

# Lawrence Berkeley National Laboratory

## Lawrence Berkeley National Laboratory

### **Title**

RAW MATERIALS EVALUATION AND PROCESS DEVELOPMENT STUDIES FOR CONVERSION OF BIOMASS TO SUGARS AND ETHANOL

### **Permalink**

<https://escholarship.org/uc/item/6k92q8gw>

### **Author**

Wilke, C.R.

### **Publication Date**

1978-06-01

To be presented at the Second Annual Symposium  
on Fuels from Biomass. DOE meeting, Troy, New York  
June 20-22, 1978

LBL-7847

c.2

RAW MATERIALS EVALUATION AND PROCESS DEVELOPMENT STUDIES  
FOR CONVERSION OF BIOMASS TO SUGARS AND ETHANOL

C. R. Wilke, R. D. Yang, A. S. Sciamanna and R. P. Freitas

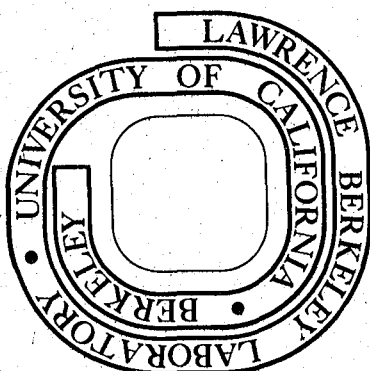
June 1978

RECEIVED  
LAWRENCE  
BERKELEY LABORATORY.

AUG 14 1978

LIBRARY AND  
DOCUMENTS SECTION

Prepared for the U. S. Department of Energy  
under Contract W-7405-ENG-48



TWO-WEEK LOAN COPY

This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 6782

LBL-7847  
c.2

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

RAW MATERIALS EVALUATION AND PROCESS DEVELOPMENT STUDIES  
FOR CONVERSION OF BIOMASS TO SUGARS AND ETHANOL\*

by

C.R. Wilke  
R.D. Yang  
A.S. Sciamanna  
R.P. Freitas

Lawrence Berkeley Laboratory  
and  
Department of Chemical Engineering  
University of California  
Berkeley, California 94720

ABSTRACT

A range of cellulosic raw materials in the form of agricultural crop residue was analyzed for chemical composition and assessed for potential yields of sugars through chemical pretreatment and enzymatic hydrolysis of these materials. Corn stover was used as a representative raw material for a preliminary process design and economic assessment of the production of sugars and ethanol. With the process as presently developed, 23 gallons of ethanol can be obtained per ton of corn stover at a processing cost of about \$1.80 per gallon exclusive of by-product credits.

The analysis shows the cost of ethanol to be highly dependent upon (1) the cost of the biomass, (2) the extent of conversion to glucose, (3) enzyme recovery and production cost and (4) potential utilization of xylose. Significant cost reduction appears possible through further research in these directions.

---

\*This paper was prepared for presentation at the Second Annual Symposium on Fuels from Biomass, Rensselaer Polytechnic Institute, Troy, New York, June 20-22, 1978.

---

This work was done with support from the Department of Energy. Any conclusions or opinion expressed in this report represent solely those of the author(s) and not necessarily those of the Lawrence Berkeley Laboratory nor of the Department of Energy.

## INTRODUCTION

Tentative processing schemes for enzymatic hydrolysis of cellulose and fermentation of sugars to ethanol have been presented by Wilke, Yang and von Stockar (1) and Cysewski and Wilke (2). In these process development studies, newsprint has been selected as a representative cellulosic substrate because of availability of information on its composition and related processing characteristics. Recently, however, other cellulosic materials, in the form of agricultural and forest biomass have received increased attention because of their availability in large quantities.

This paper will present a preliminary process design and economic assessment of the production of sugars and ethanol from a typical agricultural residue, corn stover, based on laboratory data for acid pretreatment and enzymatic hydrolysis of the material.

This study is intended to provide a preliminary assessment of the economic feasibility and to identify areas for possible process improvement through further research.

## ANALYSIS AND EVALUATION OF POTENTIAL RAW MATERIALS

A range of candidate cellulosic raw materials, mainly in the form of agricultural residues has been analyzed for chemical composition and assessed for potential yields of sugars through chemical pretreatment and enzymatic hydrolysis of these materials.

### Chemical Analysis

The approximate compositions of certain agricultural crop residues generated in California are given in Table 1. The percentage of the solids totaled to less than 100% since not all components were assayed, including protein and sugar derivatives. Also the ash content measurement suffers from inaccuracies due to oxidation and loss of volatile inorganics at 600°C. Detailed procedures for the analyses are

TABLE 1  
ASSAY OF RESIDUES IN WT%<sup>(c)</sup>

MATERIAL (A)	HEXOSANS			PENTOSANS		LIGN	ASH	AZEOT. BZ/ETOH EXT.	ACID INSOL.	OTHER
	(B) GLUC	MANN	GALAC	XYL	ARAB					
BARLEY STRAW	37.5	1.26	1.71	15.0	3.96	13.8	10.8	9.7	2(±1)	
CORN STOVER	35.1	0.25	0.75	13.0	2.8	15.1	4.3	5.5	1(±1)	4 PROTEIN
RICE STRAW	36.9	1.6	0.4	13.0	4.0	9.9	12.4	4.4	2(±1)	
SORGHUM STRAW	32.5	0.8	0.2	15.0	3.0	14.5	10.1	6.2	1(±1)	1 PROTEIN
WHEAT STRAW	32.9	0.72	2.16	16.9	2.1	14.5	9.6	7.2	3(±1)	3 PROTEIN

(A) 2MM WILEY MILLED, 40-60 MESH FRACTION, AND 100% DRY.

(B) GLUC = GLUCAN, MANN = MANNAN, GALAC = GALACTAN, XYL = XYLAN, ARAB = ARABINAN, LIGN = LIGNIN, AZEOTROPIC BENZENE ALCOHOL EXTRACTIVES, ACID INSOLUBLE MATERIAL

(C) AVERAGE OF 3-5, DET'M.

described elsewhere (3). The general scheme is shown in Fig. 1. Solid materials are first ground or milled to a suitable size. Then they are analyzed for ash, determined as the residue after ignition at 600°C, for extractives, defined as the material removed by extraction with the benzene/ethanol azeotrope; for lignin, the organic residue after a two-stage hydrolysis in 72 w/w% and 4 w/w% H<sub>2</sub>SO<sub>4</sub>; and for carbohydrates.

The carbohydrate content is determined as the monomer sugars generated by exhaustive hydrolysis of the solid, as measured by the glucose oxidase-peroxidase and gas chromatographic methods. The content of each monomer is then converted to the weight of the sugar in the polymerized form.

Liquors, such as those generated by the acid or base treatments of cellulosic materials or enzymatic hydrolyses of same, are analyzed as follows: the monomer sugar content is measured by the glucose oxidase-peroxidase and gas chromatography methods. Each liquor is then exhaustively hydrolyzed in 4 w/w% H<sub>2</sub>SO<sub>4</sub>. By this procedure, all polymerized sugar is hydrolyzed to monomer form. The resultant increase in monomer sugar content is labelled as polymerized sugar.

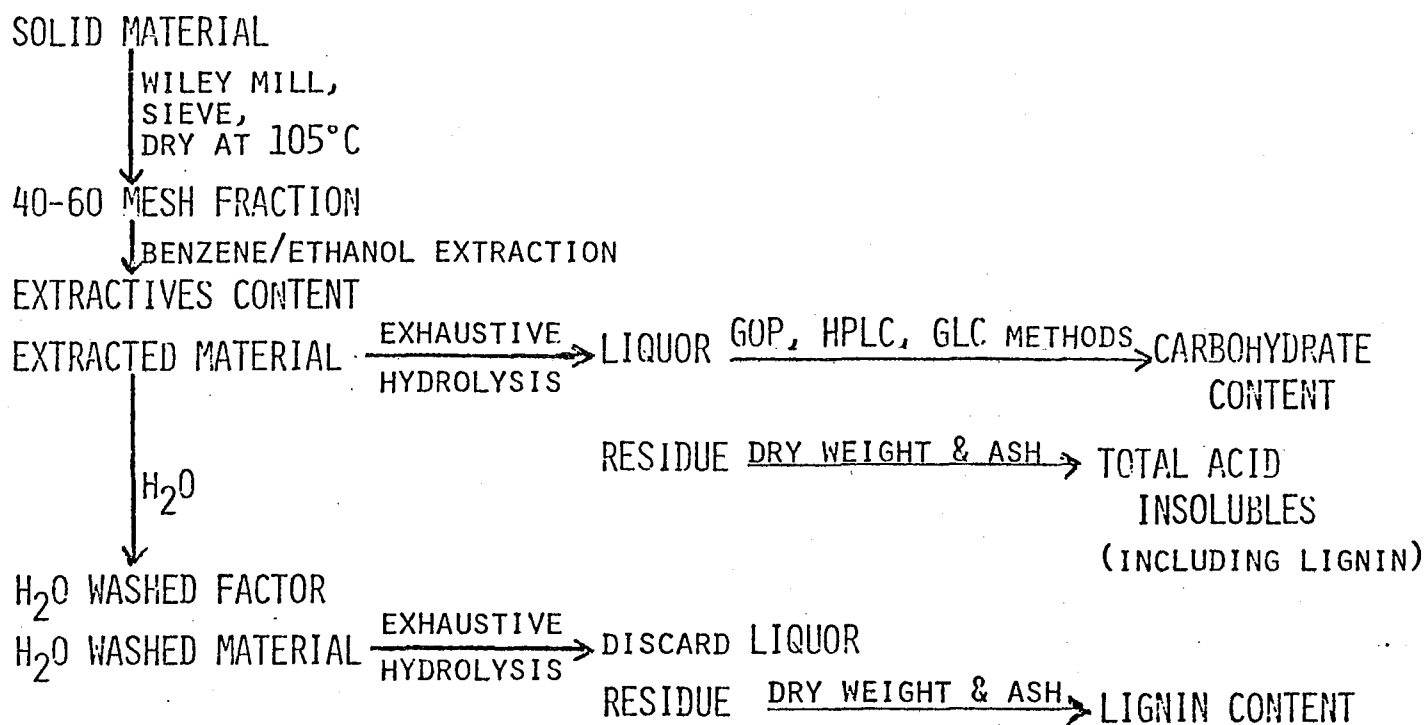
#### Acid Extraction and Enzymatic Hydrolysis of Raw Materials

Sugar yields by the direct enzymatic hydrolysis of the above agricultural residues are generally very low, ranging from 18% to 34% based on the original carbohydrate content. A series of chemical pretreatment were studied to see if sugar production might be improved (4). The results of these studies showed that pretreatment with dilute sulfuric acid extracted pentose sugars and improved glucose yield in the subsequent enzymatic hydrolysis. Carbohydrate yields obtained in this manner are summarized in Table 2. Notice that the 0.9% acid extraction converts 40-80% of the pentosans to pentoses. Yields of hexoses in the subsequent enzymatic hydrolysis increase approximately 20-70% over the hydrolysis without the acid pretreatment.

Figure 1

---

SCHEME OF SOLIDS ANALYSIS



SCHEME OF LIQUORS ANALYSIS

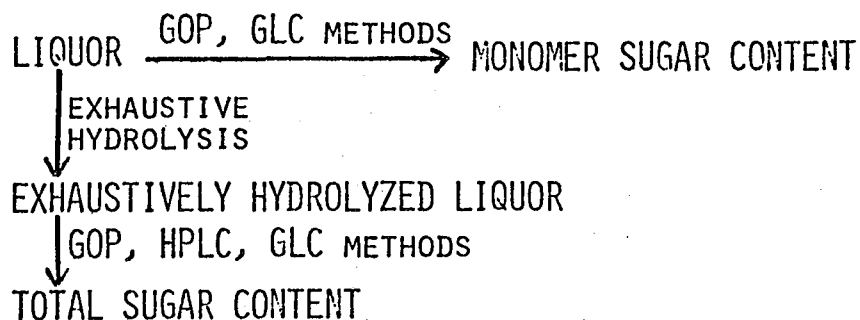




TABLE 2  
CARBOHYDRATE YIELD DATA

MATERIAL	0.9% ACID EXTRACT			ENZYMATIC HYDROLYSIS OF ACID RESIDUE		
	HEXOSES	PENTOSES	% CONVERSION TO PENTOSES	HEXOSES	PENTOSES	% CONVERSION TO HEXOSES
BRALEY STRAW	3.2	8.3	40	13.5	0.4	31
CORN STOVER	2.9	14.6	81	16.8	0.9	42
RICE STRAW	3.8	13.7	73	21.1	1.1	49
SORGHUM STRAW	2.6	9.9	50	15.0	1.0	41
WHEAT STRAW	3.7	12.9	62	13.7	2.5	35

As seen from Table 2, corn stover seems to be a suitable representative residue for further economic analysis for the production of sugars and ethanol. A laboratory corn stover processing scheme showing more detailed compositions and carbohydrate yields is given in Fig. 2. In addition to higher sugar yields obtained with acid pretreatment, as mentioned above, another advantage in terms of processing costs is that the solid processed (in the enzymatic hydrolysis section) per gram glucose produced is greatly reduced.

#### PROCESS DESCRIPTION

Figure 3 is a schematic flow diagram for the corn stover processing plant. Mass flows of the principal streams are indicated on the diagram.

##### Hydrolysis

The hydrolysis process is identical in concept to that described by Wilke, Yang and von Stockar except for the incorporation of acid pretreatment to the process (1). Table 3 gives the base case design specification.

The primary plant feed consists of 1376 tons per day of corn stover containing 6% moisture. By means of moderate shredding and hammermilling the feed is reduced to approximately -10 mesh. The size reduction is not critical so long as the material will form aqueous suspensions which can be pumped, agitated and filtered.

The milled stover is fed to the acid extraction section. Five extraction stages in series are employed with each stage consisting of an agitated stainless steel vessel providing a residence time of 1.1 hours. The extraction stages are maintained at 100°C by internal coils. In the first stage, a solid suspension of 7.5 % is employed based on the entering streams. Acid strength is maintained at 0.09 M by addition of make-up  $H_2SO_4$ . Effluent from the last stage is filtered on vacuum belt filter and a 50% of the filtrate is recycled to the first stage resulting in a new product stream containing 1.5% xylose. Yields of xylose and other sugars in the acid extract stream are assumed 75% of that obtainable

UCD CORN STOVER  
2 MM WILEY MILLED

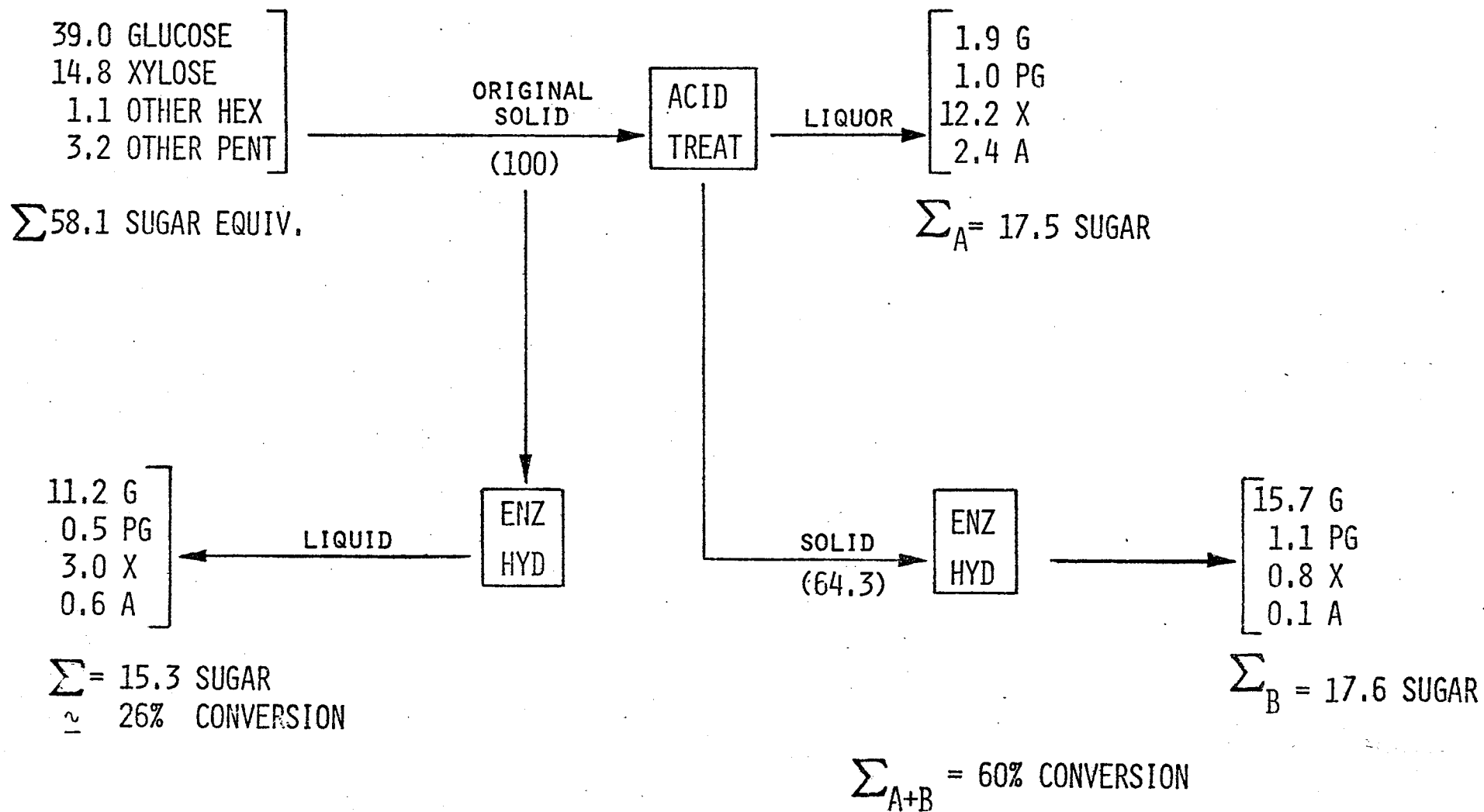


Figure 2. Schematic Diagram for the Laboratory Processing of Corn Stover.

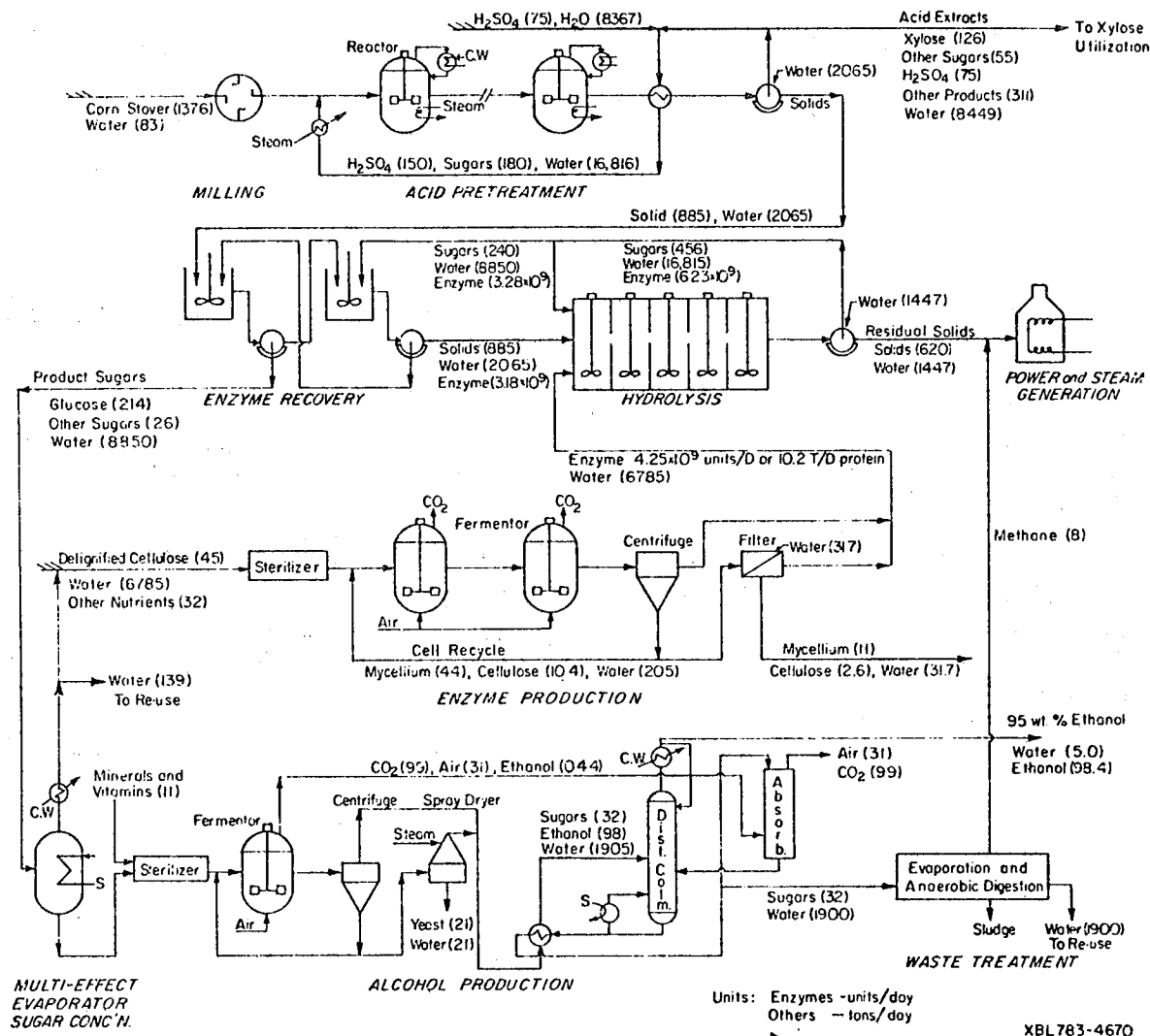


Figure 3. Material Balance Flow Diagram for Integrated Processing Scheme.

Table 3

ACID PRETREATMENT AND ENZYMATIC HYDROLYSIS OF STOVER  
BASE DESIGN CASE SPECIFICATION

---

FEED (2MM CORN STOVER)	1376 T/D
CARBOHYDRATE CONTENT	58%
ACID PRETREATMENT	0.09 M H <sub>2</sub> SO <sub>4</sub> , 7.5% SUSP. 100°C, 5.5 HR.
ACID EXTRACTS (70% XYLOSE)	181 T/D, SUGAR/ACID = 2.4
SOLIDS	885 T/D
ENZYMATIC HYDROLYSIS	3.5 FPA (0.61 U/ML, 5% SUSP. 45°C, 40 HR.
ENZYME RECOVERY	58%
ENZYME PRODUCTIVITY	0.46 U/(ML-DAY), CELL = 7 GM/L
CELLULOSE CONVERSION	40% TO GLUCOSE
HYDROLYZATE (90% GLUCOSE)	240 T/D, GLUCOSE/ENZYME = 21
SUGAR SOLUTION	2.6%

---

with no acid recycle. The cause of this yield reduction due to acid recycle is not known yet pending on further study. The sugar solution in the acid extract stream may be neutralized with lime for subsequent use as a fermentation substrate, although no further processing is assumed under this scheme.

The washed solids from the acid extraction section containing a small quantity of acid are contacted countercurrently in two mixer-filter stages with the product sugar stream from the hydrolyzer 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 97% is predicted by theory based on an adsorption distribution coefficient of 0.01 (FP units/ml soln.)/(FP units/gm stover) obtained for the corn stover.

Hydrolysis is conducted over 40 hours at 45°C at a solid suspension of 5 wt% based on inputs to the hydrolyzer. The latter consists of 5 agitated cylindrical digesters of the type used for solid waste treatment in sanitary engineering. Cellulose conversion of 40% to glucose is assumed based on the original glucose equivalent content of the stover. Enzyme strength is maintained at 3.5 Filter Paper Activity ((FPA) based on inlet streams by addition of a make-up enzyme solution from the enzyme production section. Provision is made for the recycle of a portion of the product solution (plus enzyme) back to the hydrolysis vessel. A sugar concentration of 2.6% is obtained for the case shown. A range of sugar levels is possible depending on the mode of operation and amount of recycle employed.

Make-up enzyme is produced based on our recent experimental results of two-stage cell recycle fermentation systems, employing the fungus Trichoderma viride QM 9414. The design basis is given in Table 4. (14)

The enzyme production is carried out in four lines of two fermentors connected in series. The system is operated at an overall dilution rate of  $0.027 \text{ hr}^{-1}$ , excluding the cell recycle stream. Both stages employ agitated stainless steel

Table 4

TWO-STAGE CONTINUOUS CELLULASE PRODUCTION WITH  
CELL RECYCLE DESIGN BASIS

---

INLET CELLULOSE CONCENTRATION	6.5 G/L
TEMPERATURE (BOTH STAGES)	30°C
pH (BOTH STAGES)	4.8
SEPCIFIC GROWTH RATE	0.06 HR <sup>-1</sup>
CELL RECYCLE RATIO	0.8
AVG. CELL CONCENTRATION	7 G/L
DILUTION RATE	0.027 HR <sup>-1</sup>
ENZYME CONCENTRATION	3.9 FPA (0.7 U/ML)
ENZYME PRODUCTIVITY	0.46 U/ML-DAY
CELL YIELD (MYCELIUM/CELLULOSE)	0.26
ENZYME YIELD (PROTEIN/CELLULOSE)	0.24

---

vessels operated at 30°C, pH 4.8 with aeration rates of 0.05 V.V.M. for both stages. The media containing delignified cellulose and other nutrients are sterilized and fed to the first stage. The effluent from the second stage is passed through a centrifuge from which a portion of the underflow is fed back to the first stage. The flow quantities in Fig. 2 corresponds to a cell recycle fraction of 0.8. Recycle fraction is the fraction of cells leaving the 2nd stage which is returned to the first stage. For the case shown, the use of recycle will maintain the average cell density in the system at 7 gm per liter, assuming a specific growth rate of  $0.006 \text{ hr}^{-1}$ . 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 removed 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.

#### Ethanol Fermentation

Ethanol fermentation process is similar to that described by Cysewski and Wilke (2) with the additional feature of employment of cell recycle. The design basis of the fermentation process is shown in Table 5.

Sugar concentration from the hydrolyzer is concentrated from 2.6% to 11% in a seven effect evaporator. Protein and mineral supplements mixed with the sugars are sterilized and distributed to two continuous fermentors, operating at a dilution rate of  $0.7 \text{ hr}^{-1}$ . A low flow of air ( $8.0 \times 10^{-4}$  V.V.M.) is sparged through the fermentors to maintain the oxygen tension at the optimum level of 0.07 mmHg (5). The fermented beer then passes to five continuous centrifuges and a portion of cell concentrate from the centrifuge is returned to the fermentors.



Table 5

CONTINUOUS ETHANOL FERMENTATION  
WITH CELL RECYCLE DESIGN BASIS

---

SUGAR CONCENTRATION	11.2%	90% FERMENTABLE
DILUTION RATE	0.7 HR <sup>-1</sup>	
TEMPERATURE	35°C	
CELL YIELD FACTOR, $Y_{x/s}$	0.10	
ETHANOL YIELD FACTOR $Y_{p/s}$	0.46	
CELL CONCENTRATION IN FERMENTOR	50 G. DRY WT/L	

---

This increases the cell mass concentration in the fermentors permitting a high volumetric ethanol productivity. The other portions of cell concentrate removed is subsequently dried and stored for sale as a protein feed supplement. The 4.9 per cent ethanol solution from the centrifuges plus the aqueous stream contained the ethanol removed from the carbon dioxide by an absorber are concentrated by distillation to produce 103 tons per day of 95 wt% ethanol equivalent to 23 gallons per ton of plant feed.

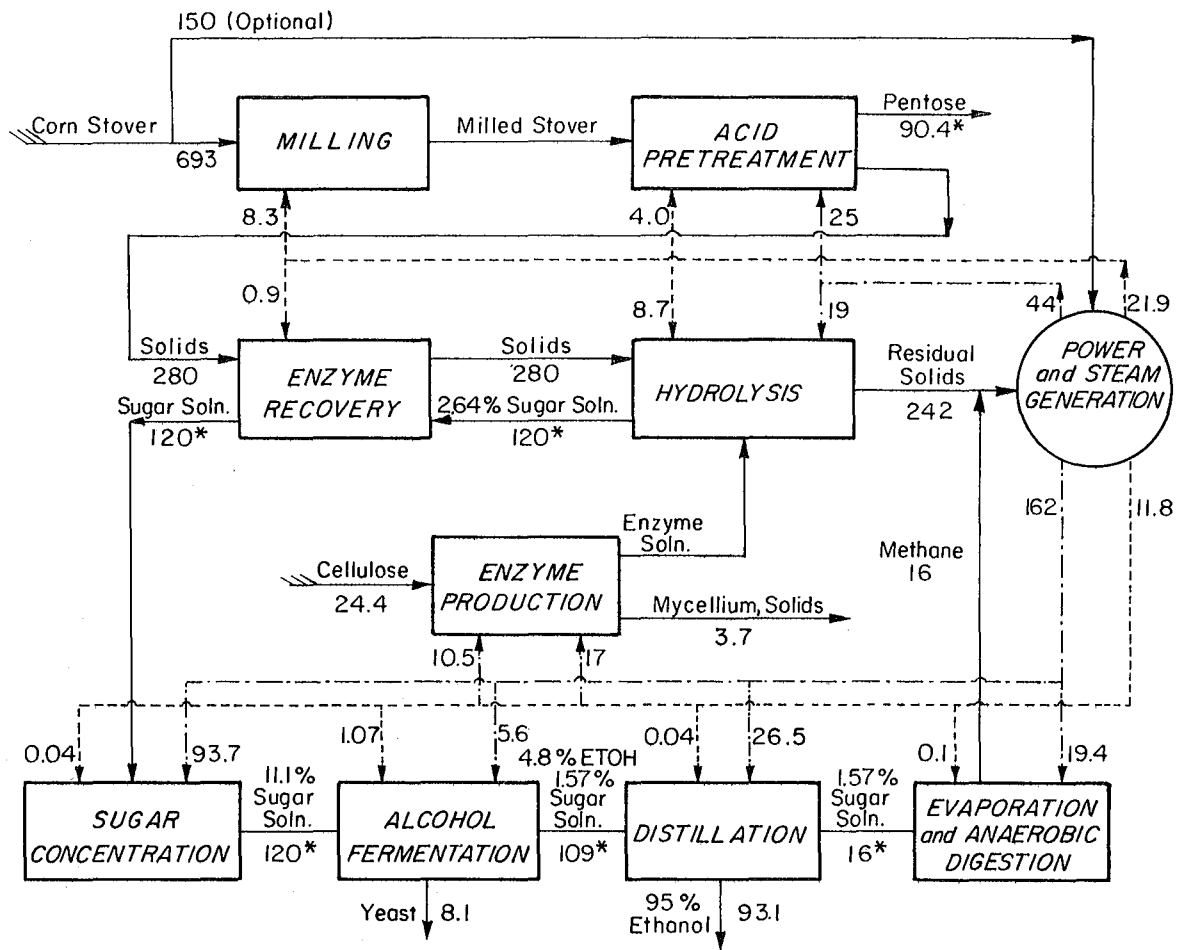
#### Methane Generation

Following yeast removal, the bottom stream from the ethanol distillation containing cellobiose, pentose and residual glucose at 1.7% is concentrated to 7.4% and sent to the anaerobic digestion system for methane generation. Methane gas produced at 384 ft<sup>3</sup>/day is sent to the furnace for process steam generation.

#### Energy Balance

Figure 4 shows the flow of energy among the various processing operations, energy quantities are expressed as heat of combustion of the process streams, except for steam which is expressed as available BTU for process heat exchange (934 BTU/lb) and electrical power which is expressed as KW or as equivalent thermal BTU's.

In contrary to the newsprint conversion case where a net energy is produced (6), the present stover process is not energy self-sufficient. However, approximately 70% of the process energy requirements, in the form of steam, can still be self-generated by using available residual solids from the hydrolyzer and methane gas from the anaerobic digester as fuels. Electricity, under the current process scheme, is assumed brought from a public utility at 3¢/KW-HR. An alternative, however, would be to self-generate the electricity in the field by feeding extra corn stover to the boiler furnace. This would be more economical only if the cost of corn stover is less than \$15. per ton.



Process Energy Flows,  $10^6$  BTU/hr

— Material  
 - - - Steam  
 - - - Power

\* Potential energy content of sugars in the solution

XBL 783-4672

Figure 4. Energy Balance Flow Diagram for Integrated Processing Scheme.

## COST ESTIMATION

For the process described above, a preliminary cost estimate was made for the required fixed capital investment, cost per pound of sugar produced in aqueous solution and cost per gallon of 95% ethanol produced.

The general cost estimation procedure was that recommended by Peters (7), Holland (8), and Guthrie (9).

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 concrete digester for which the multiple was reduced to 1.68 because the unit cost already included engineering construction fees. Estimated costs of the principal equipment items were updated from previous reports (1,2) employing a Marshall and Steven Index of 518 corresponding to the 4th quarter of 1977. The total manufacturing cost is subdivided into capital related costs, labor related costs, utilities costs, and raw materials costs. Multipliers, utility rate and chemicals costs are listed in Table 6-10. A base labor rate of \$5.60 per man-hour and a 8,500 hour year was assumed. Taxes were omitted on the assumption that the plant might be tax-exempt, but the effect of potential taxes is considered separately in a subsequent section of the paper (Table 19). Cost of process steam was estimated on the basis that it could be generated on the plant site using spent solids as fuel. Capital cost for the steam plant is not included in the fixed capital costs on the assumption that the specified unit cost includes both investment and labor charges. An on-stream efficiency of 90% is assumed, corresponding to 330 days operation per calendar year.

### Hydrolysis Process

The resulting fixed capital cost, total manufacturing costs and costs per unit of glucose in the aqueous solution are listed in Table 11 for each of the major processing sections: (1) milling, (2) acid pretreatment, (3) enzyme recovery, (4) hydrolysis, (5) enzyme production.

Table 6

CAPITAL RELATED COST FACTORS  
(ANNUAL COST=FACTOR X FIXED CAPITAL)

ITEM	COST FACTOR
DEPRECIATION	0.10
INTEREST	0.06
MAINTENANCE	0.06
INSURANCE	0.01
PLANT SUPPLIES	0.01
TAXES	0
TOTAL	0.24

Table 7

LABOR RELATED COST FACTORS  
(COST = FACTOR x LABOR COST)

<u>ITEM</u>	<u>COST FACTOR</u>
DIRECT LABOR COST	1.00
SUPERVISION	0.15
PAYROLL OVERHEAD	0.15
LABORATORY	0.15
PLANT OVERHEAD	0.50
TOTAL	1.95

Table 8

## MEDIUM CHEMICALS--ENZYME PRODUCTION

COMPONENT <sup>1</sup>	GM/L	TONS/DAY	\$/TON
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1.4	9.5	65
(NH <sub>4</sub> ) H <sub>2</sub> PO <sub>4</sub> <sup>2</sup>	2.0	13.6	180
CaCl <sub>2</sub>	0.3	2.0	75
MgSO <sub>4</sub>	0.15	1.0	180
(NH <sub>4</sub> ) <sub>2</sub> CO	0.3	2.0	160
PROTEIN NUTRIENT <sup>3</sup>	0.5	3.4	400
DELIGNIFIED CELLULOSE	6.75	4 5	100

<sup>1</sup>TRACE ELEMENTS ARE ASSUMED SUPPLIED BY THE PROCESS WATER.

<sup>2</sup>SUBSTITUTE FOR KH<sub>2</sub>PO<sub>4</sub>

<sup>3</sup>PHARMAMEDIA, TRADERS PROTEIN CORP., FT. WORTH, TEXAS

Table 9

## MEDIUM CHEMICALS--ETHANOL FERMENTATION

COMPONENT <sup>1</sup>	GM/L	TONS/DAY	\$/TON
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1.86	3.95	65
MgSO <sub>4</sub>	0.08	0.17	180
CaCl <sub>2</sub>	0.08	0.18	75
PROTEIN NUTRIENT <sup>2</sup>	2.86	6.08	1050

<sup>1</sup>TRACE ELEMENTS ARE ASSUMED SUPPLIED BY PROCESS WATER

<sup>2</sup>AMBER BYF-300 AMBER LABORATORIES, JUNEAU, WISCONSIN



Table 10

## BASE UTILITY RATE

	UNIT	UNIT COST	UNIT HR.
POWER	KW-HR.	3¢**	9875
STEAM	1000 LB.	32.5¢*	206
WATER	1000 GAL.	12.8¢	196

\* SELF GENERATED FROM RESIDUAL SOLIDS

\*\* BOUGHT FROM PUBLIC UTILITY

Table 11

	MILLING	ACID PRETREATMENT	HYDROLYSIS	ENZYME RECOVERY	ENZYME MAKE-UP	TOTAL
Fixed Capital Cost x 1000 \$	3,375	5,150	8,684	1,937	10,261	29,407
Annual Capital Related Costs x 1000 \$	810	1,236	1,798	465	2,463	6,771
Annual Labor Related Costs X 1000 \$	96	191	191	96	191	768
Annual Utilities Costs X 1000 \$	109	451	657	62	809	2,088
Annual Material Costs X 1000 \$	-	1,238	51	-	3,160	4,452
Annual Manufacture Cost X 1000 \$	1,105	3,116	2,697	623	6,623	14,100
Glucose Cost, ¢/lb	0.72	2.21	1.91	0.44	4.69	10.0

HYDROLYSIS PROCESS COST ANALYSIS--BASE CASE  
RAW MATERIAL (CORN STOVER) COST EXCLUDED

For the base case a fixed capital cost of \$29,500.000 and glucose cost of 10.0¢ per pound are obtained. Enzyme make-up is the major cost factor, comprising about 50% of the total.

Table 12 shows the distribution of costs among several categories for the hydrolysis process. As shown in Table 12, capital related and chemical costs account for about 80% of the overall cost.

Table 13 shows that xylose is produced at 5.1¢ per pound in the acid pre-treatment section. The total sugar production by the overall hydrolysis process is summarized in Table 14.

#### Ethanol Production

The fixed capital cost for the ethanol fermentation process including methane generation are shown in Table 15. A fixed capital of \$7,000.000 is required to produce 31,480 gal/day of 95% ethanol from the hydrolyzate sugars. A breakdown of ethanol production costs is shown in Table 16. Of the \$1.79/gal production cost 75.7% is related to the glucose cost of 10.0¢/lb.

The methane generation facility can be viewed as a means of waste treatment to permit reuse of water in the process. A unit treatment cost of \$14 per 1000 gallons for a scale of 200,000 GPD were updated from estimates by T.G. Shea for treating rum distillery slops by anaerobic digestion (9). In spite of relatively favorable economics of using evaporation and anaerobic digestion compared to other methods given in Table 17, other alternatives should be investigated. These might include evaporation to produce solids for animal feedstuff and the conversion of cellobiose (comprising 50% of the residual sugars) to glucose for ethanol production.

#### Overall Analysis

An overall capital investment for processing 1376 tons/day of stover for the

Table 12

## GLUCOSE PRODUCTION COSTS

---

---

	<u>¢/LB</u> <u>GLUCOSE</u>	<u>PERCENT</u> <u>OF TOTAL</u>
CAPITAL RELATED	4.8	48
LABOR RELATED	0.5	4
UTILITIES	1.5	15
CHEMICALS	<u>3.2</u>	<u>32</u>
TOTAL	10.0	100

---

---

Table 13

## XYLOSE PRODUCTION COSTS

	<u>¢/LB</u> <u>XYLOSE</u>	<u>PERCENT</u> <u>OF TOTAL</u>
CAPITAL RELATED	2.5	49
LABOR RELATED	0.4	8
UTILITIES	0.7	14
CHEMICALS	1.5	29
TOTAL	<u>5.1</u>	<u>100</u>

Table 14

## SUGARS PRODUCED FROM 1376 TONS/DAY CORN STOVER

	<u>TONS/DAY</u>	<u>¢/LB</u>	<u>LB/TON</u>
GLUCOSE	234	-	340
POLYMERIC GLUCOSE	25	-	36
XYLOSE	137	-	199
ARABINOSE	3	-	4
	<u>399</u>	<u>5.4</u>	<u>579</u>

Table 15

## CAPITAL INVESTMENT SUMMARY

	<u>\$ MM</u>	<u>% OF TOTAL</u>
SUGAR CONCENTRATION	0.8	10.5
ALCOHOL FERMENTATION	2.5	32.9
DISTILLATION	0.5	6.6
METHANE PRODUCTION	3.8	50.0
	<u>7.0</u>	<u>100</u>

Table 16

## PROCESSING COST DISTRIBUTION-ETHANOL PRODUCTION

	<u>¢/GAL</u> <u>95% ETOH</u>	<u>PERCENT</u> <u>OF TOTAL</u>
<u>SUGAR CONCENTRATION</u>	5.2	2.9
FERMENTATION	7.6	4.2
DISTILLATION	3.0	1.7
MEDIUM CHEMICALS	21.4	12.0
GLUCOSE	135.9	75.7
METHANE GENERATION	<u>6.3</u>	<u>3.5</u>
	<u>179.4</u>	<u>100.0</u>



Table 17

## COMPARISON OF WASTE TREATMENT SYSTEMS

METHOD	CAPITAL INVESTMENT \$MM	TREATMENT COST PER GAL. ETHANOL ¢	BY-PRODUCT AND ASSUMED MARKET VALUE	NET TREATMENT COST PER GAL. ETHANOL, ¢
ANAEROBIC DIGESTION	10.1	11.6	METHANE GAS 16 MMBTU/HR AT \$2.2/MMBTU	8.9
EVAPORATION FOLLOWED BY ANAEROBIC DIGESTION	3.8	6.4	METHANE GAS 16 MMBTU/HR. AT \$2.2/MMBTU	3.7
TORULA YEAST * PRODUCTION	2.6	22.0	YEAST 14.6T/D AT 15¢/LB	7.0
MUNICIPAL TREATMENT PROCESS	17.7	43.3	NONE	43.3

\* Secondary wastewater treatment is needed to achieve a low terminal BOD

for the production of ethanol and other by-products is \$37,1000,000. Table 18 summarizes the products of the overall process, product costs and estimated value of the by-products. Yeast cake is assumed to be used as a substitute for soybean as an animal feed, although debittered yeast cake may be sold as protein food supplement at a higher price (11). Mycelium is assumed to be used as a cattle feedstuff. On the basis of the assumed by-product credits, analysis indicates that 95% ethanol might be produced for about \$1.60/gal, assuming zero cost for the corn stover.

Table 19 gives the estimated incremental increase in alcohol cost per gallon under economic assumptions more representative of the private economy with respect to interest rates and taxes and with a cost of \$30/per ton for the cellulosic feed. Under these assumptions the cost of ethanol would become about \$3.50/gal.

## DISCUSSION

### Enzyme Recovery

In the base design case considered thus far, 58% enzyme recovery has been assumed based on a preliminary experiment. Subsequent laboratory results on the Filter Paper Activity of hydrolyzate suggests that the percentage of enzyme recovery may actually be smaller. Further experiments are being carried out to obtain a more precise percentage of enzyme recovery based on the actual process scheme. Therefore, ethanol costs have been estimated for a range of enzyme recovery from 20% to 60% as shown in Figure 5.

### Fermentability of Enzymatic Hydrolyzate

Preliminary experiments were conducted to determine the fermentability of enzymatic hydrolyzate of corn stover by S. cerevisiae. It was found that the fermentability decreased as the hydrolyzate was concentrated to more than 3-fold by evaporation at 100°C. It was observed, however, that when the hydrolyzate was concentrated by vacuum evaporation glucose was completely fermented. However, a

Table 18

## PRODUCT SUMMARY AND OVERALL COST ANALYSIS

(CORN STOVER FEED--1376 T/D)

	TONS/DAY	PRODUCTION* COSTS	ASSUMED MARKET VALUE	BY-PRODUCT COST CREDIT PER GALLON ETHANOL
ETHANOL (95%)	103	179 ¢/Gal	-	-
XYLOSE	126	-	-	-
OTHER SUGARS	55	-	-	-
CARBON DIOXIDE	132	-	-	-
YEAST CAKE	21	-	10¢/1b (45¢/1b) <sup>1</sup>	13¢(60¢)
MYCELLIUM	11	-	10¢/1b	7¢

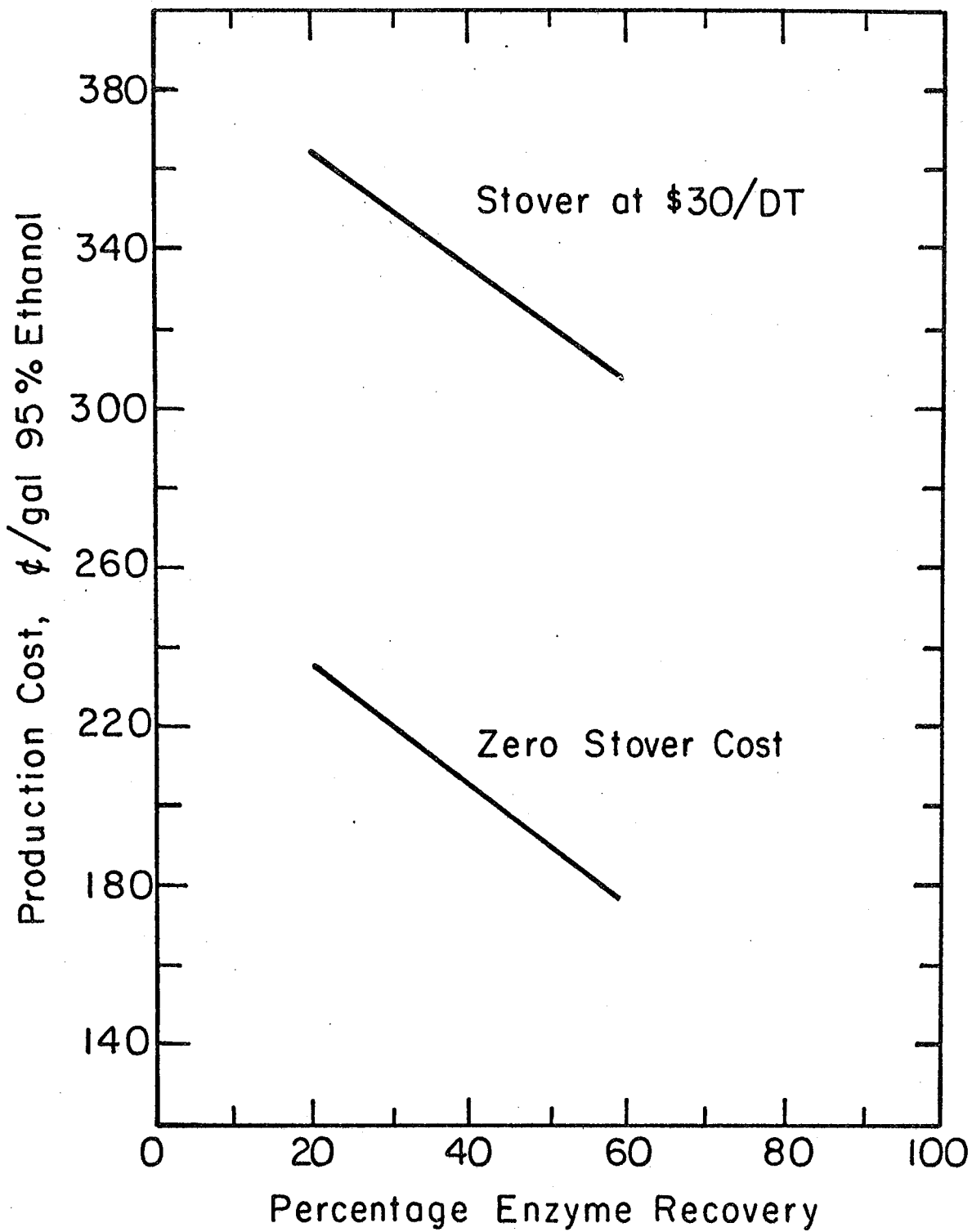
\*EXCLUSIVE OF CORN STOVER COST

1. Used as a protein food supplement

Table 19

## INCREMENTAL EFFECT OF VARIABLES ON PRODUCT COST

<u>VARIABLE</u>	<u>INCREASE OF VARIABLE</u>	<u>¢/GAL. INCREASE OF ETHANOL COST</u>
TAXES	0 TO 3%	9.3
INTEREST	6 TO 12%	18.5
COST OF STOVER	\$30/TON	131.4



XBL785-5094

Figure 5. Effect of Percentage Enzyme Recovery on Ethanol Cost.

somewhat slower rate of fermentation was observed with the glucose in the concentrated hydrolyzate relative to a pure glucose in the defined medium. Preliminary evidences indicate that these decreases in fermentability and rate of fermentation are probably due to inhibition by the increased concentration of some metabolic by-products of T. viride present in the enzyme solution. Further studies are being conducted for identification and elimination of these inhibitory substances.

### CONCLUSIONS

Based on the foregoing analysis the production of ethanol from agricultural residues such as corn stover does not appear economically feasible with the process as developed thus far.

The processing scheme is admittedly inadequate and will be superseded as research continues. Xylose, in the acid hydrolyzate, for example, is not considered for further conversion to either furfural or ethanol because the system for conversion is not yet conclusively established. Studies of the fermentation of xylose by Fusarium oxysporum are in progress (12)(13). Nevertheless, efficient conversion of xylose to ethanol would increase the overall ethanol yield by up to 70%.

Another area for major process improvement is to get a better hydrolysis yield by substrate pretreatment. One of the treatment methods we are studying currently is nitric-oxide treatment in the gas phase at room temperature (13). This method appears to open up the lignin structure and greatly improve subsequent enzymatic hydrolysis.

In connection with product yield, raw material cost is an important factor. The higher the product yield, the lesser contribution of the raw material cost to the product cost as demonstrated in Fig. 6. Each \$10 per ton of stover cost adds 18¢/gal to the ethanol cost assuming a complete cellulose conversion yielding 18% wt of ethanol from stover. An absolute maximum yield of 24 wt% can be obtained assuming a complete conversion of stover to glucose and xylose. In this case, each \$10/ton stover adds 14¢/gal to the ethanol cost. Therefore consideration must be given to lower cost sources of raw materials including utilization of solid waste and coordination of cellulose processing with agricultural operations and food production.

Other anticipated areas of process improvement include development of more effective enzyme systems, of more economic enzyme production and methods for enzyme recovery and reuse.

#### ACKNOWLEDGEMENT

This work is part of a general program on utilization of cellulose as a chemical and energy resource conducted under the auspices of the Department of Energy (DOE).

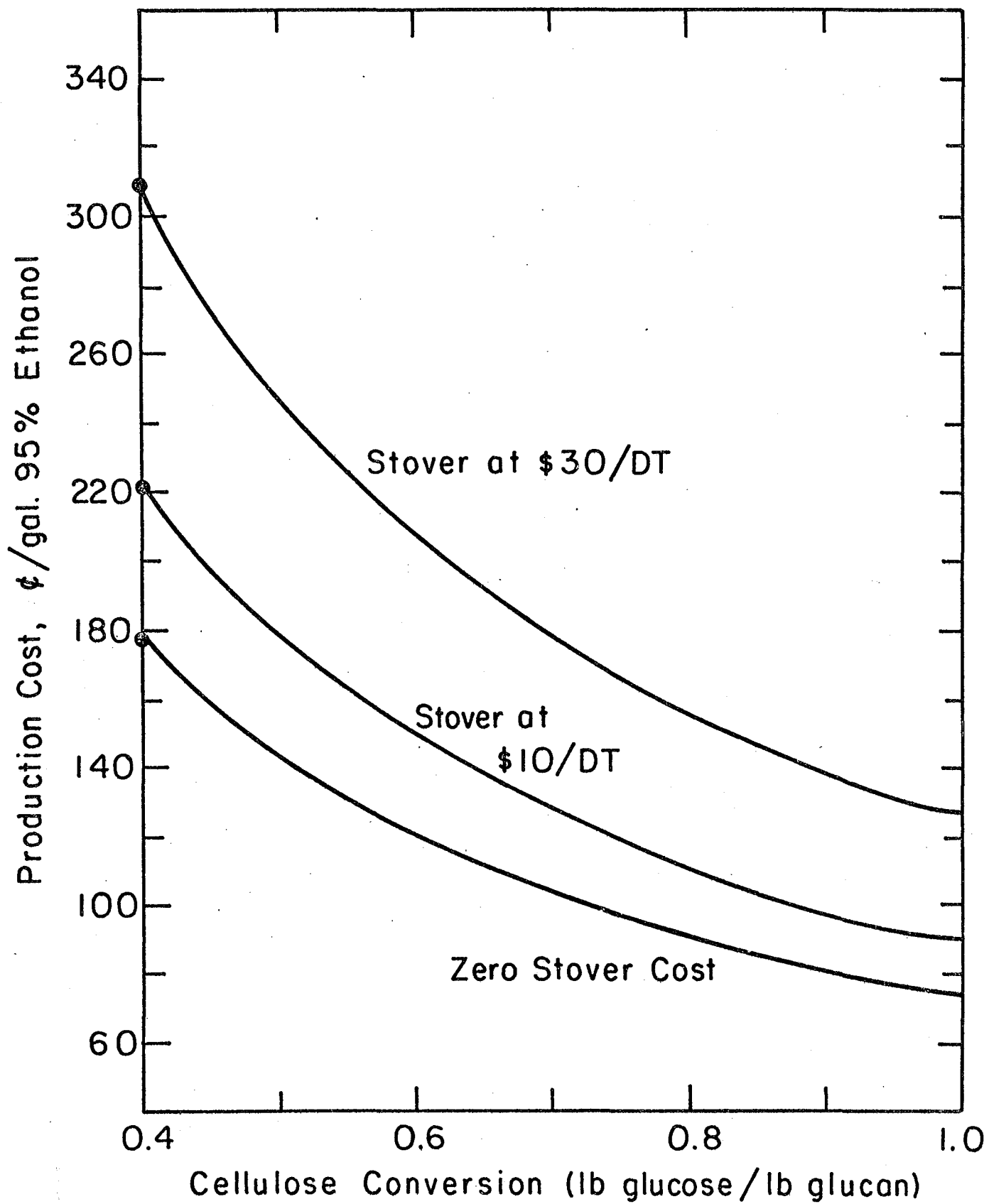


Figure 6. Effect of Cellulose Conversion on Ethanol Cost.

XBL785-5095



References

1. Wilke, Charles R., Ren Der Yang and Urs von Stockar, "Preliminary Cost Analyses for Enzymatic Hydrolysis of Newsprint," *Biotechnol Bioeng. Symp.* No. 6, 155-175 (1976).
2. Cysewski, G. R. and C.R. Wilke, "Utilization of Cellulosic Materials through Enzymatic Hydrolysis, Part. I. "Fermentation of Hydrolyzate to Ethanol and Single Cell Protein," *Biotechnol. and Bioeng.* 18, 1297 (1976).
3. Freitas, Raymond, Bill Long, Aldo Sciamanna and Charles R. Wilke, "Procedures for Analysis of Solids and Liquors from Cellulosic Sources," LBL-5967, 1978.
4. Sciamanna, Aldo, Raymond Freitas and Charles R. Wilke, "Composition and Utilization of Cellulose for Chemicals from Agricultural Residues," LBL 5966 (in press).
5. Cysewski, G.R., C.R. Wilke, "Rapid Ethanol Fermentation Using Vacuum and Cell Recycle," *Biotechnol. Bioeng.* 14, 1125 (1977).
6. Wilke, C.R., G. R. Cysewski, R.D. Yang and U. von Stockar, "Utilization of Cellulosic Materials through Enzymatic Hydrolysis, Part II. "Preliminary Assessment of an Integrated Processing Scheme," 18, 1315-1323 (1976).
7. Peters, J.S. and K.D. Timmerhaus, "Plant Design and Economics for Chemical Engineers," McGraw-Hill Book Co., New York, N.Y. (1968).
8. Holland, F.A., F. A. Watson, and J.K. Wilkinson, "Introduction to Process Economics," John Wiley and Sons, Ltd., London (1974).
9. Guthrie, K.M., Chemical Engineering, March 24, 1969.
10. Shea, T.G., E. Ramos, J. Rodrigues and G. H. Dorian, "Rum Distillery Slops Treatment by Anaerobic Contact Process," *Environmental Protection Series*, July 1974. Available from National Information Service, Springfield, Va.
11. Jackman, E.A., "Distillery Effluent Treatment in the Brazilian National Alcohol Programme," The Chemical Engineer, April 1977.
12. *Chemical Marketing Reporter*, January 23, 1978.

13. Batter, T.R. and C.R. Wilke, " A Study of the Fermentation of Xylose to Ethanol by Fusarium oxysporum," LBL-6351, filed as a M.S. thesis, June 1977.
14. Wilke, C.R., "Pilot Plant Studies of the Bioconversion of Cellulose and Production of Ethanol," LBL-6861, Sept. 30, 1977.

This work was done with support from the U.S. Department of Energy.



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.

TECHNICAL INFORMATION DEPARTMENT  
LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720