

## RECOVERY OF ENERGY FROM MSW

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### ABSTRACT

Methods for disposal of MSW that reduce the potential for groundwater or air pollution will be essential in the near future. Seventy percent of MSW consists of paper, food waste, yard waste, wood and textiles. These lignocellulosic components may be hydrolyzed to sugars with mineral acids and the sugars may be subsequently fermented to ethanol or other industrial chemicals. This paper presents data on the hydrolysis of the lignocellulosic fraction of MSW with concentrated HCl and the fermentation of the sugars to ethanol. Yields, kinetics and rates are presented and discussed. Design and economic projections for a commercial facility to produce 20 MM gallons of ethanol per year are developed. Novel concepts to enhance the economics are discussed.

### INTRODUCTION

The United States generates about 200 million tons of MSW annually, or about 4 pounds per capita per day (US EPA, 1981). The average composition of MSW is given in Table 1, and varies slightly with the season (Ng, *et al.*, 1983). This material has traditionally been disposed of in landfills. However, recent environmental concerns over groundwater pollution, leaching into waterways, and even air pollution, as well as increasing costs, have resulted in this technology becoming unacceptable in most areas. Few new landfills are being approved and the average remaining life of operating landfills is only about five years.

Alternatives to landfilling include incineration, composting, anaerobic digestion, and recycling. Incineration can result in energy recovery as steam. However, concerns over hazardous components in exhaust gases and high capital and operating costs detract from this alternative. Large areas required for composting and the ultimate use or disposal of compost with high metals content makes this technology uncertain. Very slow reaction rates and large reactors for anaerobic digestion makes this technology uneconomical at present.

Recycling of glass, metals, plastics, and paper reduces the quantity of material to be landfilled by about 60 percent, as seen from Table 1. Most states have decided that recycling offers the best solution to the environmental concerns associated with solid waste disposal and many have implemented regulations for curbside segregation of recyclable components. Markets for recycled aluminum and steel are well established, however, markets for recycled paper, glass, and plastics are not well developed. Low prices (negative in some areas for paper) will impede the application of recycling.

### Alcohol Production

The United States currently imports about half of its crude oil and must produce another 120 billion gallons of liquid fuels annually to become energy self sufficient. Ethanol can be produced from lignocellulosic matter, like paper, by hydrolysis of the polysaccharides to sugars, which can be fermented into ethanol. This technology would enable the use of the entire carbohydrate fraction of MSW (paper, yard and food waste, wood and textiles), which consti-

tutes 75 percent of the total, into a useful and valuable product. Ethanol can be blended with gasoline and, currently, nearly one billion gallons of ethanol, primarily made from corn, are used as a transportation fuel in this country. The potential market (at 10 percent alcohol) is 10 billion gallons per year. Blending of ethanol with gasoline reduces emissions and increases the octane rating. Some states, like California and Colorado where air quality has degraded seriously in metropolitan areas, are mandating the use of alcohol fuels.

The purpose of this paper is to describe a process for converting the lignocellulosic fraction of MSW into ethanol. The residue is contacted with concentrated mineral acid at room temperature to give theoretical yields of monomeric sugars, which are readily fermented into ethanol. Procedures to give high sugar concentrations are described. Data for fermentation in immobilized cell columns in a few minutes are presented. The economics of this process is then developed and key economic parameters identified.

#### HYDROLYSIS/ETHANOL PRODUCTION

The hydrolysis of biomass to sugars and fermentation of glucose to ethanol are technologies that have been commercial around the world for many years. The U. S. produced up to 600 million gallons of ethanol per year by fermentation during World War II. Also, the Germans produced fuel ethanol from wood by hydrolysis and fermentation during World War II. Today, Brazil produces most of its liquid fuel from sugar cane.

#### Hydrolysis Technology

Biomass materials are comprised of three major components: hemicellulose, cellulose, and lignin. The composition of various biomass materials is shown in Table 2. As noted, most of these materials contain 50-70 percent carbohydrate (hemicellulose and cellulose). These polysaccharides can be hydrolyzed to monomeric sugars, which can be converted by microorganisms into fuels or chemicals. The lignin cannot be hydrolyzed, but has a high heating value and can be used as a source of fuel. From Table 2, it is noted that most of the MSW biomass is cellulose.

The carbohydrate hydrolysis can be carried out by contact with cellulase or xylanase enzymes, or by treatment with mineral acids. Enzymatic hydrolysis has the advantage of operating at mild conditions and producing a high-quality sugar product. However, the enzymatic reactions are quite slow (30 hour retention time), and the biomass must be pretreated with caustic or acid to improve the yields and kinetics. The expense of pretreatment and enzyme production, and the large reactors required make this an uneconomical alternative.

Acid hydrolysis is a much more rapid reaction and various combinations of temperature and acid concentration may be used. Two methods of acid hydrolysis have been studied and developed: a high temperature, dilute acid process (Grethlien and Converse, 1982; Rugg, 1982) and a low temperature, concentrated acid process (Clausen and Gaddy, 1983; 1985). For example, complete conversion of the hemicellulose and cellulose in corn stover into monomeric sugars requires mineral acid concentrations of 2N at temperatures of 100-200°C (Clausen and Gaddy, 1982). However, acid concentrations of 10-14N yield complete conversions at room temperature (30°C).

At high temperatures, xylose degrades to furfural and glucose degrades to 5-hydroxymethyl furfural (HMF), which are both toxic to micro-organisms. Yields from dilute acid processes are typically only 50-60 percent of theoretical because of sugar losses by degradation and reverse polymerization at high temperatures. Also, equipment corrosion at high temperatures is a serious problem. Work in our laboratories has focused attention on concentrated acid

processes which produce theoretical yields at low temperatures. However, since high acid concentrations are used, acid recovery is an economic necessity (Clausen and Gaddy, 1983).

Studies in our laboratories have resulted in both single step and two-step hydrolysis processes, using concentrated mineral acids, which result in nearly 100 percent yields of sugars from hemicellulose and cellulose. The reactions are conducted at room temperature, without significant degradation or reverse polymerization (Prieto, et al., 1988a; Clausen and Gaddy, 1985). An acid recovery process has been developed and tested, yielding an energy efficient method of separating sugar and acid (Clausen and Gaddy, 1987). The resulting sugar solution has been successfully fermented to ethanol and other chemicals without pretreatment (Prieto, et al., 1988b).

Process Description. Figure 1 shows the proposed process for the acid hydrolysis of MSW, consisting simply of a mixed reactor where acid and MSW are contacted at a constant temperature. The unconverted solids (lignin and ash) are separated by filtration, washed, and used as fuel. Acid and sugars are separated and the acid returned to the reactor.

If desirable to separate the sugars, the hemicellulose, which degrades at milder conditions, may be first hydrolyzed to produce a mixture of five and six carbon sugars. The solids from this first stage reactor are separated and contacted with acid in a second step to hydrolyze the cellulose. Only six carbon sugars are obtained from cellulose in this second stage. This two step hydrolysis gives two streams; a xylose rich prehydrolyzate and a glucose rich hydrolyzate; and may be used where sugar separation is desirable. In the usual case, as with MSW, the simpler single step process will be preferred.

Hydrolysis Conditions. The two major factors which control the hydrolysis reactions are temperature and acid concentration. Studies in our laboratories have been made to define the appropriate conditions to maximize reaction rates and yields. Sugar degradation is promoted more at high temperature than at high acid concentration. Also, fast rates of hydrolysis are achieved at acid concentrations exceeding 12N. Therefore, the best conditions are a high acid concentration (80 percent H<sub>2</sub>SO<sub>4</sub> or 41 percent HCl) and a mild temperature (-40°C).

The sugar concentrations and yields from a typical hydrolysis of MSW from our laboratories are given in Table 3 (Clausen and Gaddy, 1985). The prehydrolysis step yields 8 percent of the initial MSW as xylose. The combined yield of glucose is 60 percent. These yields represent nearly complete conversion of hemicellulose and cellulose to sugars. However, very dilute (3-7 percent) sugar solutions result from these reactions.

#### Hydrolyzate Fermentation/Ethanol Production.

Glucose may be fermented to ethanol efficiently by the yeast Saccharomyces cerevisiae, or the bacterium Zymomonas mobilis (Waldron et al., 1988). Batch fermentation experiments were carried out to compare the production rates of ethanol from hydrolyzates and synthetic glucose. Saccharomyces cerevisiae (ATCC 24860) was used in the study. Identical results were found when fermenting synthetic glucose and hydrolyzate. Ethanol yields were also nearly identical. As noted in Table 4, the fermentation proceeded well in the presence of a small amount (0.25 percent) yeast extract, which can be obtained by recycle. Almost total conversion of sugars is obtained in only 16 hours. The concentrations of furfural and HMF in the hydrolyzates were found to be negligible. These low levels of by-products are believed to be the major reason for this highly efficient fermentation.

Xylose fermentation is much more difficult and the xylose might be used as a

source of energy for generating steam and power. However, future possibilities for xylose fermentation will improve the economics. Recent work with Pachysolen tannophilus shows promise for xylose conversion to ethanol (Schneider *et al.*, 1981) but, at present, this technology is not fully developed. Ethanol may also be produced by converting xylose to xylulose, followed by fermentation with yeast (Gong, *et al.*, 1981).

Continuous Fermentation. The standard technology for fermenting sugars to ethanol is in batch vessels. Batch fermentation is used so that contamination and mutation can be controlled. Sterilization between batches and the use of a fresh inoculum insure efficient fermentation. However, most batch alcohol fermentations are designed for thirty hour (or more) reaction time, which results in very large and expensive reactors.

The reactor size can be reduced substantially by using continuous flow fermenters. When fermenting acid hydrolyzates, the problems with maintaining sterile conditions are substantially reduced, since the substrate has been sterilized by contact with the acid. Therefore, the use of continuous fermentation is a natural application for producing alcohol from MSW hydrolyzates.

A number of continuous fermentation schemes have been studied, including the CSTR (Cysewski and Wilke, 1978), cell recycle reactor (Elias, 1979), flash fermentation (Cysewski and Wilke, 1977), and immobilized cell reactors (Sitton and Gaddy, 1980; Vega *et al.*, 1988). Immobilized cell reactors (ICR) show potential in substantially decreasing reactor size and decreasing substrate and product inhibition (Vega *et al.*, 1988; Gainer *et al.*, 1981; Linko, 1981; Rowe and Margaritis, 1981). Reaction rates for ethanol production in an immobilized cell reactor are as high as 10 times the values obtained in a stirred tank reactor (Sitton and Gaddy, 1980). A wide variety of immobilization techniques have been employed, including cross-linking, entrapment, and covalent bonding (Vega *et al.*, 1988).

Data are given in Figure 2 for laboratory columns with immobilized S. cerevisiae. The glucose profiles are given for initial sugar concentrations from 50-200 g/L. As noted, 90 percent conversion is achieved in one hour or less. Productivities to achieve 99 percent conversion were about 40 g/L-hr, or about an order of magnitude greater than the CSTR and 60 times more than the batch reactor. Furthermore, alcohol inhibition and toxicity to other inhibitors are reduced in the ICR. The reactor volume of the ICR for MSW hydrolyzate fermentation is about 5 percent that of the batch fermenter and substantial capital savings result.

#### Increasing the Sugar Concentration

Perhaps the single most important factor in the economics of this process is the sugar concentration that results from acid hydrolysis. Dilute concentrations increase both the equipment size and the energy required for purification. Methods to increase the sugar and ethanol concentrations have been developed.

Solids Concentration. The ultimate sugar and alcohol concentrations are direct functions of the initial solids concentration in the hydrolysis. Since fluidity in a stirred reactor is a requirement, a 10 percent mixture has been considered maximum. Therefore, the resultant sugar concentrations have been only 2-7 percent and alcohol concentrations only half as much.

If the limiting factor is considered to be fluidity in the reactor instead of the feed mixture, the feed concentration could be increased by roughly the reciprocal of one minus the solids conversion in the reactor. Of course, solids and liquid would have to be fed separately, which could also save equipment

cost. For biomass, containing 75 percent carbohydrate, the reactor size could be reduced to one-fourth the size with a ten percent feed concentration. Attendant reductions would also result in the filtration and washing units.

Equally important are the resultant increases in sugar concentrations. The glucose concentration would be quadrupled to about 280 g/L (28 percent). Energy and equipment costs in the fermentation area would be reduced proportionately. This simple alteration in the process has a profound impact on the economics. It is estimated that the capital cost is reduced by 40 percent in the hydrolysis and acid recovery sections and 60 percent in the fermentation and utilities areas. Furthermore, the energy requirements for distillation are reduced by 60 percent.

Acid Recycle. Another method to increase the sugar concentration is to recycle a portion of the filtrate (acid and sugar solution) in the hydrolysis step. The acid would catalyze further polysaccharide hydrolysis to increase the sugar concentration. Of course, recycle of the sugars would also increase the possible degradation to furfural and HMF.

Experiments have been conducted to determine the enhancement possible with acid recycle. Various amounts of the acid and sugar solution from the filtration were recycled to determine the resulting sugar and by-product concentrations. Acid and solids concentrations and temperatures were kept constant. These experiments have shown that the sugar concentrations can be increased sixfold at total recycle. It should be noted that not all the filtrate can be recycled, since a portion adheres to the solids in filtration. In order to minimize sugar decomposition, a recycle fraction of 50 percent has been used, which results in doubling the sugar composition, without significant furfural or HMF levels.

The effect of acid recycle on the economics is significant. A recycle rate of 50 percent, coupled with high solids concentrations, would result in a xylose concentration of 15 percent and a glucose concentration of over 50 percent could be achieved. Practically, sugar concentrations should not exceed 25 percent, so a smaller recycle fraction is required. It should be noted that these concentrations have been achieved in the laboratory, while maintaining furfural and HMF less than 0.05 percent. These high concentrations reduce the equipment size in the acid recovery section by 50 percent and in the fermentation section by another 60 percent. Energy consumption is also reduced another 60 percent.

Acid Recovery. Acid recovery is essential when using concentrated acid hydrolysis. Processes for recovery of both hydrochloric and sulfuric acids have been developed. A number of possible recovery schemes were examined, including electrodialysis, distillation, etc.

The recovery technology that has been selected is based upon solvent extraction. Solvents have been identified that extract HCl and H<sub>2</sub>SO<sub>4</sub> from the aqueous sugar solutions. Near complete acid recovery is possible and solvent losses are minimized. For HCl, the acid is separated from the solvent by distillation, and the solvent recycled. A hexane wash of the sugar solution is used to recover trace quantities of solvent, and hexane is separated by distillation for recycle.

Some solvent is lost in the process; however, the losses are quite small and solvent replacement costs are only \$0.02 per gallon of alcohol. Acid losses are minimized and acid costs are \$0.025 per gallon of alcohol. The total heat requirement for solvent and acid recovery is low and amounts to less than \$0.05 per gallon of alcohol. As shown later, the energy cost may be recovered from the lignin and xylose streams.

## ECONOMIC PROJECTIONS

To illustrate the economics of this process, a design has been performed for a facility to convert MSW into 20 million gallons per year of ethanol, utilizing the acid hydrolysis procedures previously described. The capital and operating costs are summarized in Table 5.

MSW would be collected and delivered to the plant site as needed. Feedstock preparation consists of plastic, metal and glass removal, shredding, grinding and conveying to the reactors. The cost of the removal of glass and metals is not included in the feed processing cost, as reports indicate that resale of these materials will offset the capital and operating costs of separation. The hydrolysis section, as shown in Figure 1, consists of continuous reactors. Acid resistant materials of construction are necessary for this equipment. Ethanol fermentation in the ICR and typical distillation units are included. The total capital cost for this plant is \$35 million, including all utilities, storage and offsites.

The annual operating costs are also shown in Table 5. These costs are also given on the basis of unit production of alcohol. As mentioned previously, no cost is included for MSW. A lignin boiler is used to reduce the energy requirements, and energy costs are only \$0.08 per gallon. Fixed charges are computed as a percentage of the capital investment and total \$5.6 million per year. The present ethanol price of \$1.50 per gallon will yield a pre-tax profit of \$18.5 per year (\$.93/gal) or 53 percent per year.

It should be noted that this process does not include utilization of the pentose stream. Acid recovery is included, but fermentation of the xylose is not provided. Xylose could be fermented to alcohol, acids or other valuable chemicals, which would improve the economics. However, since this technology is not perfected, such products have not been included.

Sensitivity analyses show that the economics are particularly sensitive to capital cost and revenue. A 20 percent reduction in capital cost raises the pre-tax return to 70 percent. Similarly, a 20 percent increase in the ethanol price increases the return to 70 percent. A tipping fee of \$20 per ton of MSW would increase the return to 65 percent. Increasing the plant size would have a similar positive affect on the economics.

## CONCLUSIONS

Concentrated acid hydrolysis of residues, such as MSW, requires mild temperatures and results in near theoretical yields. The resulting hydrolyzates, containing primarily xylose and glucose, can be fermented to ethanol or other chemicals. The acid can be recovered for reuse by solvent extraction. The sugar concentration can be increased by using high solids reactions with acid recycle. Continuous fermentation of the hydrolyzates can be achieved in an hour or less in an immobilized cell column. The capital cost for a process to produce 20 million gallons of ethanol is estimated to be \$35 million. The pre-tax profit from this facility is sufficient to encourage commercialization.

## REFERENCES CITED

- Clausen, E. C. and Gaddy, J. L., "Production of Ethanol from Biomass," Biochem. Engr. (1982).
- Clausen, E. C. and Gaddy, J. L., "Economic Analysis of Bioprocess to Produce Ethanol from Corn Stover," Biotech. and Bioenr., 13 (1983).

- Clausen, E. C. and Gaddy, J. L., "The Production of Fuels and Chemicals from MSW," Biotechnology Applied to Environmental Problems, CRC Press, (1985).
- Clausen, E. C. and Gaddy, J. L., "Acid Hydrolysis/Recovery," SERI Review Meeting, Golden, CO (October 1987).
- Cysewski, G. R. and Wilke, C. R., Biotech. Bioeng., 20, 1421 (1978).
- Cysewski, G. R. and Wilke, C. R., Lawrence Berkeley Laboratory Report 4480, (March 1976) Biotech. Bioeng., 19, 1125 (1977).
- Elias, S., Food Engineering, p 61 (October 1979).
- Gainer, J. L. et al., "Properties of Adsorbed and Covalently Bonded Microbes," presented at AIChE National Meeting, New Orleans (1981).
- Gong, C. S., McCracken, L. D., and Tsao, G. T., Biotech Letters, 3, 245-250 (1981).
- Grethlein, H. E. and Converse, O. C., "Continuous Acid Hydrolysis for glucose and Xylose Fermentation," presented at International Symposium on Ethanol from Biomass, Canertech Ltd, Winnipeg (1982).
- Linko, P., "Immobilized Microbial Cells for Ethanol and Other Applications," presented at AIChE National Meeting, New Orleans (1981).
- Ng, A. S., Wong, M. K. Stenstrom, Larson, L., and Mah, R. A., "Bioconversion of Classified Municipal Solid Wastes: State-of-the-Art Review and Recent Advances," Fuel Gas Developments, CRC Press, (1983).
- Prieto, S., Clausen, E. C. and Gaddy, J. L., "The Kinetics of Single-Stage Concentrated Sulfuric Acid Hydrolysis," Proceedings Energy from Biomass and Wastes XII, (1988a).
- Prieto, S., Clausen, E. C., and Gaddy, J. L., "Ethanol from Biomass by Concentrated Acid Hydrolysis and Fermentation," Proceedings Energy from Biomass and Wastes XII, (1988b).
- Rowe, G. and Magaritis, A., "Continuous Ethanol Production in a Fixed-Bed Reactor Using Immobilized Cell of Zymomonas mobilis," presented at AIChE National Meeting, New Orleans, (1981).
- Rugg, B., "Optimization of the NYU Continuous Cellulose Hydrolysis Process," SERI Report No. TR-1-9386-1, (1982).
- Schneider, H., Yang, P. Y., Chan, Y. K., and R. Maleszka, Biotech. Letters, 3, 89-92 (1981).
- Sitton, O. C. and Gaddy, J. L., Biotech. Bioeng., 22, 1735, (1980).
- Vega, J. L., Clausen, E. C., and Gaddy, J. L., "Biofilm Reactors for Ethanol Production," Enzyme and Microbial Tech., 10(3), 389 (1988).
- Waldron, R. D., Vega, J. L., Clausen, E. C., and Gaddy, J. L., "Ethanol Production Using Zymomonas mobilis is Cross-Linked Immobilized Cell Reactors," Appl. Biochem. and Biotech., 18, 363 (1988).
- \_\_\_\_\_ U. S. E. P. A., "Technical Environmental and Economic Evaluation of Wet Processing for Recovery and Disposal of Municipal Solid Waste," SW-109C (1981).

Table 1. Municipal Solid Waste Composition  
(Weight Percent as Discarded)

<u>Category</u>	<u>Summer</u>	<u>Fall</u>	<u>Winter</u>	<u>Spring</u>	<u>Average</u>
Paper	31.0	38.9	42.2	36.5	37.4
Yard Waste	27.1	6.2	0.4	14.4	13.9
Food Waste	17.1	22.7	24.1	20.8	20.0
Glass	7.5	9.6	10.2	8.8	9.8
Metal	7.0	9.1	9.7	8.2	8.4
Wood	2.6	3.4	3.6	3.1	3.1
Textiles	1.8	2.5	2.7	2.2	2.2
Leather & Rubber	1.1	1.4	1.5	1.2	1.2
Plastics	1.1	1.2	1.4	1.1	1.4
Miscellaneous	3.1	4.0	4.2	3.7	3.4

Table 2. The Composition of Selected Biomass Materials

<u>Material</u>	<u>Percent Dry Weight of Material</u>		
	<u>Hemicellulose</u>	<u>Cellulose</u>	<u>Lignin</u>
Tanbark Oak	19.6	44.8	24.8
Corn Stover	28.1	36.5	10.4
Red Clover Hay	20.6	36.7	15.1
Bagasse	20.4	41.3	14.9
Oat Hulls	20.5	33.7	13.5
Newspaper	16.0	61.0	21.0
Processed MSW	25.0	47.0	12.0

Table 3. MSW Acid Hydrolyzates

	<u>Concentration</u> <u>g/L</u>	<u>Yield</u> <u>g/100g</u>
Prehydrolyzate		
Xylose	9.5	8.0
Glucose	18.5	16.0
Hydrolyzate		
Xylose	0.0	0.0
Glucose	67.8	44.0
Combined		
Xylose		8.0
Glucose		60.0

Table 4. Hydrolyzate Fermentation to Ethanol  
Percent Sugar Utilization

Fermentation Time (hrs)	Hydrolyzate			With Yeast Extract
	Amino Acids	With Vitamins and NH <sub>4</sub> (PO <sub>4</sub> )	Amino Acids and NH <sub>4</sub> (PO <sub>4</sub> )	
16	15.9	21.9	27.3	97.5
23	19.3	24.9	35.8	97.5

Table 5. Economics of 20 Million Gallon Per Year  
Ethanol Facility

A. Capital Cost

	Million \$
Feedstock Preparation	3.0
Hydrolysis	5.0
Acid Recovery	8.5
Fermentation & Purification	8.0
Utilities/Offsites	6.5
Engineering	<u>4.0</u>
	35.0

B. Operating Cost

	Million \$/yr	\$/gal
MSW	-	-
Utilities	1.5	0.08
Chemicals	1.9	0.09
Labor	2.5	0.13
Fixed Charges		
Maintenance (4%)	1.4	0.07
Depreciation (10%)	3.5	0.18
Taxes & Insurance (2%)	0.7	0.02
Pre-tax Profit (53%)	<u>18.5</u>	<u>0.93</u>
	\$30.0	\$1.50/gal

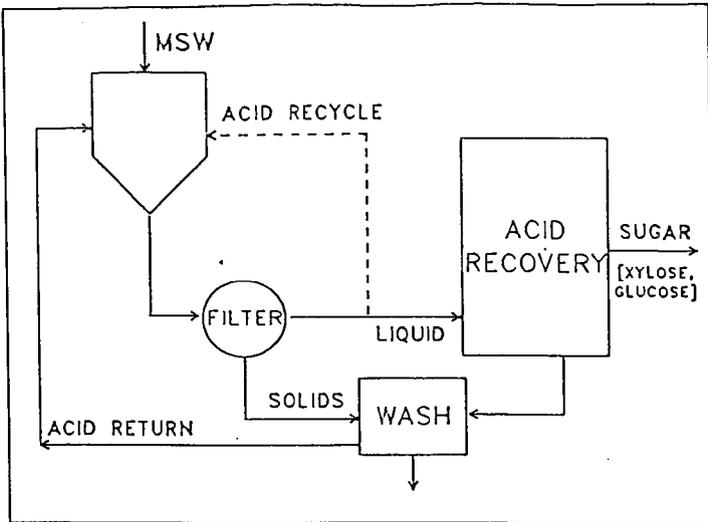


Figure 1. Schematic of Acid Hydrolysis Process

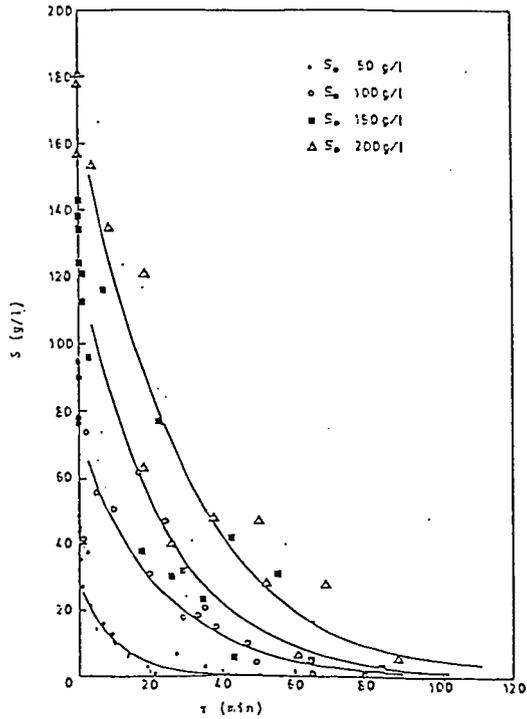


Figure 2. Glucose Profile in the ICR