# ACID SOFTENING AND HYDROLYSIS OF CELLULOSE

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# ACID SOFTENING AND HYDROLYSIS OF CELLULOSE

Final Report

Prepared for

THE NEW YORK STATE
ENERGY RESEARCH AND DEVELOPMENT AUTHORITY

Project Manager
Dr. Lawrence R. Hudson

Prepared by

Department of Chemical Engineering
RENSSELAER POLYTECHNIC INSTITUTE
Troy, New York

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# ABSTRACT

Cellulose obtained from steam-exploded wood is softened with concentrated sulfuric acid. After removal of most of the acid by washing with ethanol, the residual acid hydrolyzes the cellulose as it is added in portions to water. Very attractive features of this process are reaction speed that is many times that of enzymatic hydrolysis, simplicity, and the potential to prepare high concentrations of glucose in the hydrolysis mixture. The experiments addressed yields, glucose concentrations, and recycle of sulfuric acid because these have great impact on process economics.

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# SUMMARY

Biomass refining based on separation of the main constituents of exploded wood by extraction with water and extraction with hot ethanol appears to have good commercial potential, but only if the product mix contains high-value lignin. The extraction steps have been proven at the laboratory bench and could be scaled to pilot-plant operations with high confidence. Acid swelling and acid hydrolysis give yields of glucose from cellulose that are only fair but nevertheless are competitive with enzymatic hydrolysis because of simplicity and the low cost of acid hydrolysis. Acid recovery and reuse have been demonstrated but not optimized. There will be no request for renewal. Although this project has been reasonably successful, our group is redirecting all efforts to bioprocessing instead of the physical and chemical steps typified by this method of refining.

## Section 1

## INTRODUCTION

Refining of lignocellulosic feedstocks leads to a mix of products. A report prepared by Arthur D. Little, Inc. for the New York State Energy Research and Development Authority and SERI analyzed one of the leading contenders for biomass refining and found that coproduct credits were crucial (1). With no value derived from the other components except adding them to boiler fuel, ethanol obtained by bioconversion of the sugars from cellulose hydrolysis would have to sell for more than $4 per gallon. On the other hand, refineries that sell lignin at prices which seem reasonable for applications such as manufacture of adhesives would be profitable even if the alcohol were given away.

We want to belabor certain features that a good refining scheme should include. Our process is but one way to address some of these features and thus is a stalking horse for alternative processes to surpass. Approaches to biomass energy have been assessed in detail (2). We drew on this technology and on more recent reports to devise a scheme for biomass refining. Our approach is shown in Figure 1. The facets that will be discussed here are:

feedstock
waste treatment
pretreatment
separation
conversion to final products

### FEEDSTOCK

Only an ignorant person would take the best grades of trees and convert them to cheap fuels or chemicals. Lumber and paper pulp are much more valuable. However, inferior species and damaged trees are left and may propagate to lower the quality of the forest. When the crews and machinery are in place for harvesting the desirable trees, it costs little more to collect the poorer trees for the biomass refinery. As highly productive short-rotation tree farms are established, the increase in productivity should satisfy both pulping and biomass refining.

A challenging feedstock for biomass refining is solid waste. We hear much about the staggering problems in disposing of solid wastes in our cities, and converting trash to valuable products is a noble cause. Unfortunately, the logistics are poor in that few collection facilities are large enough to support a refinery of sufficient size to be economic. Furthermore, trash contains glass, metals, and plastics that impede biomass processing. A more promising option is to develop a biomass refinery based on a better feedstock and to see how much solid waste can be blended in. In other words, the trash may be a minor input to a large refinery but a major factor in its environmental acceptance.

Inferior grades of trees or some residues from agriculture that are readily available are the prime targets. In New York State, land formerly used to grow corn lies idle because large farms in the midwest produce corn so cheaply through economies of scale and the ease of managing flat land. Existing trees will be used for start-up, but short-rotation trees from replanting and from land now out of production would soon sustain the refinery.

## WASTE TREATMENT

A factory that uses steam explosion for size reduction and pretreatment will have wastewaters with some unreacted sugars, unchanged organic compounds found in wood, and small amounts of yeast cells and unrecovered alcohol. With no toxic or hazardous substances present, these wastes will be ideal for irrigation. We propose that the refinery be located near farms or forests so that the logistics of irrigation are favorable. The amount of wastewater will be insignificant for the thousands of hectares of woodlands, but hundreds of hectares near the refinery can be irrigated. These will be by far the most productive areas, and proximity to the refinery will result in minimum transportation costs.

Pollution will be somewhat greater for a factory that employs acid hydrolysis instead of enzymatic hydrolysis. Certain agents for swelling cellulose such as Cadoxen, a complex of cadmium salts, must be avoided because of extreme toxicity. The most likely acid for hydrolysis is sulfuric acid because of its low cost. Simple neutralization of waste acid may suffice for treatment in some cases, and ion exchange or membrane techniques can remove acid or its salts after neutralization. The wastes from bioconversion of glucose to ethanol can be used for irrigation.

# Section 2

# BIOMASS REFINING

## PRETREATMENT

The approximate composition of wood is:

| | |
|---|---|
| Cellulose | 40 to 50 percent |
| Hemicellulose | 15 to 25 |
| Lignin | 15 to 22 |
| Ash | 5 |

Cellulose is a linear polysaccharide that liberates glucose when hydrolyzed with acid or with enzymes. Hemicellulose is a polymer of several sugars, predominantly pentoses, and the sugar in greatest concentration is xylose. Lignin is a three-dimensional polymer of separate aromatic rings with side chains, ether linkages, and free phenolic groups.

All biomass processing requires subdivision. Grinding or milling is far too expensive, and neither is particularly effective in promoting subsequent steps. Steam explosion weakens cellulose, destroys hemicellulose, and melts lignin. The chips are transformed to a brown powder that is nicely sized for further processing. Explosion cellulose is relatively easy to hydrolyze. Hemicellulose is hydrolyzed to sugars during explosion, but the reactions continue on to resinous and polymeric compounds. The fractions derived from hemicellulose have potential for fermentation of the sugars, but the initial refineries will probably sell them for supplementation of cattle feed. The lignin is reduced somewhat in molecular weight, but it is highly reactive and has much more potential than do the various lignins obtained after harsh chemical pulping of wood chips.

## SEPARATION

The first separation step is extraction with water. Exploded wood will be conveyed with water, and careful recycle and management will provide semicountercurrent operation to minimize dilution. The extract must be concentrated to a syrup for sale to supplement cattle feed.

The second separation step is extraction with hot ethanol. This differs from solvent pulping in that no catalysts are added. Extraction is old, established technology, and there is no intention to seek patent protection for these steps. The water washing will be carried out in columns, and flow will be switched to ethanol at an appropriate time. Boiling ethanol extracts about 95 percent of the lignin from exploded wood. In contrast to solvent pulping, where the organic solvent must be recovered from both the treated wood and from the extracts, our scheme considers only a relatively clean lignin extract. The lignin is left behind when the alcohol is distilled. Alcohol, with the spent solids that are mostly cellulose, works its way back into liquid streams as the cellulose is further treated and hydrolyzed. There is only a small amount of final solid residue from this refinery, and this retains a negligible amount of ethanol. We propose that this residue be burned in wood-fired boilers that power the refinery.

## CONVERSION TO FINAL PRODUCTS

We consider it unwise to ferment mixed sugars from hemicellulose and cellulose to ethanol and feel that separation of these fractions is a major advantage of our process. In fermentation, glucose is used first and at a much faster rate than are the sugars from hemicellulose. In fact, the fermentation of pentoses drops off very sharply at about 4.5 percent ethanol. This means that fermentation with glucose present will accumulate sufficient ethanol to ruin the pentose fermentation. Our scheme depends on separating the cellulose and thus there is potential for a successful fermentation of the hemicellulose sugars.

We have evaluated both hydrolysis with sulfuric acid and hydrolysis with enzymes. Steam explosion is an excellent pretreatment for enzymatic hydrolysis but improves acid hydrolysis only slightly. In our laboratory, we have less complete hydrolysis with acid, but the economics compare favorably because cellulase enzymes are so very expensive to produce. Furthermore, convincing investors to construct a complicated and expensive refinery based on enzymatic hydrolysis will be much more difficult than for a relatively simple refinery using straightforward and simple acid hydrolysis.

Biomass refineries will aim for products with the best profit, and ethanol is but one possibility. However, few chemicals other than ethanol have markets large enough to realize economies of scale with large amounts of biomass. Fermentation of sugars to ethanol is old technology, but new reactor designs such as those with beds of immobilized yeasts are reducing costs through high yields in very short times. The recovery of ethanol by distillation formerly consumed most of the energy available from combustion of the product, and critics challenged the wisdom of spending more energy than could be realized. Modern distillation technology featuring vapor-phase recompression has alleviated this situation. Distillation in the most favorable region of the liquid-vapor equilibrium curve followed by vapor-phase drying to absolute ethanol, allows significant additional reduction in recovery costs. It is no longer true that fuel ethanol has a negative energy balance.

Our hypothetical refinery will collect the spent steam after explosion and use it for the evaporation to produce syrups and for distillation of ethanol. The energy balance looks favorable. The initial scale of operations must be modest because lignin, a key product, has limited markets at present. Nevertheless, a few biomass refineries that demonstrate exciting business opportunities will accelerate the timetable for a massive new biomass energy industry. To keep costs down and to amortize plants quickly, biomass refineries should employ technology akin to that of agribusiness.

Lignin recovered from the alcohol extract has some valuable applications with no further treatment, but derivatives command high prices as specialty chemicals. Lignin's reactivity makes it easy to prepare derivatives that are either water-soluble or solvent-soluble. The largest present market for lignin at attractive prices is formulation of adhesives such as those used for plywood or chipboard. It does not appear profitable to use lignin as an extender of asphalt for highways, but this large potential application provides a price floor.

Although still strictly in the research stage, lignin or crude biomass can be converted to an ignition promoter for diesel fuel. If this pans out, the markets become enormous. Instead of biomass refining limited to a few factories because economics depend on selling the lignin, we would now have two major products, each with large markets to justify many factories.

## RELATED TECHNOLOGY

The IOGEN process, currently in the pilot-plant stage at Iogen, Ltd. in Ottawa, Canada, impregnates wood chips with steam and disintegrates them as the pressure is released suddenly. This is much like the old Masonite process. Water washing to get a fraction composed of sugars from hemicellulose was suggested to us by a Soviet scientist who worked in Bungay's lab at RPI and taught this technology to the IOGEN group. Enzymatic hydrolysis of cellulose is featured.

Our group was convinced that enzymatic hydrolysis of cellulose would be superior to acid hydrolysis. Acid hydrolysis may severely damage sugars formed early in the reaction, and sugars from hemicellulose suffer greatly during prolonged hydrolysis of cellulose. Sulfuric acid has been used because of its low cost, but glucose yields of more than about 55 percent of the theoretical amount are not attained. Enzymatic hydrolysis can have yields approaching 99 percent. At the suggestion of Michael Ladisch of Purdue University, we tried acid hydrolysis after soaking in concentrated sulfuric acid and achieved yields better than 70 percent. While at first glance this seems poor compared with enzymatic hydrolysis, about 8 percent of the cellulose must be diverted to production of the enzymes. Furthermore, the outstanding yields for enzymatic hydrolysis depend on high dosages of enzymes and prolonged reaction times. A practical yield for enzymatic hydrolysis is more like 85 percent.

Some of the concentrated sulfuric acid from soaking can be recycled. The acid that is difficult to remove from the cellulose is in the correct proportion for dilute acid hydrolysis as the cellulose is added to water. There is one very great difference between our research and that of other groups; our process leads to partially purified cellulose and to fairly clean hydrolysate. Hydrolyzing wood chips or corn stover directly generates a substantial quantity of acidic sludge that presents disposal or acid recycle problems.

We think that working with fairly clean cellulose provides another very significant advantage. We add the soaked acidic cellulose in portions and add more as earlier portions dissolve. There is residue that builds up slowly and that may have to be removed. These incremental additions result in quite high sugar concentrations. Our current target is 20 percent sugar, but higher concentrations are possible. In contrast, most other processes for acid hydrolysis have low concentrations of glucose, and the costs of evaporation to a fermentable concentration can be prohibitive.

## Section 3
## CHEMICAL CONSIDERATIONS

### ORDERED STRUCTURE OF CELLULOSE

Cellulose is a straight chain polymer of D-glucose bonded by beta 1,4-glycosidic links as shown in Figure 2. The structure of cellulose that seems to average 15 percent amorphous and 85 percent crystalline is still being debated. Microfibrils aggregate to form fibrils that collectively become cellulose fibers (3). The amorphous regions may be found in the folded regions of the microfibrils. The degree of polymerization of cellulose measured by Wise and Jahn (4) by several methods can vary from 1,000 in newspaper to 10,000 in cotton. They report that this value drops quickly to a relatively constant value of roughly 100 under mild acid hydrolysis, and does not go lower. This value is often referred to as the LODP (leveling off degree of polymerization) for cellulose.

While the amorphous portion is easily hydrolyzed under mild conditions, the crystalline structure resists solvation by water thereby reducing the ability of a hydrolzing agent to break the beta 1,4 links. It is this crystalline structure and not the beta 1-4 bonds that make hydrolyzing cellulose more difficult than breaking the alpha 1,4 bonds of starch (5).

### ACID HYDROLYSIS

Acid hydrolysis of cellulose requires the breakdown of the crystalline structure of cellulose. This is accomplished by either dilute acids in excess of 180 C or concentrated acids at low temperature (6). Another method that leaves cellulose intact is use of Cadoxen or tris-(ethylenediamine)-cadmium hydroxide as a dissolving agent. Once the crystalline structure is destroyed, the amorphous residue allows complete hydration of the cellulose chains without steric hindrance.

The actual hydrolysis of the beta-1,4 bonds has been modeled as a four-step reaction mechanism as shown in Figure 3. The glycosidic oxygen is quickly protonated in the first step. This followed by the rate-limiting step which is the flexure of the ring from the chair configuration to the semi-planar configuration. The next two steps of bond breakage and addition of a water molecule follow quickly. The crystalline structure of cellulose especially inhibits the rate-limiting step by not allowing ring flexure (6,7).

Dilute Acid

The hydrolysis of cellulose by dilute acid using high temperature and pressure is readily modeled as two consecutive first-order reactions (8). The first reaction is the hydrolysis of cellulose to glucose and the second is the further hydrolysis of glucose to degradation products such as hydroxymethylfurfural or levulinic acid.

Cellulose ---> Glucose ---> Degradation Products
(C) k1 (G) k2

$$dC/dt = -k1C$$

$$dG/dt = k1C - k2G$$

Where k1 and k2 are reaction rate constants that follow an Arrhenius form. Saeman showed that the first rate constant is more temperature sensitive than the second (8). This implies that high temperature, short reaction times should produce the best yields.

Greenwald, et. al. (9), used this model to make a theoretical evalulation of existing and proposed dilute acid reactor systems. They looked at four reactor configurations: cocurrent moving bed, countercurrent moving bed, percolator, and plug flow. Using Saeman's kinetic parameters, they determined optimum yields and sugar concentrations for these types of reactors. They were able to show that the cocurrent, countercurrent and percolator systems were superior to the plug flow system on yield basis. When final sugar concentrations were evaluated, the tradeoff between yield and concentration was not as severe in the plug flow reactor. Therefore the end use of the sugar product would have to be evaluated along with the practical problems in choosing a system.

The first large-scale dilute acid hydrolysis project was a percolation system developed by Scholler in Tornesch, Germany in the 1920's. It used 0.4 percent sulfuric acid at 170 C and a pressure of 8 atmospheres. The acid solution moved in a semicontinuous fashion. This produced a 4 percent or greater sugar solution with yields in the range of 50 to 55 percent (10).

The Madison process was developed at the Forest Products Laboratory at Madison, Wisconsin towards the end of WWII. It represented an improvement on the Scholler-Tornesch process by being able to run the acid continuously and still maintain high yields. This reduced the reaction time from 15 to 18 hours to 3 to 3.5 hours (10). The sugar concentration was improved to 5 percent and the yields were raised to 60 percent (7).

Wright and coworkers (11) developed the concept of combining countercurrent operation with the percolation reaction system. Continuous solids operation was approximated by several batch reactors in series. By manipulating the valving, the reactors "moved" in sequence in the opposite direction to the liquid stream. This allows a continuous operation for both solids and liquids but still permits easy loading and discharging of solids. This system increased the yield from 65 to 80 percent when a 5 percent sugar solution was produced or produced a 10 percent sugar stream at 65 percent yield levels (11).

Grethlein and Converse (12) studied plug-flow reactors for the hydrolysis of cellulose. Many different feedstocks had maximum yields from 51.5 to 92.5 percent using a ground slurry feed in a 107 cm tube of 1.18 cm ID. The optimum reactor conditions ranged from 180 C to 250 C, with residence times varying from 0.1 to 0.23 minutes with an average of 1 percent acid. Rugg and co-workers (13) also studied the plug flow reactor system. In this case, a counter-rotating twin screw extruder was used to modify the simple plug flow design promoting good heat transfer and backmixing. It also allows easier manipulation of separate zones for optimal reaction conditions.

### Concentrated Acid

Acid hydrolysis of cellulose has been practiced for over 100 years starting with the Rheinau process patented in Germany in 1880 (10). There is balance between dissolving the crystalline structure of the cellulose, thereby making the bonds accessible for hydrolysis against degrading the glucose by further acid-catalyzed reactions (12).

Concentrated acid hydrolysis is based on the fact that concentrated mineral acids such as 72 percent sulfuric acid, 85 percent phosphoric acid, and 41 percent hydrochloric acid will dissolve crystalline cellulose at temperatures of 20 C or less (15). The original work at Rheinau led to the commercial operation of the Rheinau-Bergius process during WWII. It used 41 percent HCl, with the HCl recovered by distillation. The reported yields were in excess of 90 percent and solutions in excess of 30 percent sugar were produced (16). This system suffered from poor economics due to inefficient recovery of the acid, which in part resulted from the formation of an acid/lignin complex (10).

Concentrated HCl hydrolysis has been studied extensively by Goldstein (17), who determined that the process was diffusion controlled in the 20-50 C range. The process was enhanced by agitation and the presence of certain cations in solution such as zinc, lithium, and calcium.

Ragg and Fields (14) continued this work using $CaCl_2$ as the salt, with 40 percent HCl used under pressure to hydrolyze pretreated straw. They reported yields in excess of 85 percent, and found that the salt broke the HCl-water azeotrope at 21 weight percent. This improves the economics of the acid recovery process costs because the distillation procedure is much simpler.

Concentrated sulfuric acid has been used commercially in Japan to hydrolyze cellulose. The Hokkaido process developed after WWII, utilizied 80 percent sulfuric acid. The yields were in excess of 80 percent and produced solutions of 5-10 percent glucose. Acid recovered by dialysis with an ion-exchanging membrane was considered uneconomical because of large acid loses (10).

Further modern work (18) has shown the process to be a diffusion controlled reaction as in the HCl process. Agitation and prehydrolysis impregnation with cold sulfuric acid increased the rate and yield of the final hydrolysis at 50 C. This same group has reported preliminary work with improved acid recovery by use of electrodialysis that would add costs of only $ 0.02/lb glucose produced (19).

### Two-Step Approach

A different approach involves a two-step utilization of both concentrated and dilute acid. The original work (20) used ground corn stover with the hemicellulose previously hydrolyzed. The dried stover was impregnated with 85 percent sulfuric acid at a ratio of 53 parts acid to 100 parts stover for two minutes at 40 C. This mixture was then diluted to 8 percent acid and hydolyzed for 10 minutes at 120-130 C. With this system, a 10 percent sugar solution was obtained with an 89 percent yield.

There have been numerous subsequent projects based on this two-step approach. The Tennessee Valley Authority's Muscle Shoals Facility uses a prehydrolysis step with 20-30 percent acid for 1-2 hours at 90 C prior to hydrolysis (21). This solution is filtered and dried, and concentrated sulfuric acid (85 percent) is added at approximately 1:1 ratio. The cellulose hydrolysis step is carried out at 30 percent acid for 4 hours at a 100 C. This glucose solution is then diluted to 10 percent acid and recycled to hydrolyze the hemicellulose, producing approximately a 10 percent glucose, 10 percent xylose stream after neutralization.

Tsao and fellow workers (22) have used the Dunning and Lathrop work (20 as a guide for developing the Purdue process. The main process change in their work involves using slightly more acid in the impregnation step, with the ratio being 2.6:1 acid/stover. After impregnation, the mixture is diluted with methanol and the solids are recovered by filtering. This allows the acid to be recovered by distillation to reduce raw material costs. They observe 90 percent conversion with approximately a 9 percent glucose stream.

Bienkowski, et al., (23) followed lines similar to the TVA work, utilizing a prehydrolysis "steeping" process incorporating 20 percent acid at 100 C for 5 hours. This suspension was filtered and dried to drive the residual acid up above 72 percent with the acid/wood ratio exceeding 0.8. This removed the problem of impregnating the wood with a small volume of acid. This procedure proved difficult to reproduce because of inconsistent drying conditions and the possible instability of the cellulose during drying. Yields between 80-90 percent and sugar concentrations of up to 6.5 percent w/v were reported.

# Section 4

# EXPERIMENTAL

Exploded wood from mixed hardwood species was obtained from Iogen, Ltd. of Ottawa, Canada. The steps that were studied in this research are shown in Figure 1. Our water-washing step is very much the same as a step in the Iogen process and may be considered as demonstrated successfully at pilot-plant scale by them.

## WATER WASHING

An upflow column/fluidized bed extraction technique used a glass column three inches in diameter. A flow distributor was constructed using a funnel and glass wool. Hot tap water was the extractant for the 5-carbon sugars. After initial work, it was determined that 12-16 L of hot water was need for total hemicellulose removal per 100 g of steam-exploded wood at an approximate flow rate of 250 ml/min.

## REMOVAL OF LIGNIN

Lignin was extracted by passing hot alcohol through a jacketed column of exploded wood that had previously been washed with water. The main difference from water washing was that the column was held near the boiling point of ethanol using heating tape. The flow rate was much less than that for water in order to conserve ethanol. The flow rate was normally 30-40 ml/min, and a total of eight liters was used to delignify 200 g of wet lignocellulose. The ethanol was either bulk industrial-grade ethanol or reclaimed ethanol from previous delignification runs. After alcohol extraction, the solid designated as partially purified cellulose from the column was air-dried.

CELLULOSE PRETREATMENT

Dissolving the cellulose in cold concentrated acid was a simple batch operation. The proper concentration was prepared by diluting reagent-grade concentrated sulfuric acid with water. The alcohol and water content of the cellulose was considered in determining the correct acid concentration. The acid was chilled to -5 to -10 C and the wood was slowly stirred into the solution over 30 to 60 minutes to dissipate the heat of solution/solvation. This mixture was stored at -5 to -0 C for times ranging from 8 to 36 hours. The addition of the light brown delignified cellulose caused the solution to become very dark brown and viscous. The viscosity was very temperature dependent as sulfuric acid solutions with concentration levels of 70 to 80 percent acid froze below -10 C, and were very thin at 5 C.

The amorphous cellulose was precipitated by dropwise addition of cold ethanol to dissipate heat of mixing. The acid-cellulose mixture was kept at approximately -5 C by the use of a methanol/dry ice bath and the mixture was stirred during the entire addition procedure. After the initial addition of ethanol and the corresponding drop in acid concentration, ethanol addition proceeded rapidly to the predetermined dilution level.

After the addition of ethanol, the mixture was still opaque but the cellulose precipitate was visible. The majority of the cellulose would not settle. It was generally observed that in experiments with obvious settling, the subsequent dilute hydrolysis procedure would give poor yields, and this could usually be traced to conditions during the swelling stage. The cases where a clear zone appeared in less then one hour generally resulted in poor hydrolysis.

Two different methods were explored for separation of the amorphous cellulose from the acid/ethanol mixture. Initially, filtration was attempted using a sintered glass funnel with a 65-micron pore size. Teflon membrane filters were also used, and neither method was found particularly suitable. As was found in the settling process, a solution that filtered readily generally would not hydrolyze well, thereby implying the presence of crystalline cellulose. Diatomaceous earth was tried as a filter aid but did not help to any significant degree.

Centrifugation proved to be an acceptable means of separation and washing on a laboratory scale. A Sorvall RC2-B centrifuge with a GSA rotor at 5000 rpm was the standard procedure for separating the acid-alcohol solution from the amorphous cellulose. The acid-alcohol solution was decanted and analyzed for cellulose content. The amorphous cellulose was resuspended in clean, cold ethanol and spun down again to remove the residual acid. The collected cellulose was dark brown with a sticky, granular appearance.

The hydrolysis was normally conducted in a 250 ml two-neck round-bottomed flask warmed by a heating mantle. A condenser was attached so that reflux held the temperature at the boiling point of the dilute acid solution. Sometimes the residual acid in the wood was not sufficient to give the desired acid concentration for the dilute acid hydrolysis and additional acid was needed. Samples were taken periodically to monitor the reaction and total weight was determined and any loss of water due to evaporation was made up.

### Glucose Assay

A YSI glucose meter was used for all glucose assays. Hydrolysis samples were neutralized with concentrated NaOH with phenolphthalein as the indicator. Neutralization was needed because the buffer used in the YSI instrument was not strong enough for samples in the 3 to 6 percent acid range, and the immobilized enzyme membrane was destroyed. All final sugar concentrations used in mass balance calculations were corrected for NaOH addition. Dilution due to neutralization lowered the sugar concentration by about 10 percent.

In preparing the acid for the swelling stage, the acid/wood ratio and the percent acid need to be chosen. The percent alcohol in the alcohol-wet wood needs to be determined and included as a diluant in the calculations.

## Section 5

## RESULTS AND DISCUSSION

In the steps from steam exploded wood to a hydrolyzed sugar solution, the acid swelling of the cellulose was the pivotal procedure. Three variables were examined: acid concentration, acid/wood ratio, and total time of reaction. The amount of cellulose recovered, the hydrolysis yield based on cellulose consumed, and the overall yield were used to evaluate a set of conditions. The recovery was based on the sugar and residual cellulose at the end of the dilute hydrolysis procedure compared to the original amount of cellulose. The percent hydrolysis is based on the calculated amount of cellulose added to the dilute acid bath and not the original amount of cellulose. The overall recovery is the product of these two.

The acid concentration was found to be the most important variable for the acid swelling stage. When the acid concentration was varied from 72 percent to 76 percent, a sharp demarcation was observed at 76 percent acid, with little hydrolysis below this value. Yields and recoveries are listed in Table 1.

Table 1

Effect of Soaking Concentration on Cellulose Hydrolysis

| % Acid | % Recovery | % Hydrolysis |
|---|---|---|
| 72* | 84 | 17 |
| 76 | 73 | 26 |
| 76 | 36 | 77 |
| 76 | 83 | 25 |
| 76 | 20 | 71 |
| 78* | 61.5 | 69 |
| 80 | 40 | 65 |
| 96 | -- | negligible |

* Average values

These results show that 76 percent acid was the critical concentration for solvation of crystalline cellulose at temperatures below 0 C. The variability of results at 76 percent acid is most likely the result of slight fluctuations in actual acid concentrations. The rate of hydrolysis was also significantly different, therefore to achieve 21 percent hydrolysis at 72 percent acid, prolonged times were required. The results listed for 72 percent acid represent 48 hours of hydrolysis. The experiments utilizing 76-80 percent acid were usually complete in 8 hours. Figure 4 shows a comparison of 72 percent and 78 percent acid based on the amount of hydrolysis versus time. The use of 96 percent acid generally left a black char material which would not hydrolyze.

In contrast to the above experiments that were below 0 C, operating at room temperature with acid concentrations above 76 percent invariably left a black char material similar to runs with concentrated sulfuric acid, even with short reaction times. There was some indication that slightly lower acid concentrations (70-72 percent) could be used if the swelling temperature were 5-10 C. This result would correspond with results presented by the Purdue group (23) which reported that 72 percent acid was sufficient to dissolve crystalline cellulose.

After the initial success at 76 percent acid, the acid-to-wood ratio and time of swelling were both lowered and the effect on recovery and hydrolysis was determined. The acid-to-wood ratio was dropped from 47:1 to 24:1 without any significant adverse effects. The recovery was enhanced by the addition of increased volumes of ethanol from five times the acid weight to ten times the acid weight, but additions beyond this point had no effect. When the acid-to-wood ratio was lowered further, the mixture became too thick to mix adequately at -5 C with available laboratory equipment. The time period for swelling was varied from 36 hours to 8 hours. Swelling for less than approximately 21 hours gave increased recovery with lower yields of sugar. This opposing shift in results led to a maximum conversion of cellulose to sugar that most likely fell between 18 and 21 hours of swelling time. These results are listed in Tables 2 and 3.

Table 2

Effect of Acid:Wood Ratio on Cellulose Hydrolysis

| Acid : Wood | % Recovery | % Hydrolysis | Conversion |
|---|---|---|---|
| 47:1* | 28 | 74 | 0.21 |
| 24:1* | 61.5 | 69 | 0.42 |
| 16:1 | 72 | 55 | 0.40 |

* Average values

Table 3

Effect of Swelling Time on Cellulose Hydrolysis

| Swelling Time % | Recovery | % Hydrolysis | Conversion |
|---|---|---|---|
| 36* hr. | 28 | 74 | 0.21 |
| 25 | 48 | 69 | 0.33 |
| 21.5 | 54 | 71 | 0.38 |
| 18 | 86 | 50 | 0.43 |
| 15 | 50 | 64 | 0.32 |
| 8 | 79 | 41 | 0.32 |

* Average values

## Cellulose Recovery

The low recovery was unexpected for these experiments. Four factors were investigated for cellulose loss: sugar degradation during hydrolysis, sugar rearrangement/polymerization, residual cellulose in the ethanol wash, and residual sugar in the ethanol wash. All these possibilities except sugar loss in the ethanol wash affected the overall cellulose recovery.

Sugar degradation during hydrolysis with 4-6 percent acid to possible products such as 5-hydroxymethylfurfural and/or levulinic acid, was found to be higher than expected. In experiments with a starting concentration of 5 percent glucose, solutions with 6 or 4 percent acid turned from clear and colorless to amber over a 5-hour period, with a brown precipitate visible in the 6 percent acid solution. Table 3 has a comparison of experimental and theoretical values for various acid concentrations (23) for a 5-hour reaction time.

Table 4

Comparison of Actual and Theoretical Hydrolysis

| Acid | % Loss (Exp) | % Loss (Theory) |
|---|---|---|
| 1.87 | 1.9 | |
| 3.81 | 12.9 | 2 |
| 5.77 | 15.7 | 3 |

Most of the results presented previously were for experiments using approximately 6 percent acid. Therefore both recovery and hydrolysis were probably underestimated because of sugar degradation. Experiments were conducted at 2 and 4 percent acid levels to determine if these would be sufficient for hydrolysis. The results listed in Tables 4 and 5 contrast with experiments at similar conditions with 6 percent acid. Runs at 2 percent acid showed very little yellowing of the solution, indicating little degradation.

Table 5

Effect of Acid Strength on Hydrolysis Step

| % Acid | % Recovery | % Hydrolysis | Conversion |
|---|---|---|---|
| 2 | 80 | 45.3 | 0.36 |
| 4 | 86.2 | 50.3 | 0.43 |
| 6 | 86 | 47.5 | 0.40 |

The results of tests comparing the glucose measurement made enzymatically by the YSI glucose meter to the reducing sugar values obtained by the DNS reducing sugar test are listed in Table 6.

Table 6

True Glucose versus Reducing Sugar

| % Recovery | % Hydrolysis | Glucose (g/L) | Reducing Sugar (g/L) |
|---|---|---|---|
| 96 | 39.4 | 46.0 | 45.6 |
| 40.8 | 65.1 | 53.1 | 59.2 |
| -- | -- | 2.0 | 2.2 |

These results show that under varied conditions, the DNS test gave results from 0 to 10 percent higher. This indicates the presence of dimers and possibly higher molecular weight glucose polymers, or some possible rearrangement of glucose to other reducing sugar forms (12). These results would not account for the missing cellulose unless there was a significant concentration of trimers and above, which the DNS test would underestimate because of the availabilty of only one reducing end per chain.

The effluent from the separation of precipitated cellulose from the ethanol-acid solution was initially a clear brown solution. Upon standing for at least 15 hours, the solution would become opaque and eventually an off-white precipitate would form. Colloids of low molecular weight cellulose with degrees of polymerization of 30 glucose units and above can form in water solutions (24). Since the starting cellulose has an average degree of polymerization (DP) of 114, any hydrolysis of these chains would leave a portion of the cellulose in the colloidal size range. This precipitate was collected and characterized by hydrolysis and was found to represent 7 percent of the starting cellulose. solution. When the precipitated cellulose was recycled to the softening treatment, 79 percent rapidly hydrolyzed in 2 hours. An interesting result was that when this precipitate was separated from the solution, that had been standing for a week, the solution again went opaque overnight, but to a lesser degree. This indicates an dynamic equillibrium for the colloidal cellulose system. The effluent was also analyzed for the presence of glucose, which if present, would indicate complete hydrolysis of some cellulose to glucose during the swelling procedure. No significant amounts were detected by either sugar assay eliminating this reaction as a source of cellulose loss.

All the proposed reasons contributed to "cellulose loss" to some degree, except there was no loss of sugar in the ethanol wash. The major contributions came from the sugar degradation during the hydrolysis, which was found to be much higher than theory predicted and colloid formation in the acid/ethanol solution during the precipitation of the cellulose. The elimination of these two contributions by rough estimation would probably increase recovery by up to one-half, for conditions of low recovery and high percent hydrolysis.

### Acid Recycle

The recycle of the sulfuric acid from the swelling stage is very important in order for any hydrolysis project to be commercially viable. Although sulfuric acid is a cheap commodity chemical, the large acid-to-cellulose ratio (24:1) used in this two-step project forces recycle because of the cost of the acid and the cost of gypsum disposal if neutralization is used.

Distillation is normally considered the most viable option for recovering a volatile acid such as HCl. Hydrochloric acid has high volatility and hydrolyzes cellulose to excellent yields of glucose. Unfortunately, cost and corrosive properties make hydrolysis with HCl expensive, and it tends to complex with residual solids. There has been some success with membrane processes for acid recycle of sulfuric acid, but problems remain (19). The two-step method offers the advantage of separating the acid solution from the final product, because the amorphous cellulose is removed before the final hydrolysis. This allows simple distillation for separation of concentrated sulfuric acid.

Reusing acid several times before distillation would lower costs considerably. The acid/ethanol solution was collected from two runs and cleaned with activated charcoal to remove residual lignocellulosic material. The solution was clear and colorless with 10 percent acid and 90 percent ethanol. The ethanol was removed by a crude distillation apparatus (approximately three trays for separation) to leave concentrated acid behind. When most of the original ethanol was driven off, additional water was added and the solution was redistilled to drive off the residual ethanol. Upon reaching an acceptable acid concentration level of 76-80 percent, the solution became black and opaque with some precipitate present. This was attributed to residual cellulose that was decomposed by the hot acid solution. After coarse filtration, the solution was adjusted to a concentration of 80 percent acid and used in a normal swelling procedure. The results of final hydrolysis of 61 percent hydrolysis and 49 percent recovery were typical for runs with fresh acid for these conditions.

The possibility of acid recycle over many runs would have to be proven and optimized for a cellulose to sugar process such as this to be feasible. The initial solution should be purified as much as possible to remove any residual cellulose, and efficient vacuum distillation, if necessary, could eliminate some of the degradation.

## Section 6

## ECONOMIC ANALYSIS

This economic evaluation is novel only for the specific operations studied in our laboratory. The majority of the cost information is based on a wood-to-ethanol process analyzed in detail by Arthur D. Little, Inc. for the New York State Energy Research and Development Authority and SERI in June of 1985 (1). The original process based on enzymatic hydrolysis of cellulose using steam-exploded wood was modified for the separation methods and acid hydrolysis procedures studied in our laboratory. The cost impacts are not yet clarified for some aspects of our major advances (separation of the three main components of wood into product streams that can be optimized separately and major reductions in the amounts of acidic residues that present serious problems for treament and disposal in other schemes for hydrolysis with acid).

As in the report by A. D. Little, the costs assume processing 75,264 lbs/hr of wood at a 50% moisture. The product streams are:

| | |
|---|---|
| 5,247 | lbs/hr of denatured ethanol |
| 9,492 | lbs/hr of high-value lignin |
| 11,921 | lbs/hr of concentrated pentoses |

The plant design includes 12 major areas of processing:

I - Wood Receiving, Storage, and Handling where the main process is to debark and chip the wood.

II - Steam Explosion where the wood structure is destroyed by saturating with 600 psig steam followed by rapid decompression.

III - Washing Area where the hemicellulose is removed by water and the lignin is extracted by hot ethanol.

IV - Cellulose Decrystallization where the cellulose crystalline structure is destroyed by solvation with 78 percent sulfuric acid and amorphous cellulose is precipitated and washed with ethanol.

V - Acid Recovery where the sulfuric acid and ethanol are separated and reconcentrated.

VI - Acid Hydrolysis where 2 percent sulfuric acid hydrolyzes the amorphous cellulose producing a 10 percent glucose stream.

VII - Ethanol Fermentation where the glucose stream is converted to ethanol by a yeast fermentation.

VIII - Utilities and Waste Treatment where the waste streams are treated and the major utilities such as steam and electricty are produced.

IX - Alcohol Recovery where the ethanol from the fermentation beer is concentrated and denatured.

X - Lignin Recovery where the lignin is separated from the ethanol extractant and concentrated.

XI - Pentose Recovery where the pentose stream is concentrated and processed for furthur use.

XII - Materials, Buildings, Shipping and General Storage

Areas I, II, VII - IX, and XII are dicussed in detail in the A.D. Little report and their numbers are used directly in this economic analysis. The major design bases and assumptions are:

1 - The assumed wood composition is:

Water - 50.0
Cellulose - 18.4
Hemicellulose - 14.2
Lignin - 10.6
Bark - 5.0
Ash - 1.8
(percenteages on wet basis)

2 - The removal of hemicellulose by water extraction is assumed to be 100 percent. The conversion to pentoses and hexoses is assumed to be 90% because of some degradation of the sugars during the steam explosion process.

3 - The removal efficiency of the lignin by the ethanol extraction is assumed to be 95 percent with no degradation losses.

4 - The conversion of crystalline cellulose to amorphous cellulose was found experimentally to be only 40-60 percent. The cellulose is lost in the ethanol as a colloid suspension. It is felt that 75-80 percent could be recovered so 75 percent is used as a base case.

5 - The hydrolysis of amorphous cellulose by dilute acid generally was found to range from 60 - 80 percent. Seventy percent will be used as a base case. This process generates waste streams consisting of unreacted cellulose and lignin and another consisting of gypsum from neutralizing the acid prior to fermentation.

6 - The economics of the recovery of acid from an alcohol stream have been studied by the Department of Energy (25) based on a similar process developed at Purdue (22). It was the Purdue work that developed the fundamental idea of solvation of crystalline cellulose with concentrated acid. The DOE economic report will be used for the information in this study. It is assumed for the base case that neither acid nor ethanol will be lost in this separation step. It is not known how the presence of colloidal cellulose and other oligiosaccarides will affect this process.

7 - The lignin recovery unit is a simple flash separation system with no loss of either lignin or ethanol during the separation.

8 - The pentose recovery is a drying procedure to concentrate the stream to an acceptable level for sale as cattle feed or possibly as a fermentation ingredient.

Figure 5 presents the overall process with the 11 major units that influence the design and mass balance. The major process streams that affect the overall mass balance are labeled. Table 7 provides details on mass balances based on Figure 5.

The overall fixed capital investment is estimated to be $66,931,000 and the annual operating cost is $15,755,000. The individual components are summarizied in Tables 8 and 9 and are based as much on the A.D. Little report as possible and, when specific information was not available, standard engineering sizing and cost estimates were used.

Table 7

Overall Material Balance Based on Process Outlined in Figure 5.

| No. | Stream Name | lb/hr | Composition | |
|---|---|---|---|---|
| 1 | Roundwood | 75,264 | Water | 37,632 |
| | | | Cellulose | 13,852 |
| | | | Hemi Hexose | 2,066 |
| | | | Hemi Xylose | 8,637 |
| | | | Lignin | 7,993 |
| | | | Soluble Ash | 948 |
| | | | Insoluble Ash | 373 |
| | | | Bark | 3,763 |
| 2 | Chips | 67,738 | Water | 33,869 |
| | | | (rest same as 1) | |
| 3 | Bark | 7,526 | Water | 3,763 |
| | | | Bark | 3,763 |
| 4 | Steam | 67,738 | Water | 67,738 |
| 5 | LP Steam | 47,417 | Water | 47,417 |
| 6 | Exploded Wood | 77,897 | Water | 46,738 |
| | | | Cellulose | 13,852 |
| | | | Hemi Hexose | 1,543 |
| | | | Hemi Xylose | 6,450 |
| | | | Lignin | 7,993 |
| | | | Soluble Ash | 948 |
| | | | Insoluble Ash | 373 |
| 7 | Wash Water | 231,088 | Water | 231,088 |
| 8 | Wash Ethanol | 348,668 | Water | 34,865 |
| | | | Ethanol | 313,801 |
| 9 | Hemi Wash | 86,806 | Water | 77,865 |
| | | | Soluble Ash | 948 |
| | | | Xylose | 6,450 |
| | | | Glucose | 1,543 |

| | | | | |
|---|---|---|---|---|
| 10 | Lignin Wash | 424,601 | Water | 208,504 |
| | | | Lignin | 7,593 |
| | | | Ethanol | 509,761 |
| 11 | Air Dry | 129,997 | Water | 25,999 |
| | | | Ethanol | 103,997 |
| 12 | Cellulose | 16,250 | Water | 325 |
| | | | Cellulose | 13,852 |
| | | | Lignin | 400 |
| | | | Insoluble Ash | 373 |
| | | | Ethanol | 1,300 |
| 13 | Sulfuric Acid | 76,170 | Water | 3,047 |
| | | | Acid | 73,123 |
| 14 | Ethanol precipitate | 761,698 | Water | 76,170 |
| | | | Ethanol | 685,529 |
| 15 | Air Dry | 88,012 | Water | 8,971 |
| | | | Ethanol | 79,041 |
| 16 | Acid/Ethanol Stream | 765,579 | Water | 84,280 |
| | | | Cellulose | 3,463 |
| | | | Acid | 71,661 |
| | | | Ethanol | 606,175 |
| 17 | Cellulose | 111,616 | Water | 11,214 |
| | | | Cellulose | 10,389 |
| | | | Lignin | 400 |
| | | | Insoluble Ash | 373 |
| | | | Acid | 1,462 |
| | | | Ethanol | 80,654 |
| 18 | Dilute Acid | 65,096 | Water | 64,494 |
| | | | Acid | 154 |
| 19 | Lime | | Lime | 1,167 |
| 20 | Gypsum | 4,053 | Water | 1,216 |
| | | | Gypsum | 2,837 |
| 21 | Waste | 19,447 | Water | 15,557 |
| | | | Cellulose | 3,117 |
| | | | Lignin | 400 |
| | | | Insoluble Ash | 373 |

| | | | | |
|---|---|---|---|---|
| 22 | Sugar Stream | 80,803 | Water | 69,494 |
| | | | Ethanol | 1,613 |
| | | | Glucose | 8,080 |
| 23 | CO2 Purge | 4,056 | CO2 | 4,056 |
| 24 | Beer Stream | 74,781 | Water | 69,494 |
| | | | Ethanol | 5,247 |
| | | | Glucose | 40 |
| 25 | Denaturant | 240 | Gasoline | 240 |
| 26 | Stillage | 69,467 | Water | 69,467 |
| 27 | Product Ethanol | 5,247 | Water | 26 |
| | | | Ethanol | 5,221 |
| | | | Gasoline | 240 |
| 28 | Recovered EtOH | 673,527 | Water | 67,353 |
| | | | Ethanol | 606,175 |
| 29 | Recovered Acid | 76,235 | Water | 4,574 |
| | | | Acid | 71,661 |
| 30 | Waste | 51,076 | Water | 51,076 |
| 31 | Recovered EtOH | 435,047 | Water | 43,505 |
| | | | Ethanol | 391,542 |
| 32 | Lignin | 9,492 | Water | 949 |
| | | | Lignin | 7,593 |
| | | | Ethanol | 949 |
| 33 | Waste Water | 199,020 | Water | 199,020 |
| 34 | Recovered Pentoses | 11,921 | Water | 2,980 |
| | | | Soluble Ash | 948 |
| | | | Xylose | 6,450 |
| | | | Glucose | 1,543 |
| 35 | Waste Water | 74,885 | Water | 77,885 |

## Table 8

## Fixed Capital Investment

| | | |
|---|---|---|
| Installed Equipment | | |
| Area I | - Wood Receiving, Storage, and Handling | $ 4,067,000 |
| Area II | - Steam Explosion | 3,175,000 |
| Area III | - Hemicellulose/Lignin Extraction | 3,127,000 |
| Area IV | - Cellulose Decrystallization | 4,814,000 |
| Area V | - Acid Recovery | 13,699,000 |
| Area VI | - Cellulose Hydrolysis | 1,265,000 |
| Area VII | - Fermentation | 1,497,000 |
| Area VIII | - Utlities | 20,372,000 |
| Area IX | - Alcohol Recovery | 1,450,000 |
| Area X | - Lignin Recovery | 1,555,000 |
| Area XI | - Pentose Recovery | 841,000 |
| Area XII | - Materials, Storage, Buildings, and Shipping | 4,621,000 |
| Subtotal | - Installed Equipment | $60,483,000 |
| Land | | 400,000 |
| Contingency & 10% Installed Equipment | | 6,048,000 |
| Fixed Capital Investment (FCI) | | $66,931,000 |
| Startup + Interest | | 18,606,000 |
| Total Depreciable Capital | | $85,537,000 |
| Working Capital | | 1,882,000 |
| Total Capital Investment | | $87,419,000 |

Basis: Mid-1989 dollars

Table 9

Annual Operating Costs

| | |
|---|---|
| Raw Materials: | |
| Wood Feedstock ($20/ton) | $5,961,000 |
| Gasoline ($1.2/gallon) | 285,000 |
| Lime ($46/ton) | 4,000 |
| Sulfuric Acid ($72/ton) | 461,000 |
| Utilities: | |
| Electricity ($.06/kwh) | $2,520,000 |
| Labor: | |
| Operating | $1,769,000 |
| Foreman | 693,000 |
| Supervisor | 156,000 |
| Maintenance | 200,000 |
| Maintenance Materials | $1,367,000 |
| G & A | 1,000,000 |
| Taxes & Insurance | 1,339,000 |
| Total Operating Cost/Year | $15,755,000 |

To calculate a required selling price for the ethanol, a 15 percent rate of average return after taxes (ROAIAT) (26) is used. The capital investment and the depreciation are averaged over the 15-year life span of the plant. The depreciation schedule is the same as in the A.D. Little report i.e., 15%, 22%, 21%, 21% and 21%. By this method, the required selling price for ethanol is

$4.57/gallon. This is based on ethanol as the sole product.

This result is common to many studies in which ethanol is the sole product (e.g., 1). The two other potential products of biomass refining are lignin and the sugar syrup that comes from xylan. Markets for these products are poorly defined. Estimates for selling prices for high grades of lignin range from under $0.10 to over $0.25 per pound (27). This uncertainty makes any calculation of selling price of ethanol as a coproduct tenuous.

We can assign a target price for ethanol of $1.00 per gallon based on the rough value of gasoline and the blending benefits of adding ethanol. If the crude pentose syrup is concentrated to 75 percent solids, it can be assigned a value comparable to crude molasses used for feeding cattle. We recognize that a syrup made from washings of exploded wood may be inferior to molasses, but our assigned price of 6 to 8 cents per pound should be accurate enough for this preliminary cost estimation. If these prices for ethanol and crude syrup are accepted, the price required for our lignin fraction would be 21 to 24 cents per pound to provide a return on investment of 15 percent.

With the cost assumptions of this report, the proposed process has roughly the same commercial prospects as that analyzed in the A. D. Little report. However, there are some distinct advantages. The most dramatic difference is a potential for more ethanol because no cellulose must be diverted to the production of cellulase enzymes for enzymatic hydrolysis. The fixed capital investment and the operating costs are similar if compared in 1989 dollars, but the scale up of the fractionation steps and acid hydrolysis are much more straightforward than the scale up of enzyme production and enzymatic hydrolysis. The enzyme process also has the disadvantage of producing an inferior lignin stream that contains unreacted cellulose.

One final consideration is the relatively small amount of research and development that have been directed to this approach. Our results indicate that economics are roughly comparable to those of the standard Iotech process that has had nearly 15 years of experimentation aimed at yield improvement. An equivalent effort for improving fractionation and acid hydrolysis of the special low molecular weight cellulose has good prospects for major cost reductions.

## Section 7

## CONCLUSION

Washing with water and washing with hot ethanol are very simple steps that should pose no problems for full-scale operations. Yields can be excellent when these extractions are conducted countercurrently. There is a major advantage in separating cellulose from the sugars from hemicellulose because the latter are converted more slowly to ethanol by yeasts than is glucose, and ethanol from glucose slows the bioconversion before the fermentation of the hemicellulosic sugars even begins. Lignin precipitates from its ethanolic extract during the distillation for recovering ethanol.

Swelling partially purified cellulose with concentrated sulfuric acid is also straightforward, but refrigeration would be required in a factory based on our process. Precipitation of swollen cellulose by adding ethanol to the solution in sulfuric acid takes time to reach completion, and the precipitate filters poorly. Collection by centrifugation works well but will be relatively difficult to scale up because automated, high-speed centrifuges of large capacity are complicated and expensive.

The hydrolysis step poses no problems. While the other sulfuric acid is recycled, the acid in the hydrolysis step is neutralized and produces calcium sulfate that presents a disposal problem. This relatively harmless sludge can be handled by well-established methods for pollution control, but sizeable amounts would be generated by a large factory over a long period of time. However, the hydrolysis step can be optimized in terms of minimum amounts of sulfuric acid required.

There were only a few trials with recycled sulfuric acid, but the results seemed about the same as with fresh acid. The limits to reuse must be established because cost of acid is a major factor.

Our economic analysis is preliminary and riddled with assumptions. Nevertheless, costs of our separation scheme are very low compared with other steps in our process and are highly attractive compared to steps for enzymatic hydrolysis of cellulose. No matter what hydrolysis method is adopted, handling the components of biomass separately should be advantageous and not prohibitive in cost. Our biggest uncertainty for costs is sulfuric acid; this depends strongly on acid recycle that is not yet well defined.

The main conclusions of this study are that biomass which has been disintegrated by steam explosion is easily separated into valuable fractions and acid hydrolysis following an effective pretreatment should be a good alternative to costly enzymatic hydrolysis.

# Section 8

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## Section 9

## PUBLICATIONS RESULTING FROM THIS CONTRACT

Bungay, H. R., "The Ultimate Biomass Refinery," paper presented at the A.I.Ch.E. National Meeting, Washington, D.C., Nov. 1988

Gostomski, P., "Acid Softening and Hydrolysis of Cellulose", M.S. Thesis, RPI, August. 1989

Gostomski, P., and Bungay, H.R., "Two-step acid hydrolysis of steam-exploded cellulose", poster presented at Am. Chem. Soc. National Meeting, Miami (1989)

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