To be published in the Proceedings on International Congress on Engineering and Food, Boston, MA, August 9-13, 1976.

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LBL-5275
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Energy and Environment Division

Cellulose, Food And Energy

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November 1977

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Prepared for the U.S. Department of Energy under Contract No. W-7405-ENG-48

LBL-5275
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CELLULOSE, FOOD AND ENERGY

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The potential of cellulose as a source of energy and food is reviewed with consideration of raw material sources, processing methods and economics. A tentative scheme for production of Torula yeast and ethanol from sugars produced by enzymatic hydrolysis of cellulose is described.

Paper presented at International Congress on Engineering & Food., August 9-13, 1976, Boston, Mass.

Plant biomass consists primarily of carbohydrate polymers, lignin and small amounts of ash and extractives. The carbohydrate fraction can be characterized in various ways depending upon the methods of analysis (1) and the chemical degradation which may be caused by the separation methods employed. A detailed discussion of the complex and varied composition of plant material is beyond the scope of this paper.

For the purpose of the present discussion, the carbohydrate content of plant biomass will be viewed simply as consisting of cellulose (more correctly α-cellulose) and hemicellulose. Cellulose is a polymer of D-glucose having a degree of polymerization in the range of several thousand with the glucose units linked at the β, 1-4 position. Hemicellulose is primarily a polymer of xylose having a lower degree of polymerization in the range of several hundred. Lesser amounts of other hexoses such as mannose and of other pentose such as aribinose are often present.

Soft woods typically contain 65-73% total carbohydrate with 10-13% pentosans. Hardwoods typically contain 70-82% carbohydrate with 18-25 pentosans. The approximate carbohydrate and lignin content of some representative California agricultural crop residues is shown in Table 1 (27).

The objective of the present paper is to review briefly some methods for obtaining carbohydrates and to discuss some engineering and economic aspects of the utilization of plant biomass as a fermentation raw material. The discussion will emphasize the enzymatic hydrolysis of cellulose in which we have been engaged at

Berkeley. Acid hydrolysis will be discussed briefly as an alternative processing method.

Acid Hydrolysis

In the presence of dilute acid cellulose is hydrolyzed to glucose according to the reaction:

$$(C_6H_{10}O_5)_n + n\ H_2O \xrightarrow{[H^+]} n\ C_6H_{12}O_6 \qquad (1)$$

Unfortunately with respect to obtaining a maximum yield of sugars, acid also catalyzes the decomposition of glucose to 5-hydroxy-methy 2-furaldehyde (HMF) and thence to levulinic plus formic acids

$$C_6H_{12}O_6 \xrightarrow{[H^+]} HO\text{-}CH_2\text{-}C_4H_2O\text{-}CHO + 3H_2O \qquad (2)$$

glucose (hexose) — 5-hydroxymethyl 2-furaldehyde

$$C_6H_6O_3 + 2H_2O \rightarrow CH_3\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}OH + HCOOH \qquad (3)$$

(HMF) — levulinic acid — formic acid

To maximize the yield of glucose the effect of the competitive decomposition reactions must be minimized. Saemans (2) studied the kinetics of glucose formation from hemicellulose free wood and its decomposition by dilute sulfuric acid. Empirical rate constants for cellulose hydrolysis and glucose decomposition were determined as functions of acid concentration

and temperature. From the mathematical model obtained it was concluded that high temperature and short contact times were necessary to obtain satisfactory yields.

Fagan, et al. (3) applied Saeman's kinetic model to hydrolysis of Kraft paper and deduced first-order rate constants for the glucose formation and decomposition reactions as functions of temperature and acid concentration. Figure 1 (3) shows the predicted isothermal sugar yields expressed as a percentage of the maximum, or theoretical, yield. From these results the authors suggested as a possible operating condition the use of 1% H_2SO_4 at a contact time of 20 seconds at 230°C to obtain a maximum sugar yield of 52%. It should be noted that this analysis is not rigorous in that all sugars, including the hemicellulose sugars, are treated as a single component, glucose. However, the model is useful in indicating the effect of variables for reactor design.

Xylose undergoes similar acid decomposition to form furfural. Saemans (2) found the rate constant for xylose decomposition to be greater than for glucose so that concurrent hydrolysis of cellulose and hemicellulose results in a relatively low yield of xylose.

A number of acid hydrolysis processes for production of wood sugars and ethanol were developed prior to and during World War II. (4) Most notable among these are the process of Scholler (5,7) and the Madison Wood Sugar Process (6) developed in the U.S. Forest Products Laboratory at Madison, Wisconsin. The latter method will be described briefly as a representative example of this technology.

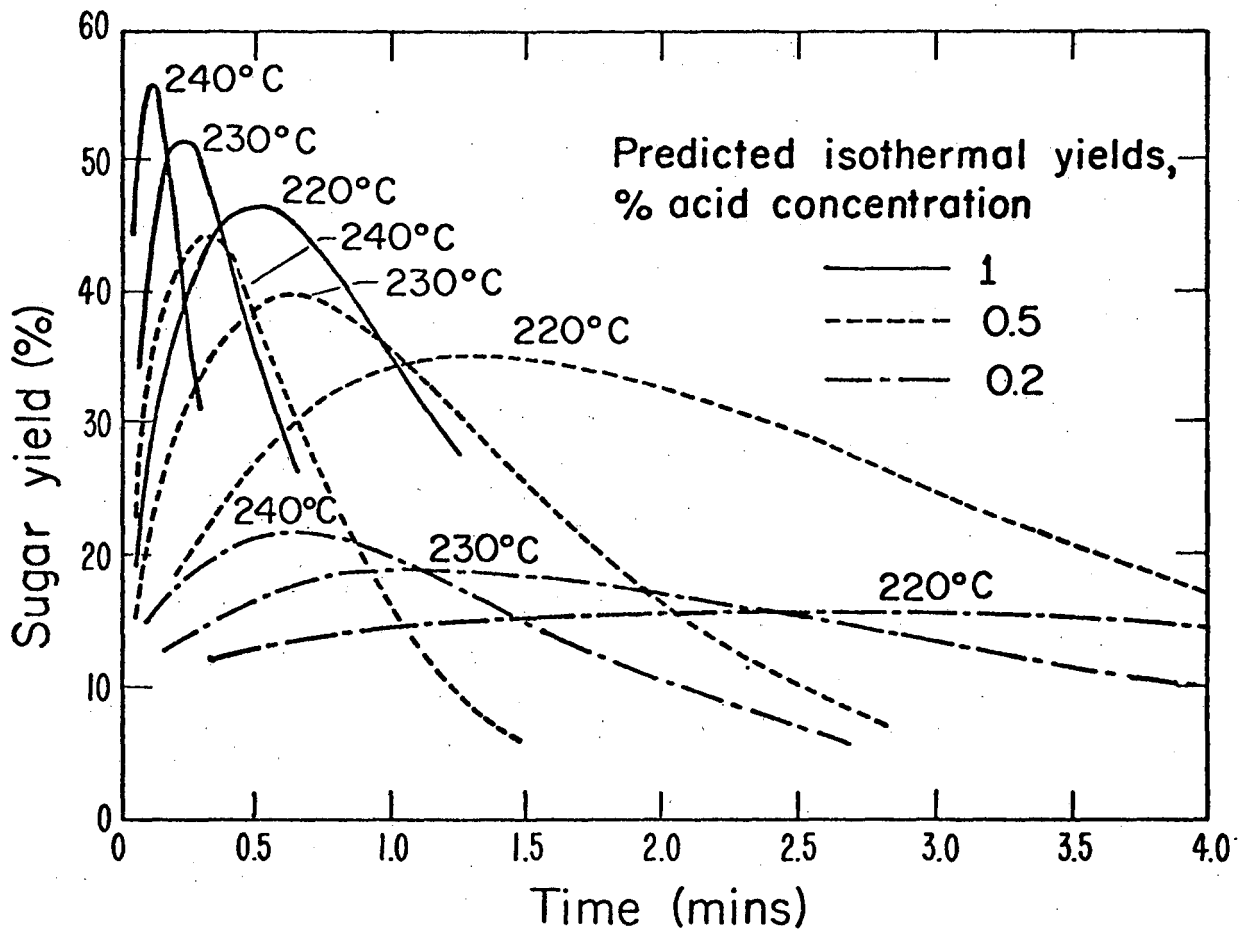

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Figure 1. Predicted isothermal sugars versus time (3)
Predicted isothermal yields, % acid concn

Sugars produced by acid hydrolysis are generally fermentable (8), although the rates may be slow due to inhibitory effects of various substances in the hydrolyzates. Hexoses may be fermented to ethanol in satisfactory yield by Saccharomyces sp. Pentose may be fermented to butanol and acetone by O. butylicum or to 2,3, butylene glycol by Aerobacter aerogenes. Various pretreatments (9) of sugar solutions have been employed to reduce inhibitory effects including addition of sodium sulfite, heat treatment, use of large quantities of inoculum, removal of lignin and furfural and clarification with activated carbon.

Harris et al. (9) studied the fermentation of Douglas Fir hydrolyzate to ethanol. It was found necessary to clarify the hydrolyzate by aeration and addition of aluminum sulfate prior to inoculation with the yeast. Also, better results were obtained by employing hydrolyzates which had been generated with a minimum of tar formation (i.e. mild hydrolyzing conditions).

The Madison Process employs 0.5 to 0.6% sulfuric acid as the hydrolyzing agent. A charge of wood chips is placed in a digester and the acid solution is caused to flow continuously through the charge while the temperature is progressively increased at a rate of 0.5°C per minute from 150°C to 185°C. In a pilot plant digester the acid-charge contact time was 11 minutes at a loading density of 11.8 pounds dry, bark free wood per cubic foot. The acid leaving the digester is flashed to 30 pounds pressure to cool the solution sufficiently to stop decomposition of the sugars and remove some methanol and furfural. When the concentration of reducing sugars in the acid reaches an average concentration of 5% the hydrolysis is discontinued. Following neutralization with lime the sugar

solution is filtered and fed to a yeast fermentation process to produce 95% ethanol as described by Harris et al. (9). Approximately 79% of the sugars are fermentable to ethanol producing 64.5 gallons of ethanol per ton of dry, bark free Douglas Fir chips.

A cost analysis for the Madison process was developed (8) for the processing of 350 tons per day of dry wood plus bark (260 tons on a bark-free basis) to produce 16,550 gallons of ethanol per day. Costs are presented in Table 2 per gallon of alcohol in 1945 dollars and in 1976 dollars, with the former updated in proportion to the change in the Marshall-Stevens chemical process industries cost index from 123 in 1945 to 464 in 1976. These data suggest that ethanol might be produced in the range of 95¢ per gallon exclusive of cost of the wood chips. The total capital investment in 1976 dollars is estimated at 10,100,000.

Assuming the fermentation cost in 1976 dollars, exclusive of sugar cost, to be 20¢ per gallon of ethanol, and assuming that 16 lb of reducing sugars are required to produce a gallon of ethanol (9), the cost of producing reducing sugars in 5% concentration by the Madison process may be estimated roughly to be 4.7¢ per pound.

It should be emphasized at this point that the foregoing cost estimates are very approximate so that a detailed re-evaluation of the process is needed to establish the process economics conclusively. Also, the yields selected in the cost analysis are among the most favorable obtained in the pilot plant studies.

One direction for future improvement of the acid hydrolysis process would be the development of a plug flow reactor to permit

use of short contact times at high solid liquid ratios. Based on a preliminary analysis by Grethlein (10) successful development of such a reactor could result in higher sugar yields, greater heat economy and lower costs than with the Madison or Scholler processes. At a residence time of 0.2 minutes at 230°C, Grethlein estimates a possible sugar production cost in 1974 dollars of 1.97¢ per lb at a solid/liquid ratio of 0.3 (w/w) and 6.5¢ per lb at a solid/liquid ratio of 0.1 for hydrolysis of municipal refuse.

Enzymatic Hydrolysis

Many microorganisms, including particularly species of fungi, produced enzyme systems or "cellulases" which depolymerize and hydrolyze cellulose to lower oligosaccharides and ultimately to glucose (11). One of the most powerful cellulase producers is the fungus Trichoderma viride in the form of the mutant QM9414 developed by Mandels, et al. at the U.S. Army Natick Laboratories. Some properties of this organism and its extracellular enzyme system and of cellulases in general will be briefly reviewed. Details of the underlying research studies have been published elsewhere (13, 14, 15, 16).

Enzymatic hydrolysis involves at least five separate types of enzyme activities as illustrated in Figure 2. An endocellulase (C_2) proposed by Halliwell and Riaz (22) cuts long cellulose fibers into short lengths and along with cellobiohydrolase (C_1) breaks down the highly polymerized crystalline parts of the cellulose to a degree of polymerization in the range of 200 or less. Two β-glucanase components (C_x) carry the degradation to cellobiose followed by action of β-glucosidase, or cellobiase, to form glucose.

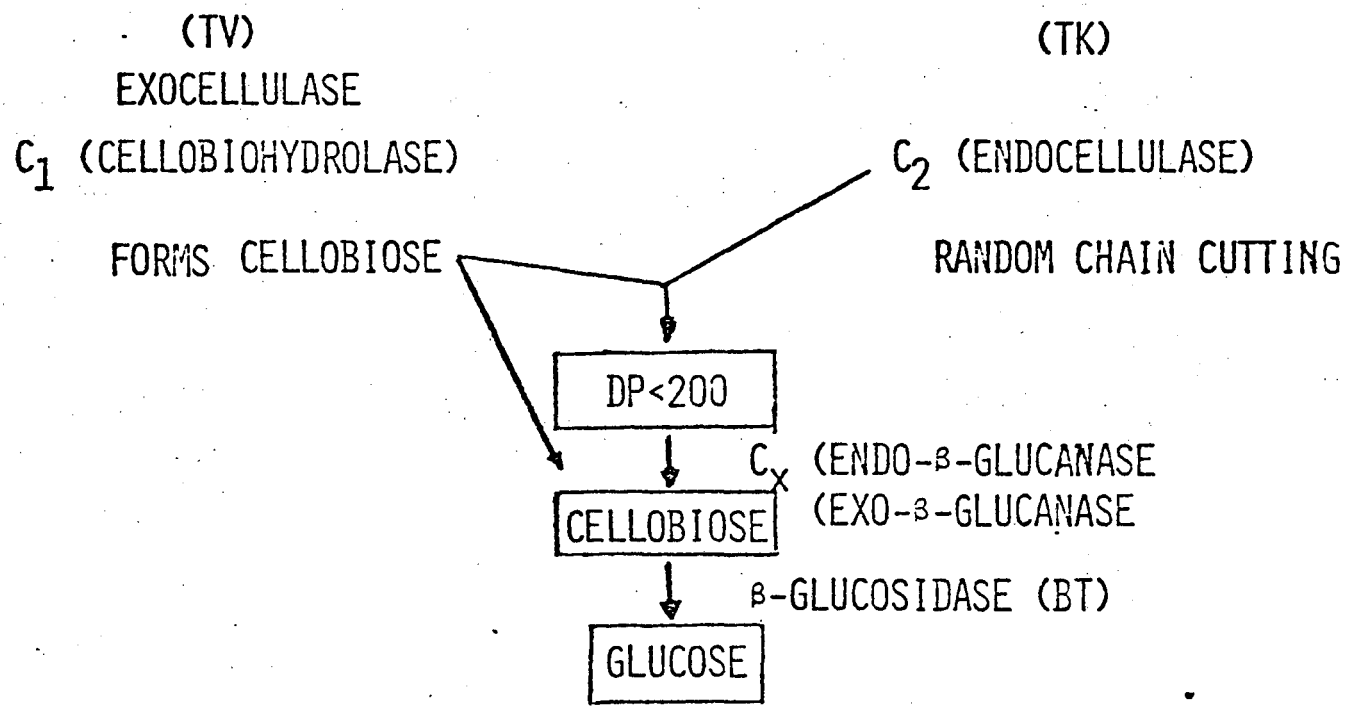

Fig. 2. Proposed mechanism of enzymatic hydrolysis.

Gel chromatography of a T. viride cellulase (17) indicated presence of three distinct protein fractions ranging in molecular weight from 10,000 to 50,000. Presence of C_x activity was found essential for C_1 activity.

An enzymatically formed hydrolyzate will typically contain glucose plus some higher oligosaccharides, primarily cellobiose with the relative amounts of each depending upon the relative strength of the various enzyme components, the degree of crystallinity of the cellulose and the hydrolysis time.

It has become customary to characterize the activity of cellulase in terms of C_1 activity (action against cotton, a crystalline cellulose) and C_x activity (action against carboxy methyl cellulose) and an overall activity (action against Whatman filter paper) or filter paper activity (FPA) according to Mandels and Weber (18).

Trichoderma viride grows rapidly at 30°C, pH 5.0 on glucose in a mineral peptone medium without production of cellulase. The maximum specific growth rate is about 0.29 hr^{-1} and maximum cell productivity occurs at a dilution rate of 0.21 in continuous culture.

In the absence of glucose T. viride grows slowly on solid cellulose (in the range of 0.02 hr^{-1} specific growth rate) and secretes cellulase into the medium. The mycelium can be readily filtered off and the filtrate used for enzymatic hydrolysis.

Figure 3 shows the relationship between soluble protein and FPA in T. viride culture filtrates. An FPA level in the range of 3-4, or about 1 gm protein per liter at 45°C is a good working condition for practical hydrolysis operations. The protein can be

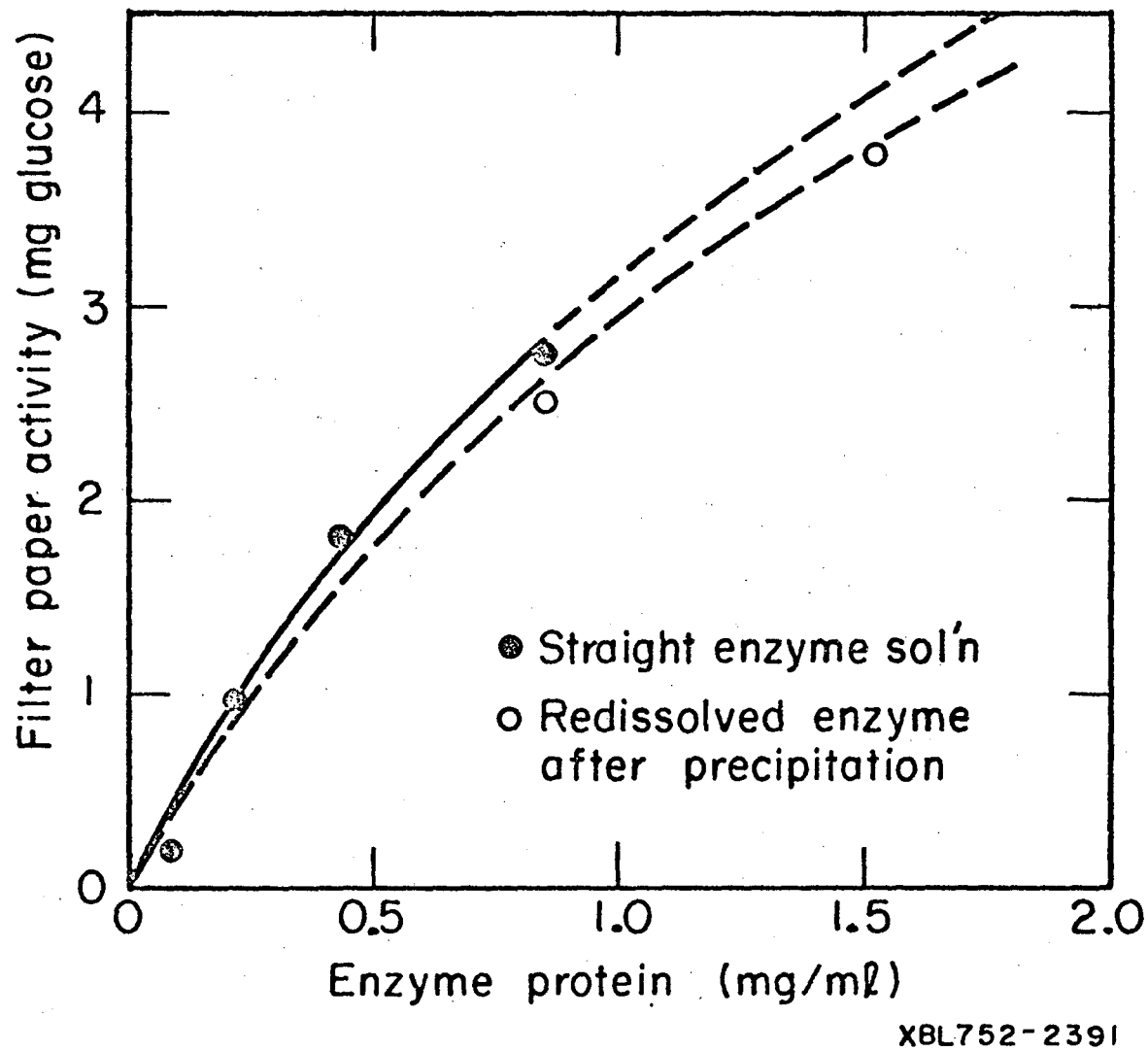

Figure 3. Filter Paper Activity vs. Enzyme Protein Concentration.

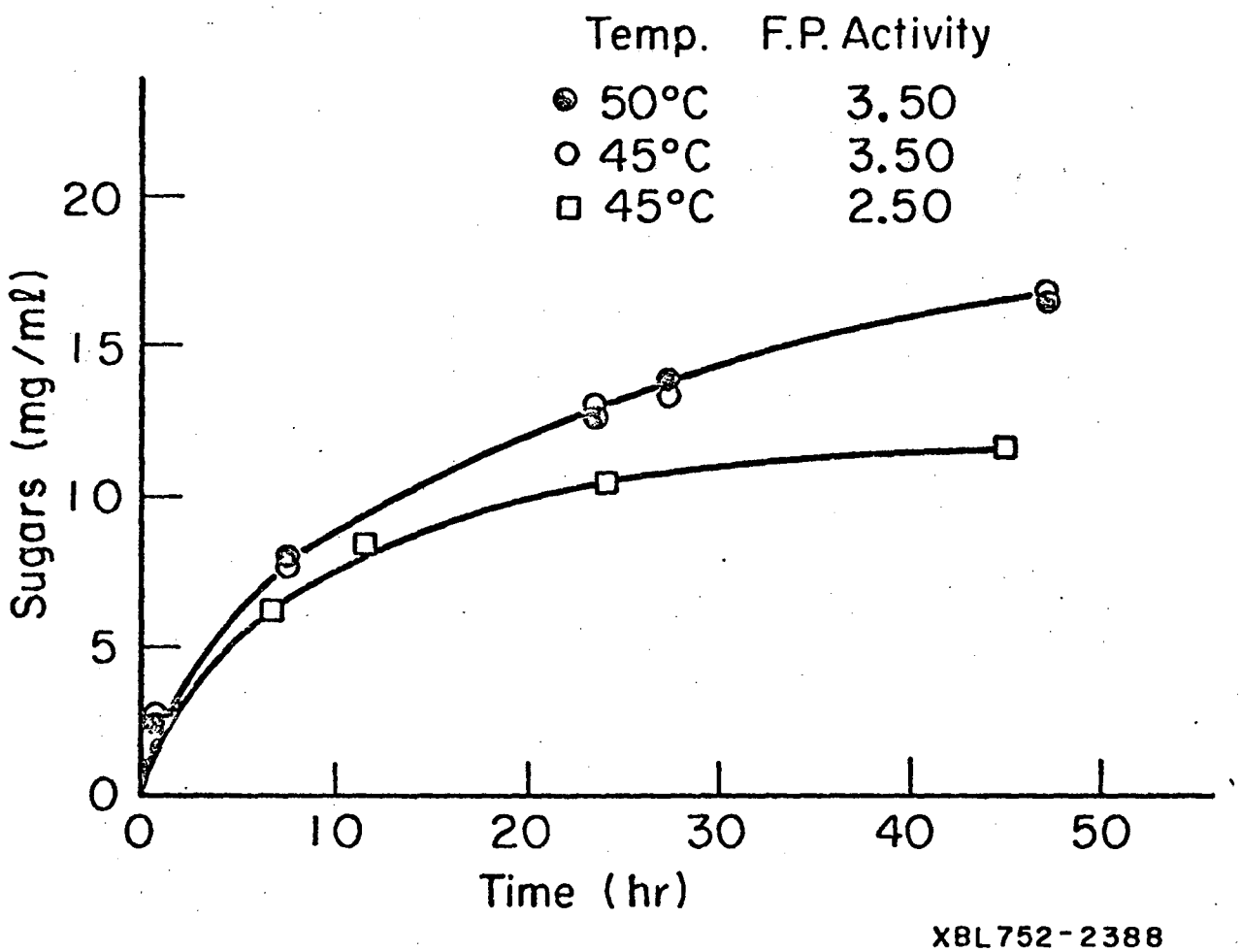

Figure 4. Hydrolysis of 5% Suspensions of -20 mesh Newsprint.

precipiatated in solid form by dilution of the filtrate with acetone (3:1 v/v) with loss of about 15% of the original activity per precipitation.

Hydrolysis of cellulosic materials results upon immersion of the substrate into the enzyme solution. The rate and extent of hydrolysis will depend upon the particular substrate and upon the type of pretreatment employed (19)(20). Chemical pretreatments must be carefully evaluated for the substrate involved since the cost of chemicals may be prohibitive. As discussed later in this paper a dilute acid pretreatment may be economical for substrates having a high hemicellulose content.

For substrates such as newsprint containing appreciable quantities of crystalline cellulose, a mechanical pretreatment such as ball milling which reduces the crystallinity improves the hydrolysis.

Figure 4 shows typical hydrolysis curves for -20 mesh Wiley milled (shredded) newsprint in 5% suspension, containing 61% α-cellulose, 16% hemicellulose and 21% lignin (14). Approximately 50% conversion of the cellulose to sugars occurs in 40 hours producing 15 lb of sugars (as glucose) per lb of enzyme protein at an activity of 3.5 FPA. A representative composition of the hydrolyzate sugars is 72% glucose, 22% cellobiose 4.4% xylose and 1.5% mannose.

Figure 5 shows data for hydrolysis of 10% suspensions of -200 mesh ball milled newsprint at 50°C (15). At 3.5 FPA, the hydrolysis is approximately 85% complete producing 54 lb of sugar per lb of enzyme protein.

Figure 6 shows the effect of delignification of ground wood by chlorite treatment (21) on its enzymatic hydrolysis. An inexpensive delignification process would be most beneficial for

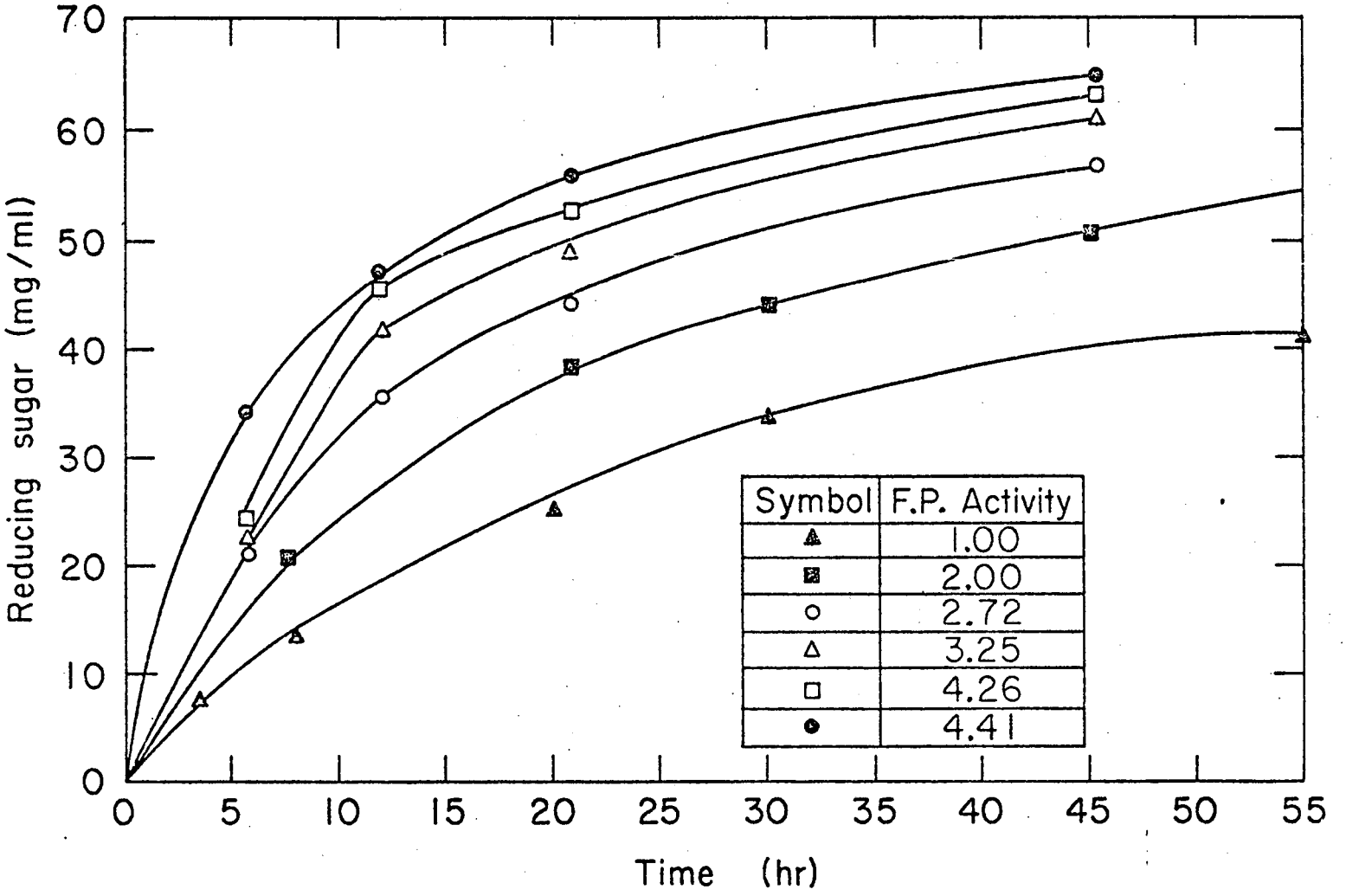

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Figure 5. Hydrolysis of 10% ball-milled (-200 mesh) newsprint.

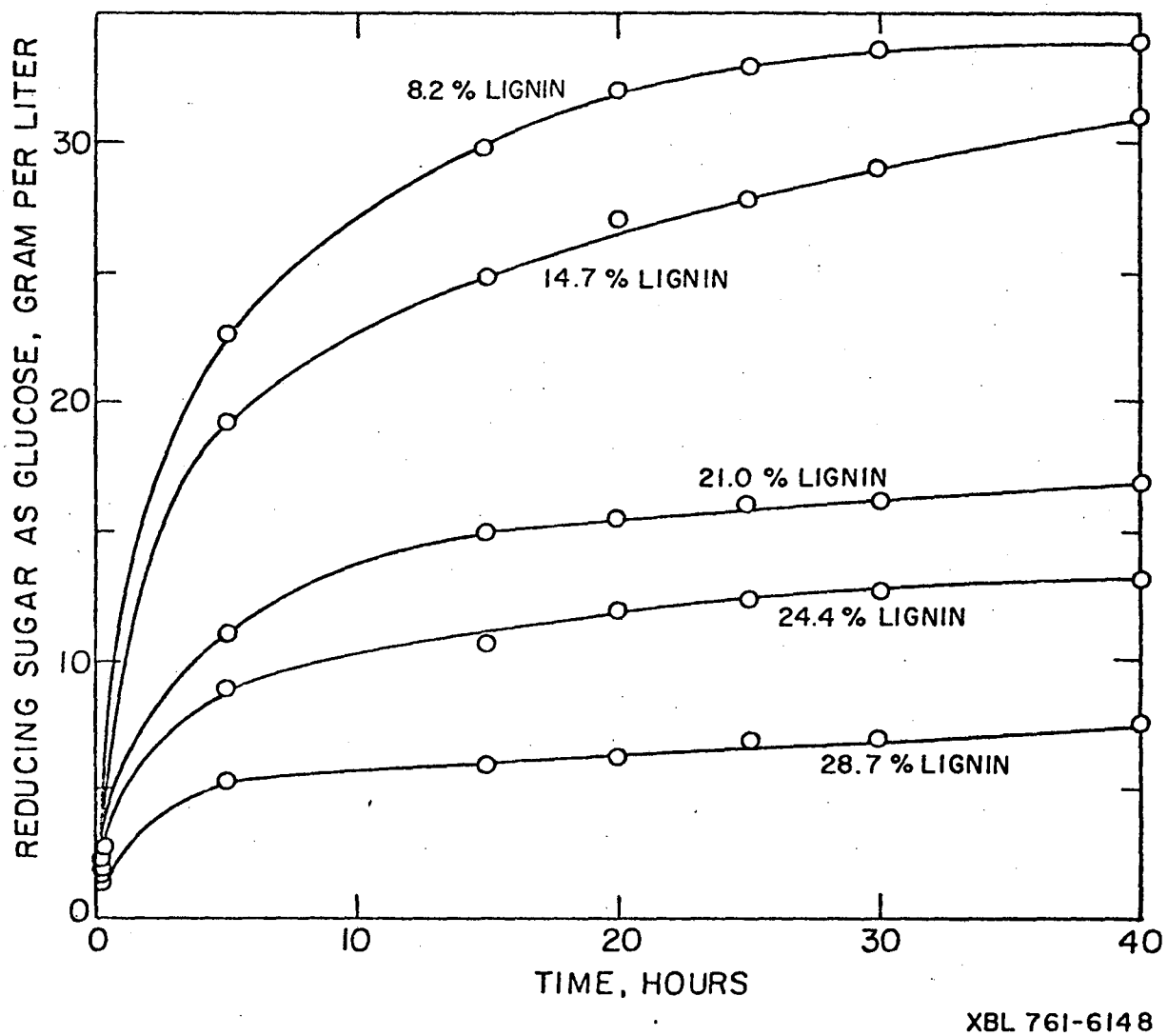

Figure 6. Effect of Lignin Removal on Hydrolysis of Ground Wood (21). Data are for treatment of suspensions containing 36 gm cellulose per liter with T. viride cellulase of 4.6 FPA.

the hydrolysis of such materials.

Although the beneficial effects are great, the cost of ball milling and lignin removal appears presently prohibitive. Therefore, a simple shredding seems the most practical pretreatment for paper-like cellulosic materials. Table 3 shows some representative conversions obtained by various investigators for materials typical of the cellulosic component of urban solid wastes.

Table 4 shows some recent results from our laboratory for the treatment of 2 mm Wiley milled wheat straw in several ways (27). In addition to glucose and xylose the original material contained 2.4% galactose, 0.75% mannose, 2.7% arabinose (other CH_2O), 12.5% lignin, 9.6% ash, 7.6% extractives and 12% unknown organic material. Treatment with 1% H_2SO_4 in 16% solid suspension for 5.5 hours at 100°C removed most of the xylose and other CH_2O with a total dry weight removal of 37.6%. Negligible acid consumption occurred. Treatment of the acid treated residue with 0.25 molar NaOH for 2 hours at 100°C removed 56% of the lignin and 26.2% of the remaining dry weight, but produced no additional carbohydrate in the extract. Approximately 57% of the NaOH was neturalized in the treatment. As shown in the table the total glucose yield obtainable by enzymatic hydrolysis increased with each of the pretreatments.

The dilute acid extraction appears particularly promising in that considerable additional carbohydrate is recoverable over that obtainable by enzymatic hydrolysis of the original material, and also the quantity of solid to be treated enzymatically per unit of glucose obtained is greatly reduced. However, it does not appear that the NaOH treatment would be practical since 0.33 pounds of base would be consumed per pound of glucose obtained, resulting

in an appreciable cost for a relatively small amount of additional sugars.

During hydrolysis the enzyme components are strongly adsorbed on the cellulosic substrate. In the case of newsprint hydrolysis, after about 50% conversion approximately one-third of the original enzyme activity remains in the liquid phase (30) from which it can be recovered by adsorption on fresh solid entering the process.

The enzyme protein remaining on the residual solids is not readily removed and must be considered as lost in the present technology. However, it would be very important economically if a low cost desorbing agent could be found.

Enzymatic Hydrolysis Economics

On the basis of available laboratory data, including those described above, Wilke, Yang and von Stockar (30) have developed a preliminary process design and cost analysis for enzymatic hydrolysis of 885 tons per day of newsprint. While confirmation of the process assumptions by pilot plant studies are needed, the analysis provides a rough economic perspective of the relative importance of various processing operations and serves as a basis for guidance of future research studies. Detailed equipment specification and justification of the process assumptions are available in the original report.

I. Process Description

Figure 7 is a schematic flow diagram of the hydrolysis process. Flow quantities correspond to the base case process specifications given in Table 5. For simplicity the facilities for milling, heat exchange, induction solids sterilization and residual

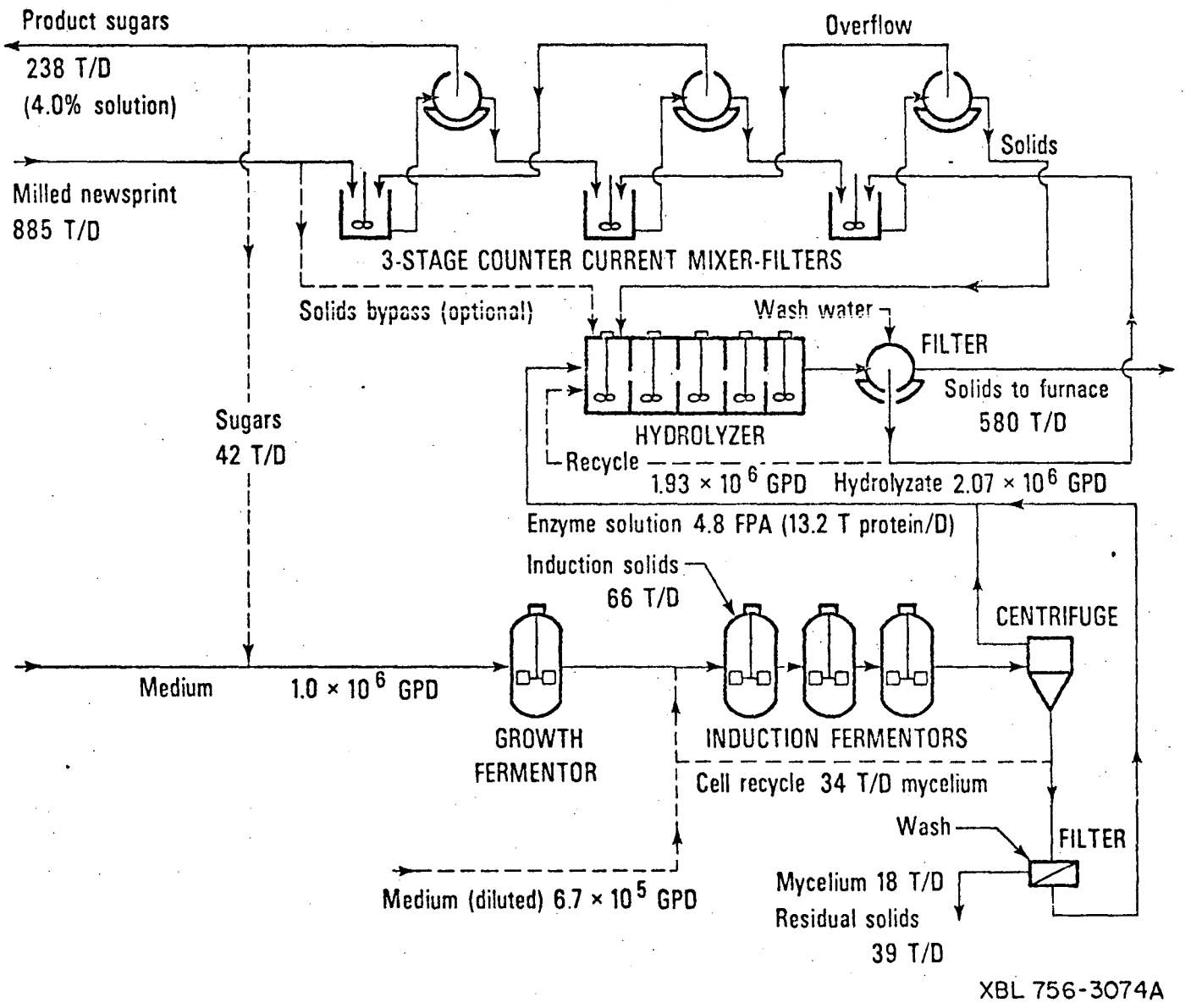

Figure 7. Flow Diagram of the Base Case Process.

solids combustion have been omitted in the flow diagram, although they were designed and are included in the processing cost analyses.

The primary plant feed consists of 885 tons per day of newsprint containing 6% moisture. By means of moderate shredding and hammermilling the feed is reduced to approximately -20 mesh. The size reduction is not critical so long as the material will form aqueous suspensions which can be pumped, agitated and filtered. An additional 66 tons per day of feed material is diverted to the first enzyme induction fermentor after sterilization with steam. The product sugar stream from the hydrolyzer is contacted countercurrently in 3 mixer-filter stages with feed solids for enzyme recovery. Each mixer filter stage consists of a mixing tank to provide 30 minutes contact time and a horizontal belt vacuum filter to separate the solids from the liquid. A total enzyme recovery of 95% is predicted by theory based on adsorption studies described previously (14)(30).

Hydrolysis is conducted over 40 hours at 45°C at a solid/liquid ratio of 1/20 w/w based on inputs to the hydrolyzer. The latter consists of 5 agitated cylindrical concrete digesters of the type used for solid waste treatment in sanitary engineering. Cellulose conversion of 50% is assumed, at an overall enzyme strength equivalent to 3.5 FPA in the hydrolyzer (13)(14). Provision is made for the recycle of a portion of the product solution (plus enzyme) back to the hydrolysis vessel. A sugar concentration

of 4.0% is obtained for the case shown. A range of sugar levels is possible depending on the mode of operation and amount of sugar recycle employed.

Make-up enzyme is produced in a two-stage fermentation system, employing the fungus Trichoderma viride QM9414 (12) obtained from the U.S. Army Natick Laboratories. Cell growth is obtained in the first stage at a dilution rate of 0.2 hr^{-1} employing a medium containing 1% product sugars plus minerals and protein nutrient (30). The induction system is operated at an overall dilution rate of 0.017 hr^{-1} excluding the cell recycle stream. Both stages employ agitated stainless steel vessels operated at 30°C with aeration rates of 0.15 and 0.015 v.v.m. in the growth and induction stages, respectively. The growth stage feed is sterilized in a heat exchange system (not shown). The induction section effluent is passed through a centrifuge from which a portion of the underflow is fed back to the first induction stage. Ten induction stages in series are employed. The flow quantities in Figure 7 corresponds to a cell recycle fraction of 0.65. Recycle fraction is the fraction of cells leaving the last induction stage which is returned to the first stage. For the case shown, the use of recycle will maintain the cell density in the induction system at 7 gm per litre, assuming negligible growth in the induction system when newsprint is employed. The resultant enzyme production is sufficient to provide an enzyme concentration

of 3.5 FPA in the hydrolyzer. A portion of the centrifuge underflow is filtered and the cells are discarded to maintain adequate cell viability. The centrifuge overflow will contain a small concentration of cells. Removal of these cells prior to hydrolysis is assumed unnecessary because T. viride will not grow at the hydrolysis temperature. However, further study of other possible problems of microbial contamination in the hydrolysis system is needed.

Spent solids from the hydrolyzer following filtration are fed to a furnace and steam-power plant to provide process steam and electricity for the process. A substantial excess of energy is available in the spent solids, sufficient to operate an alcohol fermentation plant, for example, and to produce some additional by-product power (26). No credit is assumed for this excess energy in the processing cost analysis described below, pending a more detailed study of the combustion operation.

II. Base Case Cost Estimation

For the process described above a preliminary cost estimate was made for the required capital investment and cost per pound of sugars produced in aqueous solution.

The general cost estimation procedure was that recommended by Peters (23) and by Holland (24).

The fixed capital cost is estimated as a multiple of purchased cost of the principal items of equipment. In the present case a multiplier of 3.1 was used, except in the case of the concrete digestors for which the multiple was reduced

to 1.68 because the unit cost already included engineering construction and contractor's fees. The total manufacturing cost is broken down into investment related costs, labor related costs, utilities costs, and raw material costs. Taxes are omitted on the assumption that the installation would be part of a municipal waste processing complex. No charge or credit has been assigned to the newsprint. Costs of process steam and power were estimated assuming that they could be generated on the plant site using spent solids as fuel. Capital costs for steam power facilities are not included in the fixed capital costs on the assumption that the specified unit costs for steam and electricity include both investment and labor charges. An on-stream efficiency of 90% is assumed, corresponding to 330 days operation per calendar year.

The resulting fixed capital cost, total manufacturing costs and costs per unit of product are listed in Table 6 for each of the major processing sections: (1) hydrolysis, (2) pretreatment, (3) enzyme recovery, and (4) enzyme make-up.

For this base case a fixed capital cost of $23,390,000 and a sugar cost of 5.2¢ per pound is obtained. Enzyme make-up is the major cost factor, comprising nearly 60% of the total.

Table 7 shows the distribution of costs among several categories for the overall process. As shown in Table 7, the process is highly capital intensive, with over 68% of the product cost in the investment related category.

Carbohydrate Production from Wheat Straw

A preliminary process design and economic assessment of the production of sugar from wheat straw has been made (22) based on the data for acid pretreatment and enzymatic hydrolysis of the residue shown in Table 4. The enzymatic hydrolysis operation will be identical to that described above for newsprint with flow quantities and glucose yield reflecting the different composition of straw.

The total quantity of straw to be processed, 439 T/Day, is specified to give the same solids feed to the enzymatic hydrolysis section as that shown for newsprint in Figure 7.

Figure 8 is a flow diagram for the acid extraction section of the straw processing plant. Five hydrolysis stages in series are employed with each stage consisting of an agitated stainless steel vessel providing a residence time of 1.1 hr. The extraction stages are maintained at 100°C by internal steam coils. In the first stage a liquid/solid ratio of 7.5 w/w is employed based on the entering streams. Acid strengh is maintained at 1% addition of concentrated H_2SO_4. Effluent from the last stage is filtered on vacuum belt filters with a provision for washing the solids with make-up water to the process. A major fraction of the filtrate is recycled to the first stage resulting in a new product stream containing 2.1% xylose.[1] This sugar solution is neturalized with lime for subsequent use as a fermentation substrate. The washed solids containing a small quantity of acid are fed to the enzymatic hydrolysis section.

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[1] A small concentration of furfural (0.2%) in the product will result from xylose decomposition as estimated from kinetic data of Root, et al. (31).

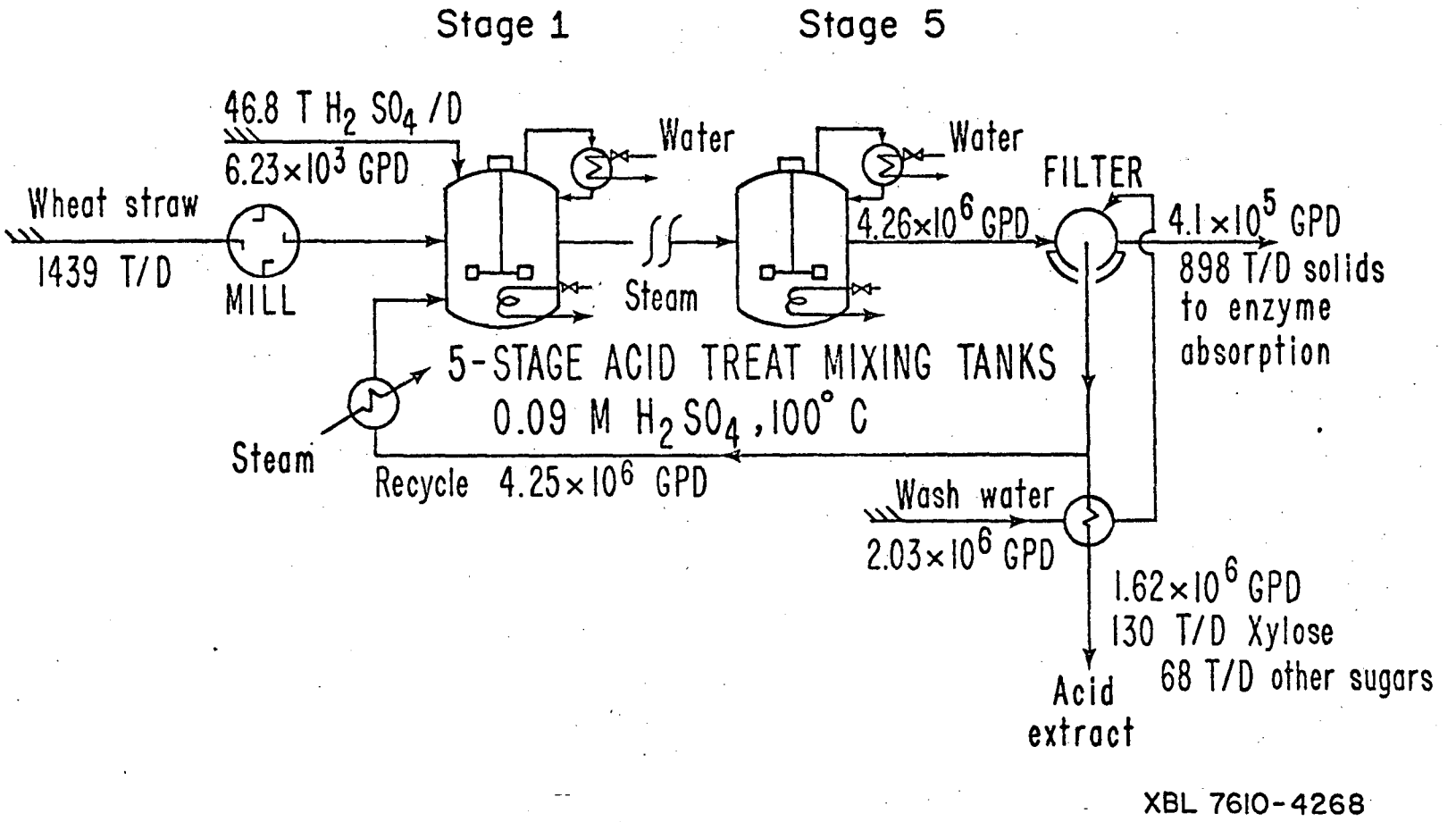

Figure 8. Acid Pretreatment of Wheat Straw.

Preliminary cost estimates were made for the straw processing operations in the same manner as described above for newsprint hydrolysis. The acid pretreatment section requires a capital investment of $5,530,000 and produces xylose at 3.0¢ per pound as shown in Table 8A. The enzymatic hydrolysis section requires a capital investment of $24,100,000 and produces glucose at 10.3¢ per pound as shown in Table 8B. Table 9 summarizes the total sugar production by the combined operations of acid extraction and enzymatic hydrolysis.

Ethanol from Enzymatic Hydrolyzates

Cysewski and Wilke studied the continuous fermentation of glucose with Saccharomyces cerevisiae and have made a preliminary process design and cost estimate for the production of ethanol and torula yeast from the enzymatic hydrolyzate of newsprint. Some results of their study will be reviewed briefly. More detailed information is available in the original reports (25)(26).

Figure 9 shows the determination of the optimum glucose concentration of 10% for continuous fermentation at a dilution rate of 0.17 hr^{-1} which gave essentially complete glucose utilization.

The fermentation process was designed to produce 24,000 gallons of 95% ethanol per day from the sugars produced from newsprint (Fig. 7).

I. Process Design and Economics

The design basis is shown in Table 10. The hydrolysis product was found to be 70% fermentable by Saccharomyces, thus requiring a 14.3% solution of hydrolyzate sugars to obtain the optimum feed of 10% fermentable sugars. Preliminary cost analysis showed it economically favorable to concentrate the sugar to 14.3%. The

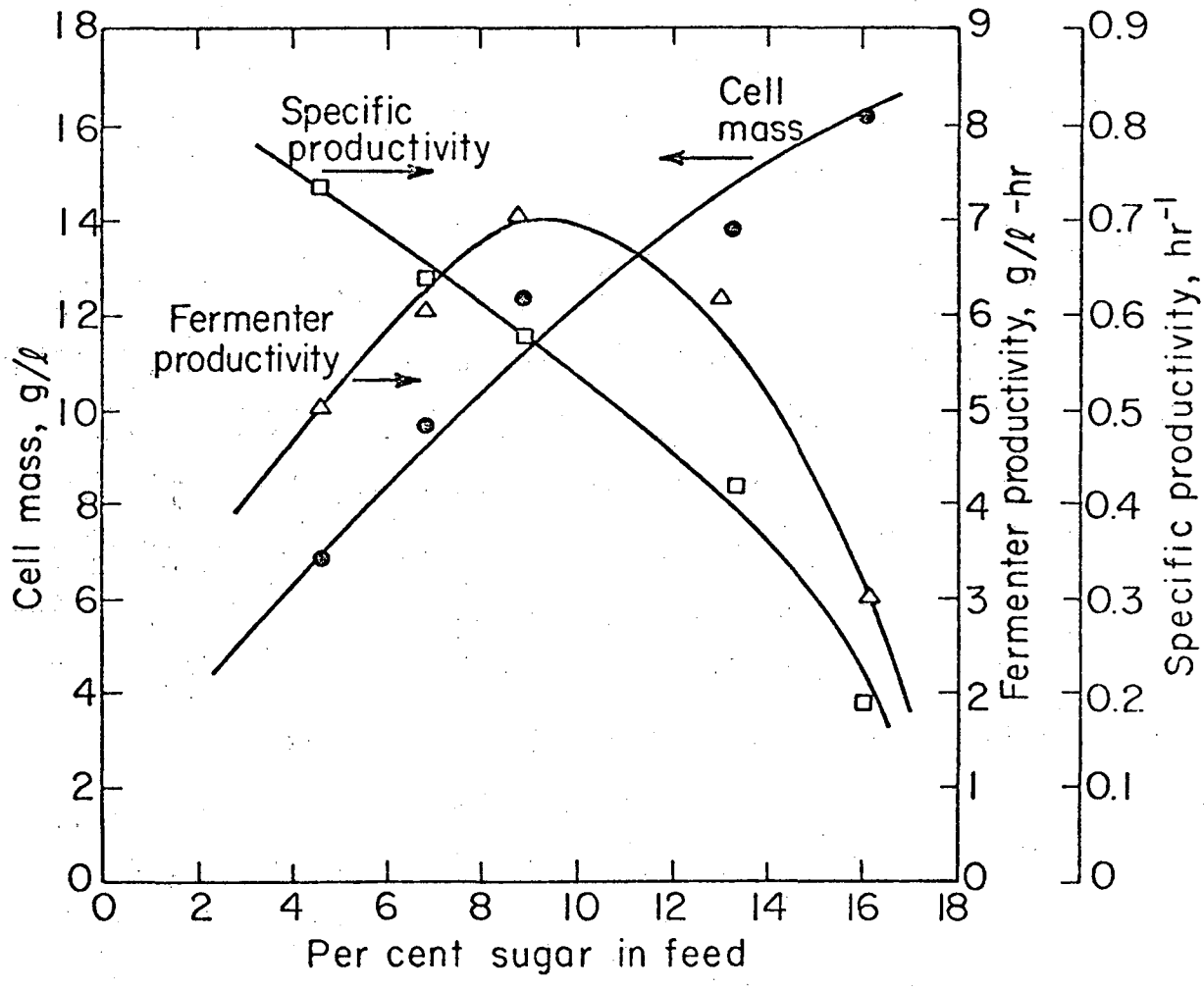

Figure 9. Ethanol Productivities and Cell Mass Concentration as a Function of Feed Sugar Concentration (adapted culture).

concentration costs of 2.7¢/gal. of ethanol produced (see below) being more than offset by the savings in fermentation and distillation costs. A computer process model was used to design and optimize the ethanol fermentation plant and a single cell protein process which consumes the residual sugars left after the alcohol fermentation.

Figure 10 shows a schematic flow diagram of the ethanol fermentation process. The evaporator which concentrates the hydrolyzate sugar solution is not shown, although it has been included in the process analysis.

After the hydrolyzate sugars have been evaporatively concentrated from 4.0% to 14.3% solution, protein and mineral supplements are mixed with the sugars. Sterilized by steam injection, the fermentation broth is distributed to five continuous fermenters, each operating at a dilution rate of 0.17 hr^{-1}. A low flow of air (8.0×10^{-4} VVM) is sparged through the fermenters to maintain the oxygen tension at the optimum level of 0.07 mmHg. The fermented beer then passes to two continuous centrifuges and the yeast is removed. The yeast is subsequently dried and stored for sale as a protein feed supplement. The clarified beer from the centrifuges is next distilled to concentrate the ethanol to 95wt%. An abosrber using the distillate bottoms as the absorbing liquid, is employed to recover ethanol lost in the exit gases (air and CO_2) from the fermenters. The ethanol rich stream from the absorber is also fed to the main distillation unit for final ethanol recovery.

Saccharomyces cerevisiae used in the ethanol fermentation will ferment only 70% of the reducing sugars in the hydrolyzate. The remaining 30% of the sugars (xylose and cellobiose) are fed to an

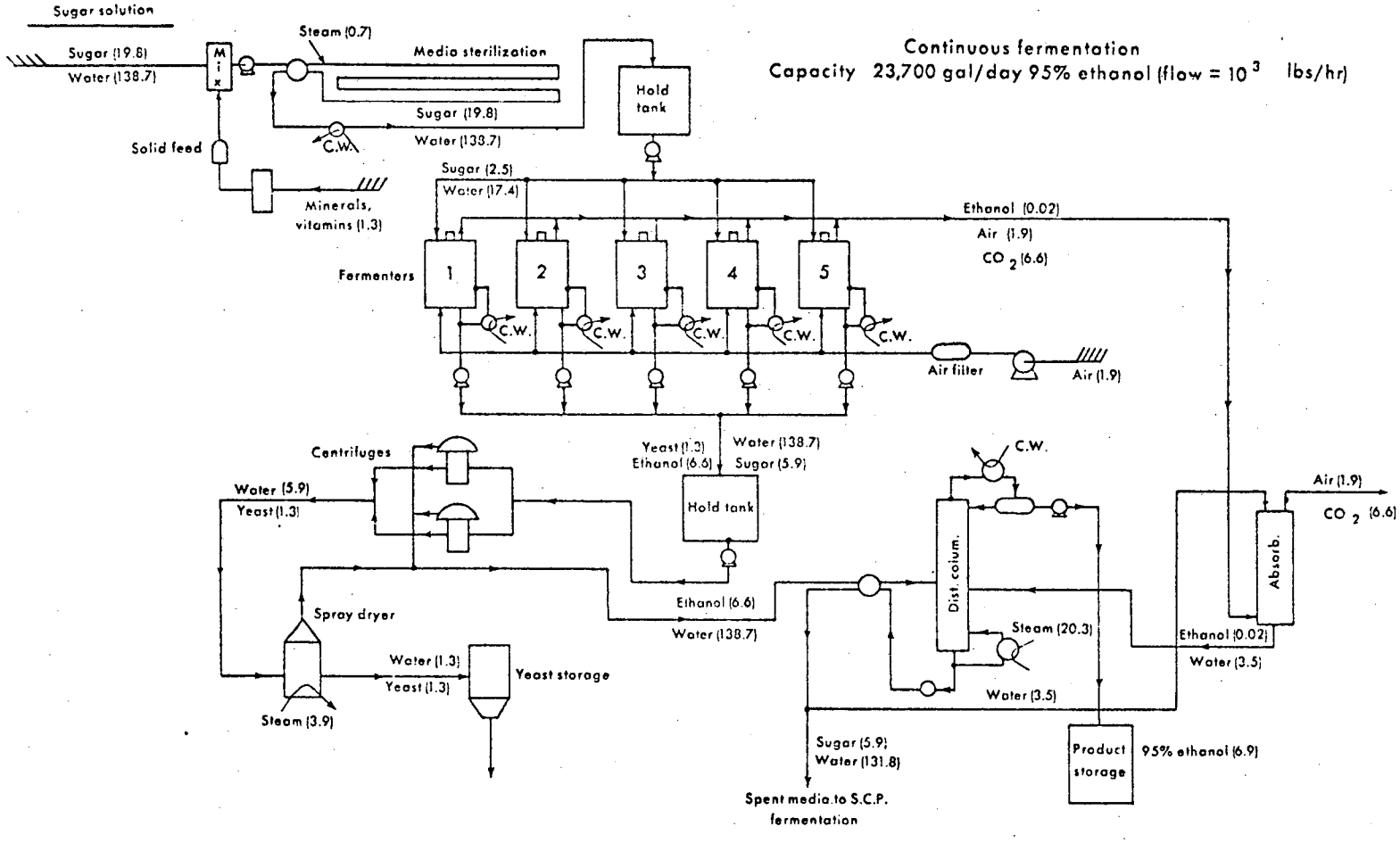

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Figure 10. Flow Diagram for Ethanol Production.

aerobic fermentation process to produce single cell protein from Torula yeast. Although Torula yeasts will ferment the remaining sugars, it is a facultative aerobe and does not produce ethanol.

The single cell protein fermentation, although not shown, resembles the alcohol fermentation process excluding the distillation and absorption columns. Of course the aeration and agitation rates are much higher for the production of cell mass. Also the fermenters were operated at a total pressure of 2.6 atm to enhance the oxygen transfer.* After the yeast has been removed from the broth by centrifugation, the yeast stream is spray dried and packaged for sale.

II. Cost Estimation

A preliminary cost estimate was made for the above mentioned ethanol and SCP fermentation processes to determine the required capital investment and cost per gallon of 95% ethanol (25).

The sugar cost was taken at a base cost of 5.2¢/lb as presented above. The steam and power costs were estimated assuming that they would be generated using spent solids from the hydrolysis process as fuel (26).

The fixed capital costs for the overall process are shown in Table 11. A total fixed capital of $\$5.37 \times 10^6$ is required to produce 24,000 gal/day of 95% ethanol from the hydrolyzate sugars. A breakdown of ethanol production costs is shown in Table 12. Of the \$1.05/gal production cost 68.6% is related to the sugar cost of 5.2¢/lb.

*These conditions were found to be optimal for the SCP fermentation from a computer model of the fermentation process.

The importance of sugar cost in the SCP fermentation is shown in Table 13. The sugar cost amounts to 39% of the yeast production cost of 30.0¢/lb. A somewhat heavy charge is made for nutrient supplements in the SCP process. The nutrient requirement was based on the yeast cell mass composition assuming no vitamin or protein components are in the hydrolyzate sugars. These media supplement costs would be reduced if agricultural or municipal wastes, which contain many vitamins and minerals, were hydrolyzed instead of the newsprint used in the base design case.

The above costs for ethanol and SCP should be considered within the context of the particular cellulose processing scheme, of which they would be a part. Such an analysis is presented elsewhere (26), in which alcohol is taken as the primary product resulting from enzymatic hydrolysis of newsprint, and cost credits are estimated for by-product yeast and electrical power.

Discussion

The processing methods and economic analyses reviewed above suggest that plant biomass can be an improtant source of chemicals and energy through utilization of carbohydrates. Cellulose may be hydrolyzed by acids or by enzymes at which seem to be approximately comparable costs based on current knowledge. The enzymatic route offers the advantage of operating under mild conditions without production of toxic by-products. Also, the enzymatic method is in a relatively earlier stage of development in which further process improvements are likely to be forthcoming. Choice of hydrolysis method may depend ultimately upon the uses intended for the product.

Further research and development studies are needed to confirm the many assumptions made in the present design concepts and to improve the current technology. Development of larger less expensive fermentation equipment than that presently used will be required for the immense scale of operation which biomass processing would involve. Maximum utilization of by-products will be necessary. Finally, consideration must be given to low cost sources of biomass including utilization of solid wastes and coordination of cellulose processing with agricultural operations and food production.

Acknowledgment

Portions of this paper are based on a program of studies of "Cellulose as a Chemical and Energy Resource" conducted at the Lawrence Berkeley Laboratory under the auspices of the Energy Research and Development Agency and the National Science Foundation.

TABLE 1

	10^6 TON/YR	HEXOSANS	PENTOSANS	LIGNIN
BARLEY STRAW	2.5	39	19	14
CORN STOVER	1.0	35	15	15
RICE STRAW	1.6	39	17	10
SORGHUM STRAW	0.7	33	18	14
WHEAT STRAW	2.4	34	17	13

% CARBOHYDRATE IN AGRICULTURAL RESIDUES
AND CALIFORNIA PRODUCTION

TABLE 2

	1945	1976
CHEMICALS	3.9	14.7
LABOR	4.0	15.1
OTHER OPERATING COSTS	3.7	14.0
AMORTIZATION (7 YEARS)	6.4	38.4
INTEREST (3%, 1945-8%, 1976)	1.3	13.1
TOTAL COST ¢/GALLON	19.3	95.3

PROCESSING COST FOR 95% ETHANOL BY ACID HYDROLYSIS
OF DOUGLAS FIR CHIPS (EXCLUSIVE OF RAW MATERIAL).

TABLE 3

MATERIAL	FPA	% ESTIMATED CONVERSION OF α CELLULOSE	% CONVERSION OF TOTAL SAMPLE	INVESTIGATORS
CORRUGATED FIBERBOARD (MULCHER 1-3CM)	4.5	73	55	MANDELS, ET AL.(29)
NEWSPAPER (MULCHER 1-3 CM)	4.5	74	42	MANDELS, ET AL.(29)
COMPUTER PRINT-OUT (HAMMER MILL)	4.5	73	51	MANDELS, ET AL.(29)
KEY PUNCH HOLES (KEY PUNCH 1MM)	4.5	80	56	MANDELS, ET AL.(29)
NEWSPRINT (WILEY MILL-20 MESH)	3.5	50	31	WILKE & YANG (13)

Representative Conversion of Materials by Enzymatic Hydrolysis

TABLE 4

	ORIGINAL STRAW	1% ACID EXTRACT	ENZYMATIC HYDROLYSIS ORIG. STRAW	ENZYMATIC HYDROLYSIS ACID RESIDUE	ENZYMATIC HYDROLYSIS NaOH TREATMENT OF ACID RESIDUE
GLUCOSE	35.6	0.1	8.9	12.5	14.6
XYLOSE	16.8	11.8	1.3	1.0	2.8
OTHER CH_2O	5.9	5.6	0.9	1.3	3.5
SOLIDS TREATED PER GM GLUCOSE	N/A	N/A	11.2	5.0	3.2
	BASIS: GM PER 100 GM DRY STRAW				

POTENTIAL CARBOHYDRATE FROM WHEAT STRAW

TABLE 5

FEED (-20 MESH NEWSPRINT)	885 TON/DAY
CELLULOSE CONTENT[1]	61% (DRY)
ENZYME ACTIVITY	3.5 FPA
CELLULOSE HYDROLYSIS	50%, 40 HR., 45°C
ENZYME RECOVERY	34%
PRODUCT (AS GLUCOSE)[2]	238 TON/DAY
PRODUCT CONCENTRATION	4%
CELL RECYCLE FRACTION	0.65

BASE DESIGN CASE SPECIFICATION

1. Assumed newsprint composition: 61% α cellulose, 21% lignin and 16% hemicellulose

2. Representative sugar composition: 72% glucose, 22% cellobiose, 4.4% xylose, 1.5% mannose.

Table 6

	HYDROLYSIS	PRETREATMENT	ENZYME RECOVERY	ENZYME MAKE-UP	TOTAL
FIXED CAPITAL COST, $	6,200,960	2,816,130	2,060,410	12,309,260	23,386,760
Annual investment related costs, $	1,482,030	673,060	492,440	2,941,910	5,589,440
Annual labor related costs, $	122,990	61,500	122,990	122,990	430,470
Annual utilities costs, $	239,415	132,290	26,560	446,850	845,115
Annual raw materials costs, $	--	--	--	1,312,190	1,312,190
ANNUAL MANUFACTURING COSTS,$	1,844,435	866,850	641,990	4,823,940	
DAILY MANUFACTURING COST, $	5,589	2,626	1,945	14,618	24,778
SUGARS COST, ¢/lb.	1.17	0.55	0.41	3.07	5.2

Process Cost Analysis--Base Case. Raw Material (Newsprint) Cost Excluded.

TABLE 7

	¢/LB SUGARS	PERCENT OF TOTAL
INVESTMENT RELATED	3.558	68.5
LABOR RELATED	0.274	5.2
UTILITIES	0.538	10.3
RAW MATERIALS	0.835	16.0
TOTAL	5.205	100

PROCESSING COST DISTRIBUTION--BASE CASE

TABLE 8A

	¢/LB XYLOSE	PERCENT OF TOTAL
CAPITAL BASED	1.5	49
LABOR BASED	0.1	5
UTILITIES	0.6	19
CHEMICALS	0.8	27
TOTAL	3.0	100

XYLOSE PRODUCTION COSTS

TABLE 8B

	¢/LB GLUCOSE	PERCENT OF TOTAL
CAPITAL BASED	7.0	68
LABOR BASED	0.5	5
UTILITIES	1.1	10
CHEMICALS	1.7	17
TOTAL	10.3	100

GLUCOSE PRODUCTION COSTS

TABLE 9

	TON/DAY	¢/LB	LB/TON
GLUCOSE	126	--	175
POLYMERIC GLUCOSE	48	--	67
OTHER HEXOSE	4	--	6
XYLOSE	170	--	236
ARABINOSE	28	--	39
TOTAL	376	4.5	523

SUGARS PRODUCED FROM 1439 TON/DAY WHEAT STRAW

TABLE 10

SUGAR CONCENTRATION	14.3%, 70% FERMENTABLE
DILUTION RATE	0.17
TEMPERATURE	35°C
CELL YIELD FACTOR, Y(X/S)	0.1
ETHANOL YIELD FACTOR, Y(P/S)	0.465

ETHANOL FERMENTATION DESIGN BASIS

TABLE 11

	10^6	% OF TOTAL
SUGAR CONCENTRATION	0.58	10.8
ALCOHOL FERMENTATION	2.36	43.9
DISTILLATION	0.39	7.3
SCP FERMENTATION	2.04	3.80
TOTAL	5.37	100

CAPITAL INVESTMENT SUMMARY

TABLE 12

	¢/GAL 95% ETOH	PERCENT OF TOTAL
SUGAR CONCENTRATION	2.7	2.6
FERMENTATION	5.4	5.1
DISTILLATION	2.5	2.4
YEAST RECOVERY	1.0	1.0
RAW MATERIALS	21.4	18.3
SUGAR	72.2	68.6
TOTAL	105.2	100

PROCESSING COST DISTRIBUTION--ETHANOL PRODUCTION

TABLE 13

	¢/LB YEAST	PERCENT OF TOTAL
INVESTMENT RELATED	1.6	5.3
LABOR RELATED	0.3	1.0
UTILITIES	0.9	3.1
RAW MATERIALS	15.5	51.6
SUGAR COSTS	11.7	39.0
TOTAL	30.0	100

PROCESSING COST DISTRIBUTION--SCP FERMENTATION

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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