FINAL REPORT

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✓ "INVESTIGATIONS FOR THE PRODUCTION OF A FERMENTABLE
FEEDSTOCK FROM BAGASSE USING THE PURDUE CELLULOSE
HYDROLYSIS (SOLVENT) SYSTEM"

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The work to be performed under this contract is completed with the submission of this report, and therefore the contract will be terminated on September 1, 1983, the date mutually agreed upon for termination of the project.

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The submitted report contains confidential information as the Division of Sponsored Research, University of Florida, Gainesville, has filed an application for a process patent under # 295,814 and under continuation # 374,949 with the U.S. Patent Office, Washington, D.C.

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INTRODUCTION

Cellulosic materials are the chief structural components which lend rigidity to plants. Units of alpha cellulose are formed as long chains of B-glycosidal linkages to yield polymers of high-molecular weight. The chains of alpha and hemi-celluloses in plant material are grouped together in bundles, which are interspersed with lignin into a common matrix somewhat comparable to rods in reinforced concrete. The major objective for the project research is to isolate the cellulosic bundles imbedded in the lignin, and thereafter hydrolyze the isolated cellulosic bundles of alpha and hemi-celluloses into sugars of mono-hexose and pentose, respectively, without significant destruction of these sugars.

OBJECTIVES FOR INVESTIGATIONS

Two approaches for obtaining the stated goals may be followed:

1. Dissolve the lignin without changing the cellulosic fraction. Separate the dissolved lignin from the fibrous bundles and hydrolyze the residual fiber into mono-sugars.
2. Dissolve the cellulosic fraction without dissolving the lignin. Hydrolyze the dissolved cellulosic fraction

without interference of lignin into mono-sugars. Remove the non-hydrolyzed lignin which is insoluble in aqueous acid solutions, and thus separate the lignin fraction from the aqueous solution containing the mono-sugars from hydrolyzing.

DISSOLVING OF LIGNIN FRACTION

Research was conducted on approach #1 using the hydrotropic solution of sodium benzene sulfonate for dissolving lignin from the matrix. (1) (2) Removal of lignin was carried out with the use of a high-pressure, stainless steel "Parr" vessel of 450 ml capacity. Ten grams of dry bagasse, 47.5g of distilled water and 150 ml with 40% concentration of sodium benzene sulfonate (hereinafter called sulfonate) were added to the "Parr" vessel for each run. The added distilled water diluted the sulfonate used to 30% concentration. Several time and

(1) McKee, Ralph. 1946. Use of Hydrotropic solutions in Industry. Industrial and Engineering Chemistry. 38(4):382-384.

(2) Hong Lau, M.S. 1941. Bamboo pulp by use of a hydrotropic solvent. The Paper:247-255.

temperature studies were conducted with the above concentrations to investigate optimum processing parameters.

After each experimental run, the treated contents were removed from the "Parr" vessel and were washed with distilled water. The fiber was dried overnight at 105 degrees F. and was weighed, and the lignin was precipitated from the obtained aliquot by dilution with distilled water (at a rate of at least 10:1 of the original volume admitted to the "Parr" vessel). The quantity of lignin precipitated and recovered by filtration was dried and weighed. The results were expressed as percent of lignin removed from the original fiber sample (dry weight). Table 1 and Diagram 1 report the data obtained for removal of lignin using the hydrotropic solution.

Table 1 shows that the highest removal of lignin is obtained when subjecting the treated samples to the following processes. Results from the first 12 samples reported in Table 1 suggest that the highest recovery of lignin in precipitate is obtained when using the following parameters for reaction:

- Use of 150 ml of sulfonate having a pH of 7.0 for treating 10 grams of fiber (dry basis).
- Stirring the mass during reaction does not appear

essential; a pre-soaking time of 30 minutes of fiber in the sulfonate prior to reaction seems beneficial for optimum removal of dissolved lignin.

- A reaction time of three hours at pressures of 80 psi (equivalent to 170 degrees C) appears optimum to maximize dissolution of lignin.

Samples 13 and 14 in Table 1 were treated differently. As a pre-treatment, the fiber was hydrolyzed with acid. The 10 grams of powdered bagasse were acidified with an 1:15 solution of sulphuric acid having a pH of 2.6, after which the mass was hydrolyzed at 185 degrees C (110 psi) for 10 minutes. The objective of the pre-treatment is to hydrolyze the hemi-cellulose and remove this product from the fiber matrix, before the residue (mostly alpha-cellulose and lignin) was subjected to the main treatment with sulfonate.

Results obtained with samples 13 and 14 (Table 1) indicate no difference in total recovery of solids. Sample 13, however, indicate an improved lignin recovery (or removal from the fiber matrix) of 9.2% with pre-treatment, in comparison with 5.9% lignin recovery without pre-treatment when sulfonate reaction was used at 170 degrees Centigrade for 3 hours.

Two additional processing methods were tried without the

use of the "Parr" vessel (without the need of high pressure and temperature for dissolution of lignin). The same components without pre-soaking were used. One sample was boiled in an evaporating flask under partial vacuum for 3 hours which understandably caused considerable foaming without any precipitation of lignin. Another sample was placed in a high-pressure bottle, stoppered and heated to 60 degrees Centigrade while shaking the contents for 3 hours. Again, no lignin was precipitated.

In conclusion, we feel that delignification of fiber by the use of sodium xylene sulfonate or another hydrotropic solution would not be economical due to the severe processing parameters for temperature and pressure required. Delignification by the said approach is technologically possible, but not practical to produce fermentable feedstocks for fuel ethanol. Therefore, our major research efforts have concentrated on the second approach: Hydrolysis using a strong acid as catalyst.

DISSOLVING OF THE CELLULOSIC FRACTION

Hydrolysis works very well when hydrolyzing long-chained carbohydrates into mono-sugars present in liquid form. The major problem still exists of how to effectively dissolve the polysaccharide polymers away from the interfering

lignin. Originally, the alpha cellulose is present in crystalline form, but when dissolved, can be changed into an amorphous form. The latter form is easier to hydrolyze into mono-sugars than cellulose in the crystalline form.

Celluloses can be dissolved in strong mineral acid of high concentration. The problem still exists that cellulosic fibers are solids, and hence are difficult to mix thoroughly and intimately with a strong mineral acid of elevated concentration due to the high viscosity of the liquid. This thorough mixing must be achieved before alpha cellulose can be dissolved.

To avoid these physical barriers sulphur trioxide was employed as catalyst, a substance which can instantly react with water to form sulphuric acid. The sulphur trioxide can be added in pre-calculated proportions to the moisture present in the fiber so that the formed sulphuric acid has 70 percent or higher concentration.

Sulphur trioxide is a dangerous substance, and its handling involves various technical and safety precautions, all well known. The substance is highly corrosive which requires stainless steel for containment and reaction vessels.

Sulphur trioxide (oleum) fumes profusely when in contact with ambient air, and will react violently when brought in

direct contact with water.

Normally, pure sulphur trioxide is converted into concentrated sulphuric acid by injecting the gas into sulphuric acid of a somewhat lower concentration than the end-product. It will not be absorbed by water when low concentrations of inert gases with sulphur trioxide are directly introduced into a water column. To investigate whether the large surface area of small fiber particles would actively absorb sulphur trioxide, the following technique was adapted for research in the laboratory:

Small stainless steel pipes were fitted on each side with stainless valves. The volume of these enclosed pipe-ends were once calibrated with water, and later used to dispense liquid sulphur trioxide for reaction with pre-determined amounts of fiber. The described procedure proved to be inaccurate for the small quantities of products involved, and during later periods, the addition of sulphur trioxide to the fiber was determined by difference in weight of the pipe-end, prior to and following the reaction with the fiber sample.

In the laboratory, severe charring of fiber occurred when a stream of inert gas with liquid sulphur trioxide was passed through a glass column packed with fiber particles. A

special reaction assembly was constructed (photograph #1) to avoid this charring of fibers. Liquid sulphur trioxide was placed in the small cylinder shown in the foreground, and compressed air or carbon dioxide was used to propel the sulphur trioxide from the small cylinder directly into the large vessel, which in turn was filled with fiber. The large cylinder was fitted at the end with a watertrap, which was connected to a waterjet condensing pump to catch excess of sulphur trioxide. The small cylinder was heated with a gas burner to vaporize the introduced sulphur trioxide prior to making contact with the fiber.

Charring of fiber was reduced when using this method, but was not entirely eliminated. Glucose recovery was low from this treatment of the fiber, and hence abrasion methods were used for fiber after reaction with the sulphur trioxide to improve glucose yield. Methods used were ball-milling with and without air pressure for the fiber treated with sulphur trioxide, and trituration with mortar and pestle. When using 3-15% sulphuric acid solutions for hydrolysis of fiber at 17 psi steam pressure during 30 minutes, a total glucose recovery (% weight on dry fiber) ranging from 16 to 24 % was obtained. The amount of acid used for the stated glucose recovery was deemed uneconomical.

To reduce charring of fiber from the sulphur trioxide introduction, additional moisture was added to the fiber prior to treatment, and the sulphur trioxide was introduced in two stages instead of one. The fiber was also tumbled on a roller mill during the addition of sulphur trioxide. Introduction of sulphur trioxide in a single dose did work best when particle size was reduced in a Wiley mill prior to treatment with sulphur trioxide, and a two stage addition of sulphur trioxide is preferred for coarser bagasse, not having passed a Wiley mill for particle reduction.

Large amounts of sulphur trioxide and the subsequently formed sulphuric acid had to be added in order to produce appreciable amounts of glucose that could be recovered from the treated bagasse after hydrolysis with steam (temperature and pressure). The reaction regime used during experimentation is the following:

- Dry fiber + sulphur trioxide + water in fiber ———>
dry fiber + sulphuric acid + residual (non-converted or reacted) water.

- Eighty parts of sulphur trioxide + 18 parts of water
————> 98 parts of sulphuric acid.

This ratio may also be expressed as:

4 grams of sulphur trioxide + 0.9 grams of water ———>

4.9 grams of sulphuric acid.

- The percent concentration of formed sulphuric acid is equal to:

$$\frac{\text{weight of formed sulphuric acid}}{\text{weight of formed sulphuric acid} + \text{weight of residual water}} \times 100$$

- Percent of sulphuric acid on bagasse (formed pure sulphuric acid in bagasse) equals:

$$\frac{\text{weight of sulphuric acid}}{\text{weight of dry fiber} + \text{weight of residual water}} \times 100$$

The latter value was later corrected to a value which more realistically represent the reaction which occurs:

- Percent of sulphuric acid on bagasse (formed pure sulphuric acid in bagasse) equals:

$$\frac{\text{weight of formed sulphuric acid}}{\text{weight of dry fiber}} \times 100$$

- To insure uniform analysis of one gram of dry bagasse, the expression "gram equivalent" was introduced.

One gram equivalent equals:

$$\frac{\text{weight of dry fiber} + \text{weight of formed sulphuric acid} + \text{weight of residual moisture in bagasse}}{\text{weight of dry fiber}}$$

When considering processing to optimize recovery of glucose from treated fiber, we found that three basic phases should be applied:

- Reaction of sulphur trioxide with the fiber to be treated.
- Abrading of fiber already treated with sulphur trioxide. This abrading is conducted under specific parameters for pressure, temperature (whether caused naturally by friction or not) and time period under which abrasion takes place.
- Hydrolysis of the abraded fiber with saturated steam at different parameters for temperature and time using the formed sulphuric acid as catalyst.

REACTION OF FIBER WITH SULPHUR TRIOXIDE

Each of the above phases have to be investigated singly and in combination to achieve maximum conversion of cellulose into mono- sugars. The following method was adapted for dispensing liquid sulphur trioxide to known weights of fiber having a pre-determined moisture content. This method caused a minimum of charring of fiber as each fiber particle was randomly exposed to the admitted sulphur trioxide:

Small, pre-weighed tube assemblies, each closed with small valves, were used to store known weights (rather than volumes) of sulphur trioxide liquid to enhance accuracy for calculations on concentration of formed sulphuric acid from

applied sulphur trioxide in the fiber mass (See photographs # 2 and 3.) The tube assembly was attached to the large vessel containing the unreacted fiber, and the connecting valve between the tube assembly and large vessel was cracked open while the entire apparatus was turning on a roller mill. The cracking of the connecting valve achieved a slow admission of sulphur trioxide and gradual exposure to the fiber in motion, thus preventing charring of the latter. Final traces of sulphur trioxide in the assembly tube were removed by blowing compressed air through the assembly tube and into the large reaction vessel containing the fiber. The sequence of treatment was as follows:

- First stage of sulphur trioxide addition with the cracked valve between the tube assembly containing sulphur trioxide and the reaction vessel, containing the fiber to be treated, while spinning on the rotary mill (15 minutes.)
- Addition of compressed air to move residual traces of sulphur trioxide in the tube assembly into the reaction vessel with fiber particles.
- Continue tumbling on the roller mill to complete the total of 30 minutes since starting.
- Reduce the particle size of the reacted material by hammermill (optional.)
- Abrade the reacted fiber material with a specially designed extrusion screw press.

- Hydrolyze the abraded material with saturated steam.

At the start, fiber with a high moisture content was treated in the above fashion, and the treated material was dried until a 70 percent or higher concentration of formed sulphuric acid was obtained. Drying of the treated material at temperatures of 60 C. degrees or higher, however, caused charring of the fiber material. Drying at the stated temperature requires a very long time, and hence drying was carried out prior to admission of sulphur trioxide during subsequent trials. Drying of the non-treated fiber was continued until reaching a moisture content which was adequate for reaction with sulphur trioxide under ambient temperatures to yield a final concentration of about 80 percent for sulphuric acid.

ABRASION OF TREATED FIBERS

Several systems for abrading the treated fibers were tested: Mortar and pestle, milling with a handgrinder, hammer milling only, and a specially designed extrusion screwpress. Abraded material with the first three methods only yielded low concentrations of mono-sugars after hydrolyzing, leading to the design of the screwpress.

The shop of the Univ. of Fla. Mechanical Engineering

Department constructed a small, laboratory-sized screwpress (photograph # 4) with a constant diameter screw and barrel. The screw was discontinued and had a narrow pitch. The barrel was fitted with "pressure screws" extending nearly to the surface of the interrupted sections on the extruding screw, thus promoting abrading of the treated fiber particles.

Experimentation, reported in more detail later, revealed that a combination of pressure and temperature during abrasion, and the degree of abrasion achieved is essential to maximize glucose formation during subsequent hydrolysis. This finding resulted when fiber treated with sulphur trioxide was individually subjected to ball milling, abrasion with mortar and pestle or hand grinder, to pressure only by hydraulic press, and to temperature only by drying in an oven; all methods yielded very low glucose content (3.6-7.8%) after hydrolyzing. In fact, heating alone showed a decrease in glucose content after hydrolyzing, indicating destruction of glucose, and suggesting that an optimum heating range during abrasion should be observed to maximize glucose recovery.

A trade-off should exist between maximizing glucose recovery from treated fiber after hydrolyzing, and the amount of sulphur trioxide on dry weight of fiber utilized

with different parameters for temperature, pressure and time of exposure during the abrasion phase.

RATES OF SULPHUR TRIOXIDE APPLICATIONS AND CONCENTRATIONS OF FORMED SULPHURIC ACID

To study these interactions and recovered glucose yields, experiments were restricted to the following parameters:

- Final concentration of sulphuric acid in percent due to admission of sulphur trioxide to react with fiber:

75,80,85, and 90 to be reported in Table II.

- Sulphuric acid formed as percent on dry weight fiber treated: 10,15,20,25,30, and 35 to be reported also in Table II.

Sulphur trioxide dosage for experimentation reported in Table II was added in two phases as to eliminate charring since the single-stage sulphur trioxide addition was not perfected at this time. During the first phase, the tube assembly, containing the smaller quantity of sulphur trioxide was heated to gasify the liquid sulphur trioxide, and the entrance tube to the reaction vessel on the roller mill was cracked open. The last traces of sulphur trioxide were propelled by compressed air from the pipe assembly. Next, an interim drying of reacted material in the oven

evaporated excess water which left only the required water needed for the second addition of sulphur trioxide. Phase two was the addition of the second part of the sulphur trioxide followed by the same sequence as in the first sulphur trioxide addition. The thus obtained treated material was abraded in a screwpress having a constant diameter and fitted with "pressure screws" (photograph # 5), and hydrolyzed to obtain the glucose and pentose fractions. The method for analysis of glucose and total quantity of reducing sugars is explained in the Appendix.

Bagasse contains roughly one-third each of alpha cellulose, hemi-celluloses and lignin. Hence, a maximum theoretical yield of about 66% of bagasse can be converted into reducing sugars, whether a hexose or a pentose. Again, half of this total amount of reducing sugars can be glucose at the most. In Table II the glucose yield obtained after hydrolysis is expressed as actual percentage for glucose obtained on fiber, dry basis. Likewise, the total for reducing sugar (glucose and pentose together) is expressed as actual percentage of reducing sugar obtained on fiber, dry basis. The last column of Table II expresses the amount of glucose obtained as percentage of the total amount reducing sugar obtained, meaning the percentage of total reducing sugar which can be fermented with yeast under anaerobic condition into fuel ethanol and carbon dioxide.

Table II reports the data obtained during experimentation with the mentioned acid concentrations and final percent of sulphuric acid on fiber, dry basis. The underlined data, graphically shown in Diagrams IA, IB, IIA, and IIB, indicate trends.

In general, the yield of glucose, obtained after hydrolysis (Table II), substantially decreased with an increase in concentration for sulphuric acid from 75 to 90% which was formed by treating fiber with sulphur trioxide. In contrast, glucose yield was positively affected when using increased amounts by weight of sulphuric acid on dry fiber (from 10 to 35%). The above conclusions strongly suggest that the quantity of formed sulphuric acid on dry fiber is relevant to better glucose yield after hydrolysis, and that the concentration of the formed sulphuric acid used during abrasion plays only a secondary role. Consequently, the lowest concentration of sulphuric acid capable to decrystallize alpha cellulose should be used for reason of economics.

The diagram IA suggests large fluctuations for obtained glucose content after hydrolysis; the least fluctuation occurred with the 75 and 85% concentrations for sulphuric acid used, while large fluctuations occurred when using the

acid concentrations of 80 and 90 percent. The results are rather inconclusive.

A rather definite trend is obtained from Diagram IB. An imaginary straight line (we did not run a regression due to the involvement of only six reference points) of obtained points should indicate a rather steep increase in glucose yield due to the larger quantity of sulphuric acid employed. Glucose yield, however, is only six percent higher when using 30% sulphuric acid than when using 10% of sulphuric acid, and such a moderate yield increase in glucose should not warrant the extra cost for higher usage of the catalyst.

Diagram IIA shows the concentrations of sulphuric acid which was formed after reaction of sulphur trioxide with fiber, and the glucose yield recovered from the abraded fiber after hydrolysis. Only a small increases in glucose yield of a few percentage points was obtained when the amount of formed sulphuric acid was tripled. The small gain in glucose yield should not warrant the added expense of sulphur trioxide to be applied.

Temperature maintained during abrading significantly influenced the final glucose yield obtained. Temperature was measured by attaching a thermometer to the outside of

the barrel of the extruding screwpress near the exit port for abraded material. Table II shows that temperature caused by friction during abrading decreased with increased utilization of formed sulphuric acid on dry fiber, regardless of acid concentration used during the abrading process. The high temperatures obtained in the extruder when using low quantities of the concentrated sulphuric acid suggest the presence of a high degree of friction due to a reduced effect for lubrication by the concentrated acid.

When using a high concentration for sulphuric acid during abrasion, the temperature in the extruding screwpress remains fairly high and constant, regardless of the quantity used per dry weight of fiber. The finding suggests that heat is released from the reaction of fiber with acid under pressure.

Sulphur trioxide is an important cost factor in the process to convert celluloses into mono-sugars, and a trade-off between sulphur trioxide addition and glucose recovery should be apparent. Table III indicates the yields recovered from different quantities of sulphur trioxide added, which resulted in varying quantities of formed sulphuric acid on dry fiber, and the range of acid concentration used to promote decrystallization. The most

economical combination for processing parameters appears to be the addition of 15% sulphur trioxide on fiber, dry basis, forming 90% concentration for sulphuric acid, and this combination yielded 29.2% of glucose after hydrolyzing. The second best combination (Table III) yielded 26.3% glucose, and was obtained from the addition of 10% sulphur trioxide on dry fiber, and abrading the treated fiber with formed sulphuric acid of 80% concentration.

Abrading by screwpress after reaction of fiber with sulphur trioxide was determined as the preferred processing method. To investigate optimum parameters for abrading, a laboratory-sized screwpress was fabricated having a "tapered and threaded" shaft and a corresponding "tapered" housing. This described design was believed to promote a greater compression for treated fiber while passing through the extrusion press. Glucose recovery was made after hydrolyzing of the fiber which was partly abraded in the conical-shaped extruder (designated as CP) and partly in the extruder with a shaft of constant diameter which barrel contained "pressure" screws (designated as CD).

At a later time the CP extruder was modified with the addition of twelve "pressure screws" placed along the entire length of the barrel in three groups of four screws

each, equally spaced around the barrel (designated as MCP.) The described laboratory-sized extruders, namely CD and MCP, are shown in photographs # 5A & # 5B, respectively.

The lowest glucose yield after hydrolyzing was obtained when using the CP design for extruding. The highest glucose content was recovered with the CD design, while the MCP design yielded a glucose value between CD and the CP designs. Also, an extruded product with optimum consistancy was produced with the MCP design at a lower temperature than when the CD design was employed (Table V). When plotting yield of mg glucose obtained versus temperature during extrusion, a positive slope was obtained for the MCP design, but not in all cases for the CD and CP designs.

In all observations (Table VI), when comparing glucose yields obtained from the conical and from the constant diameter designs for the extruder, less glucose yield was obtained with the conical press, except in one case. The plasticized consistancy of treated fiber, which is needed to optimize glucose recovery after hydrolysis, was obtained with only one pass through the conical press, while two passes were required when using the constant-diameter press.

When concentration of the formed acid in treated fiber was

lowered for abrading with the conical press, then the amount of sulphur trioxide used for the reaction with fiber (the amount of sulphuric acid formed) needed to be greatly increased to yield about the same levels of glucose recovery after hydrolysis. This trend was not obvious for the screwpress with the constant diameter barrel.

To determine the effect of the abrading phase on glucose yield finally obtained, a predetermined quantity of bagasse fiber was treated by the admission of sulphur trioxide. Treatment consisted of 25% sulphur trioxide (on fiber w/w) to fiber, having been dried prior to such an extent that formed sulphuric acid measured 80% concentration after treatment was completed.

Half of the treated fiber was abraded in the CP screwpress while the other half of the fiber sample was left unscrewpressed. The fiber which had passed through the screwpress produced more than three times the quantity of glucose after hydrolyzing with water only, when compared with the fiber which was not screwpressed. An additional increase in glucose yield was obtained when using water acidified with sulphuric acid for hydrolyzing, an observation which is in concurrence with previous reportings. The results just described are reported in

table X.

TRIALS WITH HYDROLYSIS OF ABRADED FIBER

Trials were conducted to investigate needed acid concentrations during hydrolysis (water and 5 % and 10 % sulphuric acid added to the hydrolyzing solutions). Also investigated were the volume of solutions used during hydrolysis (50,25, and 10 ml) and particle size of material leaving the screwpress. See photographs # 6 and # 7 for hydrolysis equipment. In all cases, 1.0 "gram equivalent" of reacted and screwpressed material was used for hydrolyzing.

Trends and conclusions from hydrolyzing these numerous samples can be summarized from Table VII: Of the three hydrolyzing solutions, water yielded the lowest glucose recovery. In general, the hydrolysis solutions of added 5 and 10 % sulphuric acid, respectively, yielded increasing quantities of glucose when decreasing volumes of liquid were utilized for hydrolysis (from 50-10 mL.)

Particle size reduction of abraded fiber prior to hydrolysis dramatically increased glucose recovery from hydrolysis (as shown for the sample which contained five percent by weight of sulphuric acid at 75 % acid

concentration.) In short, particle reduction of reacted fiber hydrolyzed with 10 ml of additional 5 % sulphuric acid yielded the most favorable medium for hydrolysis. Time duration for hydrolysis also has a significant effect on glucose recovery. Table VIII shows that glucose destruction takes place when time for hydrolysis is increased from 30 to 60 minutes at 17 p.s.i. with additional acid used for hydrolyzing. Destruction of glucose did not take place when only water was used to slurry the abraded fiber for the same time span and pressure during hydrolysis. The finding indicates that sufficient acid is present from prior addition of sulphur trioxide to adequately hydrolyze the subsequently abraded fiber to mono-sugars.

Table IX indicates that glucose content can be maximized at 18 % when using 15% sulphuric acid formed by prior admission of sulphur trioxide plus 5 ml of acid added (at 2.5 % concentration to slurry the abraded fiber) when hydrolyzing at 17 p.s.i. This additional dosage of acid to slurry would not be economical. Therefore, only water should be used for slurrying of abraded fiber, and to carry out hydrolysis at more elevated temperatures.

In general, glucose recovery (% glucose yield on dry fiber weight after hydrolysis) was substantially increased:

- When the volume of liquid used for hydrolyzing is reduced from 40 ml to 3.8 ml of water containing 0.5 and 5.0% sulphuric acid, respectively, per "gram equivalent" of abraded fiber.
- When the time for hydrolyzing increased from 5 to 20 minutes.
- When the pressure for hydrolyzing is increased from 25 to 75 p.s.i. (saturated steam).
- Hydrolyzing at 50 p.s.i. for 20 minutes yielded optimum glucose content; higher steam pressures applied did not result in improvement for glucose yield.

In a continued series of experimentation, the time for hydrolyzing was kept constant at 30 minutes. The average yield in mg glucose from each abraded gram of fiber was:

ml water used hydrolysis	Pressure used for hydrolysis, p.s.i.		
	35	50	75
3.8	152	163	188
4.0	128	158	178

The trial showed that glucose yield substantially increased when the liquid volume for slurring was reduced and the pressure during hydrolysis was increased with a constant time lapse for hydrolysis. Also, the single addition of sulphur trioxide proved very successful, thus eliminating the prior drying step for fiber after an initial and small

addition of sulphur trioxide.

With a single addition of sulphur trioxide, very little scorching of fiber occurred, providing the bagasse was dried to about 13% moisture content. Hammermilling of the subsequent abraded material (particle reduction) increased the surface area of the material to be hydrolyzed, and also yielded a substantial increase in glucose content. Most favorable glucose yield was obtained when hydrolyzing the abraded and hammermilled fiber at 50 p.s.i. (saturated steam) during 30 minutes, and when using 3.8 ml of water for slurring, which contained 3.4% of concentrated sulphuric acid.

A more exhaustive examination of optimum parameters for hydrolyzing of abraded fiber was conducted with three trials during 01/10/83 to 02/04/83. Tables XIII and XIV show that the most favorable glucose yield from hydrolysis was obtained with 50 p.s.i. (saturated steam) for pressure / temperature, and when using only water for slurring of the abraded and hammermilled fiber which provided a 3.3% by weight concentration of acid as catalyst.

The past experimentation with methods of hydrolysis suggested the necessity to use only water for slurring during this processing phase, for reasons of economics. By

using water only, advantage is taken of the formed sulphuric acid from prior admitted sulphur trioxide. Actual acid used during hydrolysis (% w/w) was determined as weight of sulphuric acid formed from addition of sulphur trioxide divided by the weight of water added to the slurry of the abraded and hammermilled fiber times 100. When additional sulphuric acid is supplied to the hydrolyzing solution, then this quantity of acid must be added to the acid formed from the sulphur trioxide application, and the total acid present must be divided by the total weight of water plus the combined total acid percent present times one hundred, in order to obtain the percent concentration of acid catalyst used during hydrolysis.

Acid concentrations ranging from 1.0 to 11.8 % of sulphuric acid were used when applying two pressures for hydrolysis (50 and 75 p.s.i.), during 30 minutes (Table XII). Water and dilute sulphuric acid solutions were used during hydrolysis, and results indicated a greater glucose recovery with 50 p.s.i. than with 75 p.s.i. Also, acid concentrations between 4 and 5 % of sulphuric acid for hydrolysis solution provided the highest glucose recovery. The hydrolysis was carried out in large, foam-stoppered pyrex test tubes, subjected to the desired pressure and time lapse in a thick-walled, stainless steel autoclave.

The next series of experimentation used only water as the slurring agent for abraded fiber, previously treated with sulphur trioxide. Hence, the previously formed sulphuric acid was the only acid source for the catalyst during hydrolysis. The samples were treated at different pressures: 25, 35, 50, and 75 p.s.i. (saturated steam), all for 30 minutes. This series of trials were used to determine the optimum threshold for pressure (saturated steam) during hydrolysis, and the resulting glucose yields are reported in Table XIII. Again, hydrolysis was carried out in the already mentioned autoclave with large pyrex tubes. These tubes were now covered with small glass beakers to insure a constant volume during hydrolysis; the beakers performed the stoppering function better than the previously used foam stoppers. The results from hydrolyzing indicated (Table XIII) that glucose recovery was optimum when using an acid concentration ranging from 2.6-3.3 % and at 50 p.s.i. (saturated steam). Glucose destruction apparently occurred at all at all levels for acid concentration when 75 p.s.i. was used during hydrolysis.

A steam pressure of 50 p.s.i. appears preferable to optimize glucose recovery from hydrolysis. Next, the optimum time span for hydrolysis at 50 p.s.i. should be determined. A series of time spans for hydrolysis and the subsequent glucose yields are reported in Table XIV. The

results show that hydrolysis should take place when using a steam pressure of 50 p.s.i. (saturated) during 30 minutes with an acid concentration of 3.2 % for sulphuric acid (w/w) in the slurry to be hydrolyzed for maximizing the glucose recovery from fibers. Longer time spans for hydrolysis or higher steam pressure employed will promote destruction of already formed glucose.

PILOT-PROCESSING FACILITY

To test the foregoing parameters in a continuous processing system, a small pilot plant was designed as a joint undertaking between the Facilities Engineering Division, NASA, Cape Kennedy and IFAS, University of Florida. After joint approval of the subsequent blueprints, the pilot facility was constructed at the Prototype Workshop of NASA, Cape Kennedy.

The small pilot plant consists of four main equipment components.

- A drier panel to reduce moisture in fiber with heated air.
- A reaction panel, for the admission of sulphur trioxide into an airstream into which the fiber to be treated is also introduced.
- An abrasion panel, consisting of a small extruding

screwpress.

- A hydrolyzing panel to convert abraded and treated fibrous material into a liquid stream containing glucose and xylose, and a slurry (solid) stream of liquid with lignin and residual unconverted fiber.

The different panels are shown in the photographs # 8 ,# 9, # 10 and # 11, respectively. The drier consists of a box of galvanized sheet metal subdivided into 12 compartments. An airstream passes in a zig-zag fashion through the compartments while heated by infrared lamps of 250 watt capacity each. Two lamps are controlled by one switch on the side allowing the functioning of 2, 4, 6, 8, 10 or 12 lamps simultaneously, and thus permitting 6 temperature settings for heating the air. The dryer panel has a cover for total enclosure, which was temporarily removed for taking the photograph. (See photograph # 8)

The heated air can be introduced into panel one which has provisions to introduce fiber into this airstream. The cyclone of panel one will separate dried fiber from air now saturated with moisture, and the degree of drying for the fiber can be regulated by the number of infrared bulbs utilized in the drier panel, and distribution for quantity of fiber in the air stream over time.

Panel one has a dual purpose: To dry fiber to a predetermined moisture content as explained before, and to admit sulphur trioxide to the air stream for subsequent reaction with the dried fiber to form concentrated sulphuric acid.

For the latter process phase (photograph # 9) the panel contains a rotary valve for admission of fiber, and a rotating ball valve for admission of sulphur trioxide. The entire system is kept under a slight vacuum by employing a suction ventilator after a cyclone, separating the reacted fiber and spent air. The low vacuum in the entire system is preferred to eliminate even slight leaks from admitted sulphur trioxide. The reaction of sulphur trioxide on the admitted fiber particles will take time, and for this reason a series of tubes with free-fall of fiber particles in the air plus sulphur trioxide stream is incorporated. A blueprint, designated as "A", is furnished for convenience to understand the working of design of panel one.

The fiber thus treated with sulphur trioxide is abraded in an extruding screwpress (photograph # 10) driven by a 2 hp electric motor, 3-phase. A series of belt-driven pulleys feed a permanent reduction gear, which in turn drives the shaft of the extruding screwpress. Speed for the shaft can be altered by changing the size of the pulleys on the motor

and intermediate blocks. A blueprint, designated as "B", provides the described design for panel two.

Panel three contains components for hydrolyzing the abraded fiber from panel two with saturated steam (photograph # 11). Vessels with conical bottoms are used for hydrolysis, each fitted with a progressive cavity pump which is capable of emptying the contents of the vessel, passing the slurry through a wet cyclone which in turn separates this slurry stream into a thin liquid phase and a slurried solid phase. The latter stream travels to feed the next vessel, while the former stream proceeds to the preceeding vessel.

Abraded fiber from panel two is first passed through a hammermill to obtain suitable particle size reduction, after which the material is slurried for entrance into the first hydrolyzing vessel by means of a separate progressive cavity pump. The final product, consisting of a liquid phase with dissolved glucose and xylose, leaves the system through a condensing unit to reduce the liquid to atmospheric pressure without flash. Likewise, the other final stream, a slurry consisting of lignin and non-reacted fiber particles also passes through a condensing coil for the same purpose. A blueprint designated as "C" is supplied for clarity, as well as a blueprint designated as "D", which explains the flow diagram for the entire processing system.

After interconnecting of the different panels for steam water and electric power, additional experimentation during 18-24 months will be conducted to establish proper parameters for continuous processing. This time period for investigations will continue beyond September 1, 1983 and as such, is not included within the scope for reporting , since this report presents the findings for the now concluded contractual obligation.

PRINCIPAL CONCLUSIONS AND SUMMARY

From the extensive experimentation, the following main conclusions can be summarized:

1. Sulphur trioxide when introduced into an air stream of ambient temperature will react with subsequently introduced fiber particles and will coat these particles at random with a thin layer of formed sulphuric acid.
2. A minimum of 5-10 % of sulphur trioxide by weight on dry fiber weight is required to accommodate optimum glucose formation after subsequent hydrolysis, without a need for additional sulphuric acid as catalyst to maximize mono-sugar content after hydrolysis.
3. A minimum of 75% concentration for formed sulphuric acid is required to adequately decrystallize alpha cellulose and to optimize glucose yield during subsequent hydrolysis.
4. To reach the desired acid concentration for sulphuric acid on fiber particles, the latter have to be dried to such a moisture content that sulphur trioxide addition and residual moisture in fiber after drying are in equilibrium to result in a minimum acid concentration of 75 % for

formed sulphuric acid.

5. Abrading of treated fiber should preferably take place in an extruding screw press having a constant diameter for the shaft. The screw flight of the latter is interrupted in several places to accommodate "pressure screws" to maximize the effect from abrading of fiber particles which were coated already with sulphuric acid of at least 75 % acid concentration.

6. The degree of abrading must result in a plasticized appearance of the end-product leaving the extruding screwpress. The required product appearance may result in different temperatures to be maintained during extrusion, and different lengths of time period for extrusion for types of fiber abraded. The stated parameters for extrusion with a screwpress having constant diameter shaft should involve length and RPM for the extruder shaft, and cooling or heating of the barrel during extrusion. The pitch on the shaft should also play an important role.

The needed parameters will be fully investigated in the constructed pilot plant where temperature elevation by friction from processing large fiber samples can be properly monitored.

7. The abraded and partly decrystallized fiber mass should

be passed through a hammermill to achieve adequate reduction of particle size prior to hydrolysis.

8. Hydrolyzing of the abraded fibrous material should take place without further addition of an acid catalyst. The added sulphur trioxide resulting in sulphuric acid prior to abrading is adequate to facilitate proper hydrolysis with saturated steam only.

9. Hydrolyzing takes place with saturated steam at 50 psi during a maximum of 30 minutes. Higher temperatures and longer time periods will cause destruction of formed glucose. Actual time limit for hydrolysis is dependent on the type of fiber crop utilized, and may be less than 30 minutes in certain cases to optimize glucose yield.

The above findings were utilized to formulate, design and actually fabricate a laboratory-sized pilot facility, capable to treat at least 50 pounds of fiber (dry basis) per day.

APPENDIX

METHODS OF ANALYSIS

I) Total Reducing Sugar Determination Procedure (Luff-Schoorl)

The Schoorl method as discussed in a technical report titled "Diazyme Assay" * was used. This method employs Fehling's solution from which the reduced copper is determined indirectly by iodometric titrations of the unreduced copper salt remaining after the sugar oxidation. Add to a 300 or 400 ml Erlenmeyer flask, 10 ml of the sample. Treat it cold with 10 ml of Fehling Solution A and 10 ml of Fehling Solution B and, add 15 ml of distilled water. Boil the solution for five minutes, assuring that the solution begins to boil after two minutes so that the total boiling time is three minutes. Along with the sample, a blank determination is

* Technical information bulletin, Miles Laboratories, Inc.,
Marshall Division, Elkhart, IN 46514.

also carried out , the only change being that 25 ml of distilled water is used in lieu of a sample.

After cooling the boiled sample to room temperature under tap water, the following solutions are added in order: 10 ml of 30% potassium iodide and 10 ml of 26% sulphuric acid. Once the sample is so treated, it must be immediately titrated against a 0.1 N solution of sodium thiosulfate. As soon as the 25% acid is added, the solution will change color from a clear blue (with some red precipitate in the bottom of the flask) to a rusty, brownish-red or an orange color, depending upon the concentration of reducing sugars present. As the solution is titrated with the thiosulfate, the solution will begin to have a slight yellowish tinge. At that moment the starch indicator solution should be added. The solution will then turn a very dark purple or almost black color. When the end-point is reached, the solution will turn to a creamy white color and should stay at that color point for at least 30 seconds.

Solutions used for the Luff-Schoorl test.

Solution A. Copper sulfate solution.

Dissolve 34.639 g reagent grade copper sulfate in 400 ml of distilled water and adjust to 500 ml in a volumetric flask.

Or, dissolve 2 x 34.639 g copper and adjust to 1000 ml in a volumetric flask.

Solution B. Alkaline tartrate solution.

Dissolve 173 g of reagent grade Rochelle salts (sodium potassium tartrate) and 50 g of reagent grade sodium hydroxide in 400 ml of distilled water and bring it up to 500 ml in a volumetric flask and allow to stand for two days. Or, double the quantities of reagent used and bring up to 1000 ml in a volumetric flask.

Solution C. 30% Potassium iodide (KI).

Dissolve 300 g of reagent grade KI in 900 ml of distilled water and bring to volume in 1 L of distilled water.

Solution D. 26% Sulphuric acid.

CAREFULLY: add 145 ml of 37 N sulphuric acid to about 750 ml of distilled water. Allow the solution to cool, and bring to volume in a 1 L volumetric flask with distilled water.

Solution E. 0.1 N Sodium thiosulfate.

Dissolve 24.85 g of the thiosulfate in 500 ml of distilled water which has recently boiled. Add 1 ml of 0.1 N sodium hydroxide (or 0.1 g of sodium carbonate) and bring to volume in a 1 L volumetric flask with boiled water (to

remove carbon dioxide). Let the solution stand for at least 24 hours before using.

1% Starch indicator solution.

Dissolve 150 g of sodium chloride in 300 ml of boiling distilled water to which 5 g moisture-free soluble starch is slowly added. After boiling for 5 minutes the volume is adjusted to 500 ml in a volumetric flask with distilled water.

Calculations.

The thiosulfate solution must be standardized against potassium iodate as follows:

Weigh carefully, between 0.1200 g and 0.1700 g of iodate and dissolve it into 50 ml of distilled water which was boiled and cooled to room temperature. Next, weigh 2.0 g of potassium iodide and make a solution consisting of 10-13 ml of distilled water to which one ml of concentrated hydrochloric acid (HCl) has been added. Pour the iodide into the solution containing the iodate, and as soon as the iodate is dissolved, pour in the HCl and immediately begin titrating with the thiosulfate. As soon as HCl is added, the solution will attain a very dark color. Do not add the indicator until the solution begins to get a yellowish tinge. The color of the solution will subsequently change

to a deep blue color which will gradually begin to clear. When the solution is totally clear, the end-point has been reached and the volume of thiosulfate used is recorded and plugged into the following formulae in order to get the "X" factor:

$$\frac{\text{mg of iodate}}{0.03567 \text{ g/m.e.}} = \text{milli equivalent (m.e.)}$$

$$\frac{\text{m.e.}}{\text{ml of thiosulfate}} = \text{Normality (N)}$$

$$\frac{N}{15.49 \times 0.1} \times 50 = \text{X factor}$$

With the "X" factor thus calculated, the weight per unit volume of reducing sugars can be calculated as follows:

Take the absolute value of the ml of thiosulfate needed to reach the end-point with the blank minus the ml of thiosulfate needed to reach the end-point of the sample. Multiply the resulting value by the "X" factor. Finally, multiply this value by the appropriate adjusting factor for volume.

Example:

Assume that the sample aliquot equals 3.8 ml and the result is to be expressed as mg/gallon. Then the adjusting factor for volume would be 1,000, since 3,800 ml = 1 gallon. Also the following values are assumed:

$$X \text{ factor} = 3.27$$

$$\text{ml of blank} = 35.5$$

$$\text{ml of sample} = 21.3$$

The mg of reducing sugar per gallon then equals:

$$(35.5 - 21.3)(3.27)(1000) = 46,434 \text{ mg/gallon}$$

II) Glucose Determination Procedure

Since the total reducing sugar determination includes the glucose, a method for isolation of only glucose is desired. This was accomplished by using an Industrial Glucose Analyzer Model 27 of Yellow Springs Industries, fitted with a dextrose detecting membrane. Following the operating manual's instructions, an automatic digital readout of concentration (mg/dl) is obtained after injection of the sample solution into the instrument.

Table I. Analysis results from treating bagasse with sodium xylene sulfonate at different temperatures and time periods.

Sample #	Treatment duration in hours	Temp., degrees C.	Pressure, psi	----- Solids in sample -----			
				Filtrate residue		Lignin recovered	
				g.	%	g.	%
1	1	180	90-100	-	-	-	-
Comments: Scorching of fiber; liquid volume too small; 40% xylene conc. used; precipitate formed							
2	2	180	90	4.78	47.8	1.04*	10.4
Comments: Two precipitates formed. * Washed precipitate a) 0.621 Lignin precipitate b) 0.423							
3	2	160	40	5.51	55.1	0.442	4.4
Comments: No charring; no second precipitate.							
4	2	160	40	5.65	56.5	0.393	3.9
Comments: Not stirred.							
5	1	160	40	-	-	-	-
Comments: No precipitate; Xylene at pH 7.0							
6	2	160	60	5.68	56.8	-	-
Comments: No precipitate; Xylene at pH 7.0							
7	2	160	40-50	4.75	47.5	0.258	2.6
Comments: 30min. for fiber pre-soak; Xylene at pH 7.0.							

Table I. Analysis results from treating bagasse with sodium xylene sulfonate at different temperatures and time periods. Continued.

Sample #	Treatment duration in hours	Temp., degrees C.	Pressure, psi	----- Solids in sample -----			
				Filtrate residue		Lignin recovered	
				g.	%	g.	%
8	2	170	80	6.20	62	0.637	6.4
Comments: Wash made alkaline.							
9	3	170	80	6.12	61.2	0.943	9.4
Comments: 30 min. for fiber pre-soak.							
10	4	170	80	4.77	47.8	0.604	6.04
Comments: 30 min. for fiber pre-soak.							
11	5	170	80	4.93	49.3	0.958	9.6
Comments: One hour for fiber pre-soak.							
12	6	170	80	6.91	69.1	0.567	5.7
Comments: 30 min. for fiber pre-soak.							
13	3	170	70	9.90	49.5	1.846	9.2
Comments: Pre-hydrolysis with acid; 30 min. for fiber pre-soak; 20 g of powered bagasse used.							
14	5	170	60	5.44	5.44	0.596	5.9
Comments: Pre-hydrolysis with acid; 30 min. for fiber pre-soak.							

Table II. Effect of acid concentrations on glucose recovery,
using 75% of sulphuric acid as final concentration.

Sulphuric acid on dry fiber, %	Conversion temp., C.	Glucose, mg/dl	Glucose on dry fiber, %	Schoorl, mg/dl	Tot. red. sug. on dry fiber, %	Glucose as percent of total reducing sugars
-----	-----	-----	-----	-----	-----	-----
10	73	44	8.8	153	30.6	29
		113	22.6	168	33.6	67
		108	21.6	175	35.0	62
		119	23.8	191	38.2	62
15	85	52	10.4	149	29.8	35
		124	24.8	173	34.6	72
		112	22.4	152	31.0	72
20	60	32	6.4	150	30.0	21
		60	12.0	149	29.8	40
		122	24.4	191	38.2	64
25	65	42	8.2	123	24.6	33
		124	24.8	178	37.6	66
30	64	39	7.8	128	25.6	30
		119	23.8	194	38.8	61
		139	27.8	219	43.8	63
35	50	42	8.4	138	27.6	30
		110	22.0	215	43.0	51
		120	24.0	213	42.6	56

Please note: Tot. red. sug. - Total reducing sugars.

Table II. Effect of acid concentrations on glucose recovery,
using 80% of sulphuric acid as final concentration.

Sulphuric acid on dry fiber, %	Conversion temp., C.	Glucose, mg/dl	Glucose on dry fiber, %	Schoorl, mg/dl	Tot. red. sug. on dry fiber, %	Glucose as percent of total reducing sugars
10	90	33	6.6	114	22.8	29
		105	26.6	115	28.8	91
		18	3.6	52.8	10.6	34
15	70	41	8.2	130	26.0	32
		71	14.2	176	35.2	40
		120	24.0	188	37.6	64
20	75	36	7.2	113	22.6	32
		123	24.6	171	34.2	72
25	--	47	9.4	136	27.2	35
		107	21.4	144	28.8	74
		38	7.6	155	31.0	25
30	--	40	8.0	147	29.4	27
		118	32.6	196	39.2	60
		160	32.0	262	52.4	61
35	75	47	9.4	113	22.6	42
		136	27.9	174	34.8	78
		127	25.4	171	34.2	74

Please note: Tot. red. sug. - Total reducing sugars.

Table II. Effect of acid concentrations on glucose recovery,
using 85% of sulphuric acid as final concentration.

Sulphuric acid on dry fiber, %	Conversion temp., C.	Glucose, mg/dl	Glucose on dry fiber, %	Schoorl, mg/dl	Tot. red. sug. on dry fiber, %	Glucose as percent of total reducing sugars
-----	-----	-----	-----	-----	-----	-----
10	85	32	6.4	99	19.8	32
		53	10.6	109	21.8	49
		88	17.6	122	24.2	73
15	80	37	7.4	142	28.4	26
		118	23.6	221	44.2	53
		105	21.0	186	37.2	56
		113	22.6	215	43.0	53
20	65	113	22.6	169	33.8	67
		119	23.8	181	36.2	66
25	--	32	6.4	113	22.6	28
		93	18.6	172	34.4	54
		88	17.6	146	29.2	60
30	60	45	9.0	119	23.8	38
		100	25.0	130	32.5	77
35	60	57	11.4	151	30.2	38
		154	30.8	215	43.0	72
		153	30.6	209	41.8	73
		153	30.6	217	43.4	71
		158	31.6	229	45.8	69

Please note: Tot. red. sug. - Total reducing sugars.

Table II. Effect of acid concentrations on glucose recovery,
using 90% of sulphuric acid as final concentration.

Sulphuric acid on dry fiber, %	Conversion temp., C.	Glucose, mg/dl	Glucose on dry fiber, %	Schoorl, mg/dl	Tot. red. sug. on dry fiber, %	Glucose as percent of total reducing sugars
-----	-----	-----	-----	-----	-----	-----
10	--	37	7.4	127	25.4	29
		96	19.2	149	29.8	64
		109	21.8	163	32.6	67
		108	21.6	165	33.0	65
		107	21.4	142	28.4	75
15	80	57	11.4	145	29.0	39
		146	29.2	189	37.8	77
20	80	42	8.4	162	32.4	26
		39	7.8	157	31.4	25
		98	19.6	186	37.2	53
		94	18.8	201	40.2	47
25	70	52	10.4	125	25.0	43
		146	29.2	216	43.2	68
		153	30.6	238	47.6	64
		151	30.1	239	47.8	63
30	70	36	9.0	109	27.3	33
		132	26.4	170	34.0	78
35	65	60	12.0	147	29.4	41
		159	31.8	195	39.0	82

Please note: Tot. red. sug. - Total reducing sugars.

Table III. Feasibility of glucose recovery based on the required quantity of sulphuric acid.

Feasibility	Sample number and acid concentration used	Glucose present, %	Sulphuric acid on dry fiber used, %
Least	II 80	32.0	30
	IV 90	31.8	35
	III 85	31.6	35
Medium	IV 90	30.6	25
	I 75	27.8	30
	IV 90	26.4	30
	III 85	25.0	30
Most	IV 90	29.2	15
	II 80	26.3	10
	I 75	24.8	15
	II 80	24.0	15

TABLE IV. Screwpress design and glucose recovery.

Concentrations	----- Glucose (mg/dl) -----			Trend
	CD	CP	MCP	
* 5-75	137	68	95	CD>MCP>CP
5-90	110	103	115	MCP>CD>CP
10-75	119	78	105	CD>MCP>CP
10-90	109	91	97	CD>MCP>CP

* 5% Sulphuric acid on dry wt. of fiber

75% Sulphuric acid concentration formed from sulphur trioxide addition

Table V. Screwpress design and conversion temperatures for glucose formation.

Sulphuric acid concentration and press design	Temperature, degrees C	Glucose, mg/dl	Glucose recovery trend
10-75/CP	110	78	CP>CD>MCP
10-75/MCP	70	105	
10-75/CD	73	119	
10-90/CP	55	91	MCP>CP
10-90/MCP	60	97	
5-90/CD	125	110	CD>MCP>CP
5-90/CP	75	103	
5-90/MCP	98	115	
5-75/CD	143	137	CD>MCP
5-75/CP	---	68	
5-75/MCP	98	95	

Table VI. Comparative glucose recovery using different configurations for screwpress.

----- Constant Diameter (CD) -----				----- Conical (CP) -----			
Sulphuric acid on dry fiber, %	Sulphuric acid conc. %	mg of Glu./ %	mg of Sch./ %	Sulphuric acid on dry fiber, %	Sulphuric acid conc, %	mg of Glu./ %	mg of Sch./ %
5	75	137/24.4	178/35.6	5	75	68/13.6	124/24.8
5	80	129/25.8	193/38.6	5	80	90/18.0	190/38.0
5	85	82/16.4	211/42.2	5	85	63/12.6	169/33.8
5	90	92/23.0	125/31.3	5	90	103/20.6	159/31.8
* 10	75	119/23.8	191/38.2	10	75	78/15.6	208/41.6
* 10	90	109/21.8	163/32.6	10	90	91/18.2	126/25.2
* 20	80	123/24.6	171/34.2	20	80	115/23.0	205/41.0
* 30	75	139/27.8	219/43.8	30	75	95/19.0	210/42.0

Please note: * = Previous data; Glu = Glucose, mg/dl; Sch = Schoorl, total reducing sugars, mg/dl.

Table VII. Hydrolysis study using three types of hydrolyzing solutions.

Sample	With water			With 5% sulphuric acid			With 10% sulphuric acid		
	Glucose mg/%	Schoorl mg/%	Glucose/ Schoorl*	Glucose mg/%	Schoorl mg/%	Glucose/ Schoorl*	Glucose mg/%	Schoorl mg/%	Glucose/ Schoorl*
50 ml Hydrolysis									
5-75**	14/2.8#	41.0	34.0	62/12.4	183	34.0	84/16.8	164	51.0
5-75##	17/3.4	59.0	29.0	141/28.2	164	86.0	127/25.4	177	72.0
5-90	9/1.8	31.0	29.0	65/13.0	152	43.0	63/12.6	162	39.0
10-75	14/2.8	37.0	38.0	76/15.2	107	71.0	79/15.8	95	83.0
10-90	14/2.8	49.0	29.0	69/13.8	131	53.0	81/16.2	128	63.0
25 ml Hydrolysis									
5-75	13/2.6	42.0	31.0	88/17.6	175	50.0	107/21.4	154	69.0
5-75 ##	15/3.0	46.0	33.0	85/17.0	159	53.0	139/27.8	185	75.0
5-90	18/3.6	47.0	38.0	108/21.6	162	67.0	85/17.0	167	51.0
10-75	14/2.8	31.0	45.0	75/15.0	108	69.0	81/16.2	99	82.0
10-90	19/3.8	37.0	51.0	100/20.0	144	69.0	74/14.8	118	63.0
10 ml Hydrolysis									
5-75	16/3.2	50.0	32.0	94/18.8	173	54.0	98/19.6	175	56.0
5-75 ##	14/2.8	52.0	27.0	157/31.4	164	96.0	123/24.3	165	75.0
5-90	20/4.0	60.0	33.0	116/23.3	152	76.0	97/19.4	152	64.0
10-75	25/5.0	44.0	57.0	114/22.8	113	100.0	86/17.2	89	97.0
10-90	19/3.8	47.0	40.0	85/17.0	128	66.0	106/21.2	144	74.0

Key: * glucose as % of total reducing sugars (Schoorl); ** 5% of formed sulphuric acid on dry fiber; # glucose as % dry fiber weight; ## particle size reduced to 50-80 mesh by mortar and pestle.

Table VIII. Time study for hydrolyzing finely divided (90-100 mesh) and abraded bagasse treated with 10% sulphur trioxide on dry fiber and 90 % concentration of formed sulphuric acid.

Hydrolyzing solution -----	1 hr @ 17 psi in mg. for Glucose/Schoorl -----		1/2 hr @ 17 psi in mg. for Glucose/Schoorl -----	
	5 ml -----	10 ml -----	5 ml -----	10 ml -----
Water	50/78	41/158	39/71	32/93
5% Sulphuric acid	102/143	113/143	113/139	118/143
10% Sulphuric acid	91/120	109/141	119/149	122/119

Table IX. Results from hydrolysis of bagasse with a single dose of sulphur trioxide using various amounts of formed sulphuric acid on dry fiber for hydrolysis.

---All samples with 80% conc. sulphuric acid on dry wt. of fiber---

% Sulphuric acid on dry fiber, %	Type of hydrol. sol.	5ml Hydrol. Sol.		10ml Hydrol. Sol.	
		Gluc.	Schoorl	Gluc.	Schoorl
5	water	18	N/A	19	42
	sulphuric acid, %				
	2.5	93		116	180
	5.0	111		117	179
	10.0	100		126	192
10	water	15	30	11	37
	sulphuric acid, %				
	2.5	60	99	61	111
	5.0	63	105	75	113
	10.0	69	119	76	105
15	water	20	66	17	61
	sulphuric acid, %				
	2.5	93	154	98	178
	5.0	92	135	105	178
	10.0	97	147	105	152

Please note:

Bagasse used contained 13% moisture. Reacted material was hammermilled after screwpressing for particle size reduction. All figures expressed as mg/dl unless otherwise stated. All volumes are 200 ml. Hydrolysis was carried out at 17 psi for 30 minutes.

Table IX. Table IX. Results from hydrolysis of bagasse with a single dose of sulphur trioxide using various amounts of formed sulphuric acid on dry fiber for hydrolysis, (continued)

-- All samples with 80% conc. sulphuric acid on dry wt. of fiber---

% Sulphuric acid on dry fiber, %	Type of hydrol. sol.	5ml Hydrol. Sol.		10ml Hydrol. Sol.	
		Gluc.	Schoorl	Gluc.	Schoorl
20	water	55	184	41	125
	sulphuric acid, %				
	2.5	83	206	108	140
	5.0	99	239	113	176
	10.0	106	244	114	229
25	water	53	224	43	189
	sulphuric acid, %				
	2.5	77	294	100	259
	5.0	97	262	105	---
	10.0	88	249	107	---

Please note:

Bagasse used contained 13% moisture. Reacted material was hammermilled after screwpressing for particle size reduction. All figures expressed as mg/dl unless otherwise stated. All volumes are 200 ml. Hydrolysis was carried out at 17 psi for 30 minutes.

Table X. Effect of screwpressing for fiber treated with sulphuric acid on obtained yield of glucose.*

Screwpressing	No screwpressing	Hydrolyzing solution, 10 ml		yield of glucose, mg/dl in solution
		water	10% sulphuric acid	
	X	X		20
X		X		74
	X		X	72
X			X	123

* Hydrolysis at 75 psi for 10 min.

Table XI. Glucose content from different parameters for hydrolysis using 20-80* bagasse with varying amounts of distilled water as hydrolyzing solution during three time periods.

% sulphuric acid in a water sol'n.**	25 psi with 100ml dilution						50 psi with 100ml dilution					
	5 min.		10 min.		20 min.		5 min.		10 min.		20 min.	
	Glu.	Sch.	Glu.	Sch.	Glu.	Sch.	Glu.	Sch.	Glu.	Sch.	Glu.	Sch.
0.5% (40 ml)	44	81	53	103	65	203	91***	306	99	224	131	290
1.0% (20 ml)	73	105	55	110	78	163	101	270	129	274	159	310
2.0% (10 ml)	49	111	82	143	88	155	126	322	138	280	169	329
5.0% (3.8 ml)	71	174	112	182	122	211	147	306	154	375	179	305

* 20-80= 20% sulphuric acid on dry fiber at 80% concentration.

** Weight of the sample = 1 g equivalent.

*** Weight of the sample = 1/2 g equivalent

Glu - Glucose, mg/dl.

Sch - Schoorl, total reducing sugars, mg/dl.

Table XI. Glucose content from different parameters for hydrolysis using 20-80* bagasse with varying amounts of distilled water as hydrolyzing solution. during three time periods, (continued)

% sulphuric acid in a water sol'n.**	75 psi with 100ml dilution					
	5 min.		10 min.		20 min.	
	Glu.	Sch.	Glu.	Sch.	Glu.	Sch.
0.5% (40 ml)	137	287	145	253	187	341
1.0% (20 ml)	164	331	160	303	169	304
2.0% (10 ml)	190	336	161	302	188	328
5.0% (3.8 ml)	180	316	151	265	179	323

* 20-80= 20% sulphuric acid on dry fiber at 80% concentration.

** Weight of the sample = 1 g equivalent.

*** Weight of the sample = 1/2 g equivalent

Glu - Glucose, mg/dl.

Sch - Schoorl, total reducing sugars, mg/dl.

Table XII. Average glucose content from hydrolysis using water and dilute acid as solutions for 30 minutes at 50 and 75 p.s.i.

sulphuric acid hydrolysis solution on dry fiber, % w/w.	Type of solution	----- Glucose (mg/dl)-----	
		30" @ 50 p.s.i.	30" @ 75 p.s.i.
0.0 152	no water	174 *	
2.6	3.8 ml water	161	161
1.0	10 ml water	-	162
4.0	10 ml of 2.5 % sulphuric acid	186	165
6.9	10 ml of 5.0 % sulphuric acid	129	89
10.0	10 ml of 10.0 %	88	26

* The reaction tube was uncovered.

Please note:

All samples were covered with a foam stopper unless otherwise noted and were 10-80 passed through the conical type screwpress.

Table XIII. Average glucose content from two hydrolysis at various pressures for 30 minutes using water as the hydrolysis solution.

Water, ml -----	Sulphuric acid on dry fiber, % -----	at 25 p.s.i. -----	at 35 p.s.i. -----	at 50 p.s.i. -----	at 75 p.s.i. -----
10.0	1.0	85	141	144	148
5.0	2.0	98	147	147	141
3.8	2.6	101	137	161	142
3.0	3.3	112	145	164 149*	137
2.5	4.0	128	143	143	126
2.2	4.5	112	142	154	126

* Cover broke and allowed steam to enter the reaction tube, thus altering the true concentration of the acid in the hydrolyzing solution.

Please note: All samples are 1 g equiv.; 10-80 for sulphur trioxide addition and abraded in the conical press.

Table XIV. Average glucose from hydrolysis using water as solution and carried out at 50 p.s.i. during several time periods.

water, ml -----	acid on dry fiber % w/w -----	----- Time periods in minutes -----			
		5 ---	10 ---	15 ---	20 ---
10.0	1.0	66	91	96	108
5.0	2.0	79	108	108	109
3.8	2.6	76	105	103	112
3.0	3.3	80	104	98	110
2.5	4.0	92	102	104	111
2.2	4.5	89	107	104	107

Table XIV. Average glucose from hydrolysis using water as solution and carried out at 50 p.s.i. during several time periods, continued

-----Time periods in minutes-----				
water, ml	acid on dry fiber % w/w	25	30	40
-----	-----	---	---	---
10.0	1.0	108	144	110
5.0	2.0	113	147	100
3.8	2.6	107	161	103
3.0	3.3	105	164	96
4.0	2.5	111	143	97
2.2	4.5	100	154	91

* Previous data from Table XIII.

Diagram I. Materials flow for delignification process with data supplied by sample # 14 of table I.

GLUCOSE PRODUCED AT VARIOUS % DRY WEIGHT OF H_2SO_4 %

DIAGRAM
I-A

KEY OF SYMBOLS
FINAL CONC. OF H_2SO_4 ; %

75% ○

80% □

85% △

90% ✕

GLUCOSE PRODUCED IN
1 g. equiv. OF DRY FIBER; %

H_2SO_4 BASED ON DRY WEIGHT OF FIBER ; %

COMPOSITE AVERAGES OF:

GLUCOSE PRODUCED AT VARIOUS % DRY WEIGHT OF H_2SO_4 %

GLUCOSE PRODUCED IN
g. equiv. OF DRY FIBER; %

H_2SO_4 BASED ON DRY WEIGHT OF FIBER; %

KEY OF SYMBOLS

% OF SO_3 BY DRY WEIG

10% $\triangle$

15% $\square$

20% $\circ$

25% $*$

30% $\bullet$

35% $\star$

GLUCOSE PRODUCED IN
1 g. equiv. OF DRY FIBER; %

GLUCOSE PRODUCED AT VARIOUS FINAL CONC. OF H_2SO_4 ; %

II-B

GLUCOSE PRODUCED IN
lg. equiv. OF DRY FIBER

1. Assembly for reaction of fiber with SO_3 diluted by an inert gas.

2. Tube assembly with stainless steel valves connected to small volume reaction vessel.

3. Tube assembly with stainless steel valves connected to large volume reaction vessel.

4. Laboratory-sized extruder with constant diameter screw and barrel, and with pressure screws.

5. Different view of extruder described in photograph #4.

5A. Constant diameter extruder as seen in photograph #5.

5B. In contrast to 5A, the modified conical extruder with pressure screws.

6. Close-up view of hydrolysis autoclave.

7. General view of equipment used to hydrolyze.

8. Overall view of dryer panel for pilot facility.

9. Overall view of reaction panel for SO_3 admission on fiber for pilot facility.

10. Overall view of extruder press for pilot facility.

11. Overall view of the counter-flow hydrolyzing panel for pilot facility.