFLUENT SOLIDS (PERCENT):          95.0
                CENTRIFUGED SOLIDS CONCENTRATION (PERCENT):          40.0
                SOLIDS CONCENTRATION FOLLOWING REPULPING (PERCENT):          20.0
                WATER WASH FACTOR ON WATER AND SOLUBLES IN POLISH FILTER SOLIDS:          1.5
                SOLUBLES ON FILTERED SOLIDS REMOVED BY WASH (PERCENT):          93.8
                UNREACTED SOLIDS RECYCLED (PERCENT):          40.0
                GLUCOSE FORMATION KINETICS:       5.331E16  (A)*1.14 EXP(-36995/RT)
                GLUCOSE DECOMPOSITION KINETICS:   3.841E09  (A)* .57 EXP(-20988/RT)
                XYLOSE DECOMPOSITION KINETICS:    8.780E15  (A)*1.00 EXP(-33560/RT)
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                                    SUMMARY OF INPUT DATA (CONTINUED)
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NEUTRALIZATION AND CONCENTRATION BLOCK

                    CONCENTRATION IS BYPASSED
                    pH OF FERMENTATION FEED:           4.0

INPUT FEED CONCENTRATIONS AND MOLECULAR WEIGHTS

                                     Molecular    Process Fe
                                     Weights      ed

                    Water                 18.0          50.0
                    Cryst. Cellulose     162.0          20.7
                    Amorph. Cellulose    162.0           3.7
                    Pentosan             132.0          10.9
                    Hexosan              162.0           4.4
                    Insoluble Lignin     100.0           8.3
                    Insoluble Protein    100.0            .0
                    Ash                  100.0            .1
                    Extractives          100.0           1.9
                    Soluble Lignin       100.0            .0
                    Pseudolignin-5        78.0            .0
                    Pseudolignin-6       108.0            .0
                    Soluble Protein      100.0            .0
                    Carbohydrates        342.0            .0
                    Furfural              96.0            .0
                    HMF                  126.0            .0
                    Xylose               150.0            .0
                    Glucose              180.0            .0
                    Ethanol               46.0            .0
                    Sulfuric Acid         98.0            .0
                    Calcium Hydroxide     74.0            .0
                    Calcium Sulfate      136.0            .0
                    Benzene               78.0            .0
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                                         PREHYDROLYSIS BLOCK SUMMARY
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                                      SOLAR ENERGY RESEARCH INSTITUTE
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                    FEED TO PR   AFTER DILU   AFTER REAC   FROM FLASH   SOLUBLES E   SOLID FILT
                    EHYDROL.     TION         TION                      FFLUENT      ER CAKE

Water                215518.7    1166674.4    1156783.6    1112283.5    1255844.5     180778.1
Cryst. Cellulose      89397.1      89397.1      89339.9      89339.9        435.5      88904.4
Amorph. Cellulose     15776.0      15776.0           .0           .0           .0           .0
Pentosan              46823.6      46823.6           .0           .0           .0           .0
Hexosan               19125.1      19125.1           .0           .0           .0           .0
Insoluble Lignin      35776.1      35776.1      35776.1      35776.1        174.4      35601.7
Insoluble Protein          .0           .0           .0           .0           .0           .0
Ash                     431.0        431.0        431.0        431.0          2.1        428.9
Extractives            8189.7       8189.7       8189.7       8189.7       7754.9        434.8
Soluble Lignin             .0           .0           .0           .0           .0           .0
Pseudolignin-5             .0           .0           .0           .0           .0           .0
Pseudolignin-6             .0           .0           .0           .0           .0           .0
Soluble Protein            .0           .0           .0           .0           .0           .0
Carbohydrates              .0           .0           .0           .0           .0           .0
Furfural                   .0           .0        258.4        258.4        244.7         13.7
HMF                        .0           .0        543.9        543.9        515.1         28.9
Xylose                     .0           .0      52804.8      52804.8      50001.3       2803.5
Glucose                    .0           .0      38065.5      38065.5      36044.5       2021.0
Ethanol                    .0           .0           .0           .0           .0           .0
Sulfuric Acid              .0       5903.8       5903.8       5903.8       5590.4        313.5
Calcium Hydroxide          .0           .0           .0           .0           .0           .0
Calcium Sulfate            .0           .0           .0           .0           .0           .0
Benzene                    .0           .0           .0           .0           .0           .0

TOTAL                431037.3    1388096.9    1388096.9    1343596.8    1356607.4     311328.5


WATER ADDITION TO PREHYDROLYSIS IS:      951155.7
ACID ADDITION TO PREHYDROLYSIS IS:         5903.8
WATER ADDED TO CENTRIFUGE REPULPING IS:      298174.3
WATER ADDED TO FILTER WASH IS:      26164.8
VAPOR REMOVED BY FLASH IS:      44500.0
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                                                        HYDROLYSIS BLOCK SUMMARY
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                                                    SOLAR ENERGY RESEARCH INSTITUTE
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                          HYDROLYSIS  AFTER DILU  AFTER REAC  FROM FLASH  SOLUBLES E  SOLIDS REC  SOLIDS PUR
                           FEED       TION        TION                    FFLUENT     YCLE        GE

Water                       180778.1    897617.7    899255.0    681131.4    782123.1     49811.2     74716.8
Cryst. Cellulose             88904.4     99841.5     27476.7     27476.7       133.9     10937.1     16405.7
Amorph. Cellulose                 .0          .0          .0          .0          .0          .0          .0
Pentosan                          .0          .0          .0          .0          .0          .0          .0
Hexosan                           .0          .0          .0          .0          .0          .0          .0
Insoluble Lignin             35601.7     59106.7     59106.7     59106.7       208.1     23527.4     35291.1
Insoluble Protein                 .0          .0          .0          .0          .0          .0          .0
Ash                            428.9       712.1       712.1       712.1         3.5       283.5       425.2
Extractives                    434.8       445.2       445.2       445.2       419.2        10.4        15.6
Soluble Lignin                    .0          .0          .0          .0          .0          .0          .0
Pseudolignin-5                    .0          .0          .0          .0          .0          .0          .0
Pseudolignin-6                    .0          .0          .0          .0          .0          .0          .0
Soluble Protein                   .0          .0          .0          .0          .0          .0          .0
Carbohydrates                     .0          .0          .0          .0          .0          .0          .0
Furfural                        13.7        57.0      1048.3      1048.3      1740.1        43.3        64.9
HMF                             28.9       514.4     20744.9     20744.9     19530.7       485.7       728.5
Xylose                        2803.5      2803.7         4.7         4.7         4.4          .1          .2
Glucose                       2021.0      3303.7     54808.3     54808.3     51600.5      1283.1      1924.7
Ethanol                           .0          .0          .0          .0          .0          .0          .0
Sulfuric Acid                  313.5      9138.8      9138.8      9138.8      8603.9       213.9       320.9
Calcium Hydroxide                 .0          .0          .0          .0          .0          .0          .0
Calcium Sulfate                   .0          .0          .0          .0          .0          .0          .0
Benzene                           .0          .0          .0          .0          .0          .0          .0

TOTAL                       311328.5   1073540.7   1073540.7    855417.1    864447.6     86595.7    129893.6


WATER ADDITION TO HYDROLYSIS IS:      474192.1
STEAM ADDITION TO HYDROLYSIS IS:      192869.4
ACID ADDED FOR HYDROLYSIS IS:       8611.6
WATER ADDED TO CENTRIFUGE REPULPING IS:      207326.8
WATER ADDED TO FILTER WASH IS:       18192.9
VAPOR REMOVED BY FLASH IS:     218123.6
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                                        NEUTRALIZATION AND CONCENTRATION BLOCK SUMMARY
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                                              SOLAR ENERGY RESEARCH INSTITUTE
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                       FEED TO NE   AFTER NEUT   FROM FLASH   FILTER EFF   FILTER CAK   CONC. SUGA
                       UTRAL.       RAL.                      LUENT        E            RS

Water                   2037967.7    2043173.9    2019082.7    2033977.1      29364.0    2033977.1
Cryst. Cellulose            569.5        569.5        569.5         28.5        541.0         28.5
Amorph. Cellulose              .0           .0           .0           .0           .0           .0
Pentosan                       .0           .0           .0           .0           .0           .0
Hexosan                        .0           .0           .0           .0           .0           .0
Insoluble Lignin            462.6        462.6        462.6         23.1        439.4         23.1
Insoluble Protein              .0           .0           .0           .0           .0           .0
Ash                           5.6          5.6          5.6           .3          5.3           .3
Extractives                8174.1       8174.1       8174.1       8167.2          6.9       8167.2
Soluble Lignin                 .0           .0           .0           .0           .0           .0
Pseudolignin-5                 .0           .0           .0           .0           .0           .0
Pseudolignin-6                 .0           .0           .0           .0           .0           .0
Soluble Protein                .0           .0           .0           .0           .0           .0
Carbohydrates                  .0           .0           .0           .0           .0           .0
Furfural                   1984.8       1984.8       1984.8       1983.2          1.7       1983.2
HMF                       20045.8      20045.8      20045.8      20028.9         16.9      20028.9
Xylose                    50005.7      50005.7      50005.7      49963.6         42.2      49963.6
Glucose                   87645.0      87645.0      87645.0      87571.1         73.9      87571.1
Ethanol                        .0           .0           .0           .0           .0           .0
Sulfuric Acid             14194.3         21.8         21.8         21.7           .0         21.7
Calcium Hydroxide              .0           .0           .0           .0           .0           .0
Calcium Sulfate                .0      19668.0      19668.0        983.4      18684.6        983.4
Benzene                        .0           .0           .0           .0           .0           .0

TOTAL                   2221055.0    2231756.7    2207665.5    2202748.0      49175.9    2202748.0


CALCIUM HYDROXIDE ADDED IN NEUTRALIZATION IS:        10701.7
VAPOR REMOVED BY FLASH IS:       24091.2
WATER ADDED AT WASH IN FILTER IS:        44258.3
WATER REMOVED IN EVAPORATOR IS:              .0
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                                        FERMENTATION BLOCK SUMMARY
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                                     SOLAR ENERGY RESEARCH INSTITUTE
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                         FERMENTATI   FROM CARBO   YEAST RECY   FROM FERME   SOLUBLES F   SOLIDS FRO   YEAST PURG
                         ON FEED      N BEDS       CLE          NTATION      RM CENTRI    M CENTRI     E

Water                     2033977.1    2033977.1      38233.1    2072210.4    2027458.8      44751.6       6518.5
Cellulose                      28.5         28.5           .5         29.0         28.4           .6           .1
Yeast                            .0           .0       7095.9       8742.8        437.1       8305.7       1209.8
Pentosan                         .0           .0           .0           .0           .0           .0           .0
Hexosan                          .0           .0           .0           .0           .0           .0           .0
Insoluble Lignin               23.1         23.1           .4         23.6         23.1           .5           .1
Insoluble Protein                .0           .0           .0           .0           .0           .0           .0
Ash                              .3           .3           .0           .3           .3           .0           .0
Extractives                  8167.2       8167.2        153.5       8320.7       8141.0        179.7         26.2
Glycerol                         .0           .0         48.4       2624.0       2567.3         56.7          8.3
Pseudolignin-5                   .0           .0           .0           .0           .0           .0           .0
Pseudolignin-6                   .0           .0           .0           .0           .0           .0           .0
Soluble Protein                  .0           .0           .0           .0           .0           .0           .0
Carbohydrates                    .0           .0           .0           .0           .0           .0           .0
Furfural                     1983.2           .0           .0           .0           .0           .0           .0
HMF                         20028.9           .0           .0           .0           .0           .0           .0
Xylose                      49963.6      49963.6        939.2      50902.7      49803.4       1099.3        160.1
Glucose                     87571.1      87571.1         32.3       1752.1       1714.2         37.8          5.5
Ethanol                          .0           .0        783.6      42469.2      41552.0        917.2        133.6
Sulfuric Acid                  21.7         21.7           .4         22.2         21.7           .5           .1
Carbon Dioxide                   .0           .0           .0           .0           .0           .0           .0
Calcium Sulfate               983.4        983.4         18.5       1001.9        980.3         21.6          3.2
Benzene                          .0           .0           .0           .0           .0           .0           .0

TOTAL                     2202748.0    2180735.9      47305.8    2188098.8    2132727.6      55371.2       8065.4


FRESH YEAST ADDITION TO FERMENTATION IS:        788.4
CARBON DIOXIDE RECOVERED IS:       40731.7
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                                         PURIFICATION BLOCK SUMMARY
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                                      SOLAR ENERGY RESEARCH INSTITUTE
                                      ===== ====== ======== =========


                        PURIFICATI   TO AZEO CO   AQUEOUS ST   AZEO COL R   WASTE WATE   ETHANOL PR
                        ON FEED      LUMN         ILLAGE       EFLUX        R            ODUCT

Water                    2027458.8       2632.7    2024826.1       4475.6       2632.7           .0
Cellulose                     28.4           .0         28.4           .0           .0           .0
Yeast                        437.1           .0        437.1           .0           .0           .0
Pentosan                        .0           .0           .0           .0           .0           .0
Hexosan                         .0           .0           .0           .0           .0           .0
Insoluble Lignin              23.1           .0         23.1           .0           .0           .0
Insoluble Protein               .0           .0           .0           .0           .0           .0
Ash                             .3           .0           .3           .0           .0           .0
Extractives                 8141.0           .0       8141.0           .0           .0           .0
Glycerol                    2567.3           .0       2567.3           .0           .0           .0
Pseudolignin-5                  .0           .0           .0           .0           .0           .0
Pseudolignin-6                  .0           .0           .0           .0           .0           .0
Soluble Protein                 .0           .0           .0           .0           .0           .0
Carbohydrates                   .0           .0           .0           .0           .0           .0
Furfural                        .0           .0           .0           .0           .0           .0
HMF                             .0           .0           .0           .0           .0           .0
Xylose                     49803.4           .0      49803.4           .0           .0           .0
Glucose                     1714.2           .0       1714.2           .0           .0           .0
Ethanol                    41552.0      41136.5        415.5      24616.1           .0      41136.5
Sulfuric Acid                 21.7           .0         21.7           .0           .0           .0
Carbon Dioxide                  .0           .0           .0           .0           .0           .0
Calcium Sulfate              980.3           .0        980.3           .0           .0           .0
Benzene                         .0           .0           .0     194690.8         14.6           .0

TOTAL                    2132727.6      43769.2    2088958.3     223782.5       2647.3      41136.5


BENZENE MAKEUP TO DEHYDRATION IS:          14.6
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                              HEAT GENERATION BLOCK SUMMARY
                              ==== ========== ===== =======

                             SOLAR ENERGY RESEARCH INSTITUTE
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                     HYDROLYSIS   BY-PROD LI   STILLAGE B   NEUTRAL FE   FROM NEUTR   EVAP CONDE   BOILER FEE   SOLID WAST
                      SOLIDS      GNIN         OTTOMS       ED           AL           NSATE        D            E

Water                   74716.8           .0           .0      74716.8      74834.7      29588.3      45246.4      29364.0
Cellulose               16405.7           .0           .0      16405.7      16405.7           .0      16405.7        541.0
Yeast                        .0           .0           .0           .0           .0           .0           .0           .0
Pentosan                     .0           .0           .0           .0           .0           .0           .0           .0
Hexosan                      .0           .0           .0           .0           .0           .0           .0           .0
Insoluble Lignin        35291.1           .0           .0      35291.1      35291.1           .0      35291.1        439.4
Insoluble Protein            .0           .0           .0           .0           .0           .0           .0           .0
Ash                       425.2           .0           .0        425.2        425.2           .0        425.2        430.5
Extractives                15.6           .0           .0         15.6         15.6           .0         15.6          6.9
Glycerol                     .0           .0           .0           .0           .0           .0           .0           .0
Pseudolignin-5               .0           .0           .0           .0           .0           .0           .0           .0
Pseudolignin-6               .0           .0           .0           .0           .0           .0           .0           .0
Soluble Protein              .0           .0           .0           .0           .0           .0           .0           .0
Carbohydrates                .0           .0           .0           .0           .0           .0           .0           .0
Furfural                   64.9           .0           .0         64.9         64.9           .0         64.9          1.7
HMF                       728.5           .0           .0        728.5        728.5           .0        728.5         16.9
Xylose                       .2           .0           .0           .2           .2           .0           .2         42.2
Glucose                  1924.7           .0           .0       1924.7       1924.7           .0       1924.7         73.9
Ethanol                      .0           .0           .0           .0           .0           .0           .0           .0
Sulfuric Acid             320.9           .0           .0        320.9           .0           .0           .0           .0
Carbon Dioxide               .0           .0           .0           .0           .0           .0           .0           .0
Calcium Sulfate              .0           .0           .0           .0        445.4           .0        445.4      19130.0
Benzene                      .0           .0           .0           .0           .0           .0           .0           .0

TOTAL                  129893.6           .0           .0     129893.6     130135.9      29588.3     100547.6      50046.5


CALCIUM HYDROXIDE ADDED TO NEUTRALIZATION IS:        242.3
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WASTE TREATMENT BLOCK SUMMARY

SOLAR ENERGY RESEARCH INSTITUTE

	FLASH VAPORS	FLASH CONDENSATE	EVAP CONDENSATE	OTHER BY-PROD	YEAST PURGE	TO WASTE POND	BY-PRODUCT
Water	24091.2	262623.6	32221.0	2024826.1	6518.5	2343761.9	6518.5
Cellulose	.0	.0	.0	28.4	.1	28.4	.1
Yeast	.0	.0	.0	437.1	1209.8	437.1	1209.8
Pentosan	.0	.0	.0	.0	.0	.0	.0
Hexosan	.0	.0	.0	.0	.0	.0	.0
Insoluble Lignin	.0	.0	.0	23.1	.1	23.1	.1
Insoluble Protein	.0	.0	.0	.0	.0	.0	.0
Ash	.0	.0	.0	.3	.0	.3	.0
Extractives	.0	.0	.0	8141.0	26.2	8141.0	26.2
Glycerol	.0	.0	.0	2567.3	8.3	2567.3	8.3
Pseudolignin-5	.0	.0	.0	.0	.0	.0	.0
Pseudolignin-6	.0	.0	.0	.0	.0	.0	.0
Soluble Protein	.0	.0	.0	.0	.0	.0	.0
Carbohydrates	.0	.0	.0	.0	.0	.0	.0
Furfural	.0	.0	.0	.0	.0	.0	.0
HMF	.0	.0	.0	.0	.0	.0	.0
Xylose	.0	.0	.0	49803.4	160.1	49803.4	160.1
Glucose	.0	.0	.0	1714.2	5.5	1714.2	5.5
Ethanol	.0	.0	.0	415.5	133.6	415.5	133.6
Sulfuric Acid	.0	.0	.0	21.7	.1	21.7	.1
Carbon Dioxide	.0	.0	.0	.0	.0	.0	.0
Calcium Sulfate	.0	.0	.0	980.3	3.2	980.3	3.2
Benzene	.0	.0	14.6	.0	.0	14.6	.0
TOTAL	24091.2	262623.6	32235.6	2088958.3	8065.4	2407908.8	8065.4

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                      OVERALL MATERIAL BALANCE SUMMARY
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                      SOLAR ENERGY RESEARCH INSTITUTE
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         PRODUCTS, LBS/HR

     Ethanol                     41136.5
     Carbon Dioxide              40731.7
     SCP                          1209.8


         RAW MATERIALS, LBS/HR

     Aspen Wood                 431037.3
     Sulfuric Acid               14515.4
     Calcium Hydroxide           10944.1
     Yeast                         788.4
     Benzene                        14.6


         PROCESS UTILITIES CONSUMED, LBS/HR

     Steam, 600 psia            192869.4
     Steam, 55 psia                   .0
     Process Water             2019465.0
     Boiler Feedwater           192869.4


         PROCESS UTILITIES PRODUCED; LBS/HR

     Steam, 600 psia            192869.4
     Steam, 200 psia            130386.0
     Steam, 30 psia             262623.6
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                     PLANT CAPITAL COST SUMMARY
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                  SOLAR ENERGY RESEARCH INSTITUTE
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                        (FIRST QUARTER 1982)
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                                                  DOLLARS
                                                  -------
PURCHASED EQUIPMENT COSTS
     RAW MATERIAL HANDLNG                          257379
     DELIGNIFICATION                                    0
     PREHYDROLYSIS                                3505080
     HYDROLYSIS                                   2859141
     NEUTRALIZATION                               1637726
     FERMENTATION                                 5998032
     PURIFICATION                                 2126866
     HEAT GENERATION                               356954
     WASTE TREATMENT                                30583
                                                 --------
TOTAL PURCHASED EQUIPMENT COST                   16771760

TOTAL INSTALLED EQUIPMENT COST                   38268652

ENGINEERING AND CONST. OVERHEAD                   5769486
ENGINEERING FEE AND CONTINGENCY                   6239095

CO2 RECOVERY SYSTEM PACKAGE                       8371825
                                                 --------
TOTAL PLANT ISBL COST                            58649058

OFFSITES CAPITAL COSTS
     ETHANOL STORAGE  14 DAYS                      834837
     CALCIUM HYDROXIDE STORAGE  7 DAYS             407276
     SULFURIC ACID STORAGE  14 DAYS                227192
     FEEDSTOCK STORAGE  14 DAYS                   2851985
     BYPRODUCT STORAGE  14 DAYS                    191653
     YEAST STORAGE  14 DAYS                         68032
     600 PSIA LIGNIN STEAM BOILER                21725060
     600 PSIA STEAM BOILER                       23301689
     COOLING WATER SYSTEM                         1761736
     ELECTRICAL                                   2571368
     BUILDINGS  3 PERCENT ISBL                    1759472
     GENERAL UTILITES  5 PERCENT ISBL             2932453
     SITE DEVELOPMENT  3 PERCENT ISBL             1759472
     PIPING  3 PERCENT ISBL                       1759472
     POLLUTION CONTROL  2 PERCENT ISBL            1172981
                                                 ---------
TOTAL OFFSITES COST                              63324677
                                                 ---------
TOTAL PLANT CAPITAL COST                        121973735
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                                   OVERALL UTILITIES SUMMARY
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                                SOLAR ENERGY RESEARCH INSTITUTE
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                           STEAM, M LBS/HR                                          POWER,     COOLING     PROCESS
                     15 PSIA    30 PSIA    55 PSIA   200 PSIA   600 PSIA             HP      WATER, GPM  WATER, GPM

RAW MATERIAL HANDLNG      .0         .0         .0         .0         .0             .0          .0          .0
DELIGNIFICATION           .0         .0         .0         .0         .0             .0          .0          .0
PREHYDROLYSIS             .0      ¯44.5         .0      244.8         .0         1984.7          .0      2548.3
HYDROLYSIS                .0     ¯218.1         .0         .0      192.9         1970.3          .0      1398.0
NEUTRALIZATION         ¯24.1         .0         .0         .0         .0         1068.1          .0        88.4
FERMENTATION              .0         .0         .0         .0         .0         8119.7     11557.9          .0
PURIFICATION              .0         .0         .0      385.6         .0          124.7      4027.6          .0
HEAT GENERATION           .0         .0        8.9     ¯130.4     ¯192.9           47.9      1082.9          .0
WASTE TREATMENT           .0         .0         .0         .0         .0             .8      1867.1          .0

TOTAL                  ¯24.1     ¯262.6        8.9      500.0         .0        13316.1     18535.5      4034.7


TOTAL BOILER FEEDWATER REQUIRED, GPM:         385.3
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TABLE 1

COST OF PRODUCTION ESTIMATE FOR ETHANOL
PROCESS- ACID HYDROLYSIS

CAPITAL SUMMARY

BASIS
Location: U.S. Gulf Coast
First Quarter, 1982
Capacity: 50.0 million gallons/yr
149,335 metric tons/yr
Str.Time: 8000 hours per year

CAPITAL COST	$MILLION
Battery Limits	58.6
Offsites	63.3
Total Fixed Inv.	122.0
Working Capital	11.8

PRODUCTION COST SUMMARY

RAW MATERIALS	UNITS PER GAL	PRICE, ¢/UNIT	ANNUAL COST, $M	CENTS PER GAL	DOLLARS/ MET TON
Aspen Wood, Lb	68.9660	1.0	34,483		
Sulfuric Acid, Lb	2.3225	4.3	4,993		
Calcium Hydr., Lb	1.7510	2.0	1,751		
Catalyst & Chemicals			3,188		
TOTAL RAW MATERIALS			44,416	88.83	297.42
UTILITIES					
Power, Kwh	1.58238	4.6	3,639		
Cooling Water, M Gal	.17794	7.3	649		
Process Water, M Gal	.03873	65.0	1,259		
Boiler Feedwtr, M Gal	.00370	113.0	209		
Steam, 200psia, M Lb	.08000	480.0	19,201		
Steam, 55psia, M Lb	¯.04445	470.0	¯10,447		
TOTAL UTILITIES			14,511	29.02	97.17
OPERATING COSTS					
Labor, 46 Men @ $ 26,000		10 M/S	1,196		
Foremen, 9 Men @ $ 29,600		1 M/S	266		
Supervision, 1 Man @ $ 35,600		1 Man	36		
Maint., Material & Labor	6% of ISBL		3,519		
TOTAL OPERATING COST			5,017	10.03	33.60
OVERHEAD EXPENSES					
Direct Overhead	45% Lab. & Sup.		674		
Gen. Plant Overhead	65% Oper. Costs		3,261		
Insurance, Prop. Tax	1.5% Tot. Fix. Inv.		1,830		
TOTAL OVERHEAD EXPENSES			5,765	11.53	38.60
BY-PRODUCT CREDIT					
Carbon Dioxide, Lb	6.51707	2.8	¯9,124		
SCP, Lb	.19357	15.0	¯1,452		
TOTAL BY-PRODUCT CREDIT			¯10,576	¯21.15	¯70.82
CASH COST OF PRODUCTION			59,133	118.27	395.97
Depreciation	20% ISBL + 10% OSBL		18,062		
NET COST OF PRODUCTION			77,195	154.39	516.92
SALES PRICE AT 15% DCF				215.3	720.8