The NYU Continuous Acid Hydrolysis Process - Hemicellulose Utilization Preliminary Data and Comparative Economics for Ethanol Production

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INTRODUCTION

There has been a recent increased interest in the possible commercial utilization of waste biomass for both material and energy recovery due to the steadily rising price of fossil fuels. Currently employed methods for dealing with these solid residues are inadequate for the cost effective utilization of their latent energy values; waste cellulose conversion via acid hydrolysis to xylose and glucose followed by fermentation to ethanol offers an attractive alternative. Additionally, as is shown in Figures 1 and 2, the xylose and glucose from cellulosic wastes could be used as the basic raw material for the manufacture of many "petrochemicals", or more precisely volume chemicals which are presently obtained from petrochemical feedstocks.

Ethanol production from biomass sources is proposed to increase due to various government incentives to meet projected "Gasahol" production levels by 1985. A reliable, high yield, energy efficient process based on waste cellulose would have many advantages as compared to the more conventional grain processing technology now being utilized. The economic viability of ethanol from cellulose does not exclusively depend on by-product values, as does ethanol from grain, but would be most sensitive to the cost of the waste cellulose feedstock.

The NYU continuous acid hydrolysis process has been utilized in the past primarily for the conversion of crystalline α-cellulose to glucose. Under the rather severe conditions of high temperature required for this process, the amorphous hemicellulose fraction primarily composed of pentosans in hardwoods is converted beyond the sugars to furfural. It has been the objective of our recent experiments to show the feasibility of performing a continuous two stage hydrolysis which would allow for a more complete utilization of carbohydrate content. Conceptually, the process is shown in Figure 3. By using a mild prehydrolysis and extraction, it is possible to reclaim a major portion of the hemicellulose fraction as xylose. Subsequently it is proposed to hydrolyze continuously the remaining hexosan fraction to glucose by the usual process.

HISTORICAL REVIEW

Acid hydrolysis of cellulose has been extensively studied for the better part of a century,particularly in connection with the manufacture of ethanol from wood wastes. (1,2,3) Attempts to commercialize this technology in Europe and the U.S. occurred only at wartime when petroleum was cut off. A significant effort has been ongoing in the USSR.

Cellulose derived from forestry, agricultural or municipal residues has three main components; crystalline α-cellulose, amorphous hemicellulose and lignin. The cellulose fractions in these residues react differently when exposed to acid hydrolysis conditions because of their relative degree of molecular order or accessibility. The amorphous hemicellulose reacts to form sugars at conditions much less severe than those required for the crystalline α-cellulose conversion to glucose.(4) Therefore, in order to extract the maximum carbohydrate value from cellulose residues, studies to accomplish a two stage hydrolysis in which the hemicellulose fraction is prehydrolyzed and extracted prior to a concentrated sulfuric acid α-cellulose hydrolysis have been reported by Dunning et. al. and by Sitton et. al. (5,6)

There exist, both economic and technical factors which favor dilute acid hydrolysis of α-cellulose to glucose to be conducted at high temperatures for short times so as to maximize the glucose yield. Numerous kinetic studies, initially by Saeman and later Porteous, Fagan, Converse and Grethlein have been useful in the characterization of heterogeneous hydrolysis of various cellulose feedstocks. Porteous predicted a maximum sugar yield of 55% with 0.4% acid at 230°C, the yields being based on percentage conversion of available α-cellulose to glucose. The Fagan experiments were carried out with rather small samples (0.5 gms) of ball mill Kraft paper and verified the Porteous predictions. Such kinetic studies are of considerable value for the development of improved process designs and economic data of waste cellulose and/or ethyl alcohol production facilities (2,7,8,9, 10).

Grethlein has recently proposed and built a plug flow pipe reactor in which nearly isothermal conditions can be maintained. Verification of previously developed data based on a batch reactor is currently underway. The kinetic model indicates that high temperature, short time dilute acid hydrolysis reactions favor the production of glucose versus its degradation. Yields of 80-90% of the available glucose may theoretically be obtained under ideal conditions. (11,12)

Experimental investigations on the dilute acid hydrolysis of waste cellulose to glucose have been carried out at the Department of Applied Science of New York University over the past five years. The waste cellulose feedstock employed in the initial studies was newspaper pulp. This experimental work involved an evaluation of the cost effectiveness of various pretreatments for enhancing the accessibility of the cellulose and the determination of the optimum reaction conditions for maximizing the sugar yields.

The hydrolysis experiments were initially carried out batchwise with two differently sized stirred stainless steel autoclave reactors. The optimum reaction conditions were determined to be temperatures around 220°C-230°C and reaction times of less than 30 seconds with about 1 wt% of sulfuric acid. (13) These results agree quite well with the results of the kinetic rate studies which were previously reported by Porteous and Fagan. (9)

More recently, over the past three years, studies at NYU have resulted in the design, costing and construction of a continuous waste cellulose to glucose pilot plant with a nominal 1-2 ton/day capacity. This pilot plant is based on the concept of employing an intensive screw mixer/conveyor for continuously reacting waste cellulose at suitably elevated temperatures in the presence of acid.

The key to successful operation of a continuous acid hydrolysis process is the design of the hydrolysis reactor. This reactor must be capable of feeding, conveying and discharging hydrolyzable cellulosic materials continuously while maintaining appropriate temperatures and associated pressures in a reaction zone. Because this hydrolysis requires exposure of the reactor components to dilute acids at high temperatures and pressures, all materials of construction have to be resistant to corrosion especially in the reaction zone.

A Werner & Pfleiderer ZDSK53 (53mm) twin screw extruder (Werner & Pfleiderer Corporation, Ramsey, N. J.) was selected on account of its capacity for conveying, mixing and extruding the required amounts of cellulosic feedstock. This machine allows accurate control of temperature, pressure, residence time, etc., within the previously established acid hydrolysis operating conditions while continuously feeding and discharging material.

This equipment was obtained and installed at the Antonio Ferri Laboratories of New York University (Westbury, Long Island, N.Y.) and considerable progress has been achieved in the development and characterization of reaction conditions. Conversions of 50-60% yield based on available α-cellulose have been reported. (14) Experiments have been run with diverse feedstocks such as paper pulp (10% solids) and hardwood sawdust (95% solids). It is anticipated that significant increases in yield will result with improved process control.

CONTINUOUS ACID HYDROLYSIS STUDIES-HEMICELLULOSE UTILIZATION

In the course of recent experiments to improve the level of carbohydrate utilization for the continuous acid hydrolysis process, the feedstock used was a mixed hardwood sawdust; A representative analysis of this is shown in Table 1.

Table 1: Analysis of Mixed Hardwood Sawdust. (4)

	% by wt.	
α-cellulose (crystalline)	45	
hemicellulosic glucan	3	34
glucomannan (acetate)	5	
arabiogalactan	1	
4-O-methyl-glucurono (arabino) xylan (acetate)	25	
lignin	21	
Total	100	

Analytical procedures for this complex system are being developed using high pressure liquid chromatography (HPLC). Initial determinations of sugar yields from hemicellulose, however, utilized a dual-wavelength spectrophotometric technique with orcinol reagent (15); this and similar early methods are unfortunately, subject to significant interferences.

Initial prehydrolysis experiments for the hardwood sawdust were directed toward the determination of reaction conditions (acid concentration, temperature and residence time) for satisfactory utilization of the hemicellulose fraction. Preliminary findings are presented in Figure 4. Subsequently, it is proposed to hydrolyze the residual α-cellulose fraction by previously described methods (13, 14)

YIELD ANALYSIS - SUGARS AND ETHANOL

For the purpose of a preliminary analysis to determine the impact on ethanol yield of hemicellulose prehydrolysis, the chemical composition for hardwood sawdust is given in Table 1. The data given in Table II assumes 80% conversion of the hemicellulose to sugar (glucose, mannose, or xylose) and 60% conversion of the α-cellulose to glucose. A 45% conversion of all sugars is assumed to ethanol. Based on these assumptions, one could expect a yield of 72.2 gallons of anhydrous alcohol per ton of dry hardwood sawdust.

PRELIMINARY ECONOMIC ANALYSIS

A preliminary cost analysis of a plant processing 2000 tons/day of sawdust producing 48MM gallons of fuel grade ethanol is presented in Figure 5. The total plant investment cost was estimated at $75MM in 1980. The plant scheme assumes the energy saving advantages of continuous fermentation and energy efficient distillation. The ligno-cellulosic residue is

TABLE II: YIELD ANALYSIS; BASIS 100 LB HARDWOOD SAWDUST

Hemicellulose fraction (assume 80% conversion to sugars)

3 lb glucan x (180/162)[a] x .8 = 2.26 lb glucose

5 lb glucomannan (Ratio of glucose/mannose = 1/4)

1 lb glucan x (180/162)[a] x .8 = 0.89 glucose

4 lb mannon x (180/162)[a] x .8 = 3.55 lb mannose

25 lb 4-O-methyl-glucurono (arabino) xylan (acetate)
(approximately 70% of weight due to xylan)

25 lb x .7 x (150/132)[b] x .8 = 15.96 lb xylose

α- cellulose froction (assume 60% conversion to glucose)

45 lb x (180/162)[a] x .6 = 30 lb glucose

Hydrolysis Summory

Glucose = 33.55 lb
Mannose = 3.55 lb
Xylose = 15.96 lb
} total sugars = 53.06 lb

Fermentation Yield (assume 45% conversion of sugars to ethanol

53.06 lb x .45 = 23.88 lb ethanol/100 lb sawdust

or 23.88/661 = 3.61 gallon ethanol/100 lb sawdust

or 3.61 x 20 = 72.2 gallons ethanol/ton sawdust

[a] ratio of molecular weight of glucose/glucan = mannose/mannan

[b] ratio of molecular weight of xylose/xylan

utilized to generate high pressure steam for continuous acid hydrolysis while the total plant is assumed to operate at a 91% capacity factor. The results of the analysis are quite promising assuming a $30/ton feedstock sawdust cost; at the current market price of $1.77/gal for anhydrous ethanol the plant would earn $40.8MM the first year. IF an 80/20 debt/equity ratio is assumed, a conservative payback for the plant would be 1.84 years.

CONCLUSION AND FUTURE WORK

The development of the NYU continuous acid hydrolysis process has been most favorable. The characterization of preferred reaction conditions for both hemicellulose prehydrolysis and extraction followed by α-cellulose hydrolysis is continuing. Potential alcohol yield with hemicellulose utilization is estimated to increase 70% beyond that without prehydrolysis.

A data base for the utilization of various waste cellulose feedstocks is being developed. Preliminary studies on the fermentation of waste cellulose acid hydrolyzates is underway.

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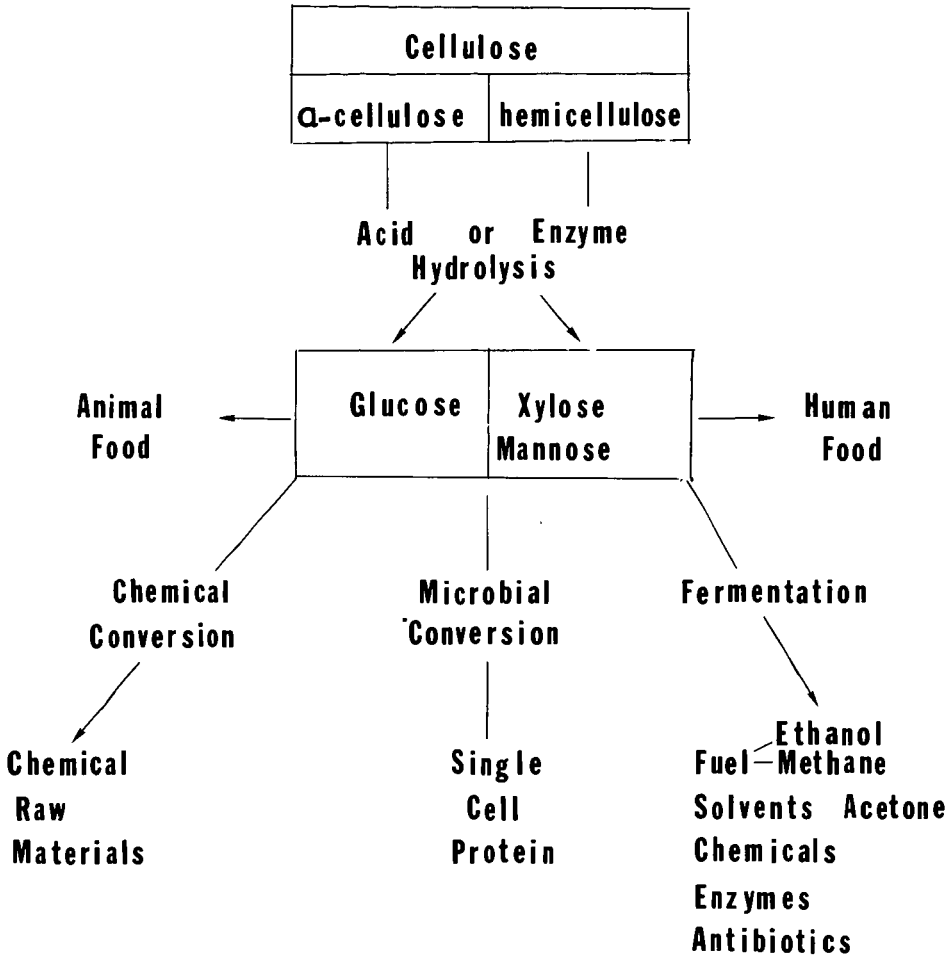


Fig. 1: Waste Cellulose Utilization Routes

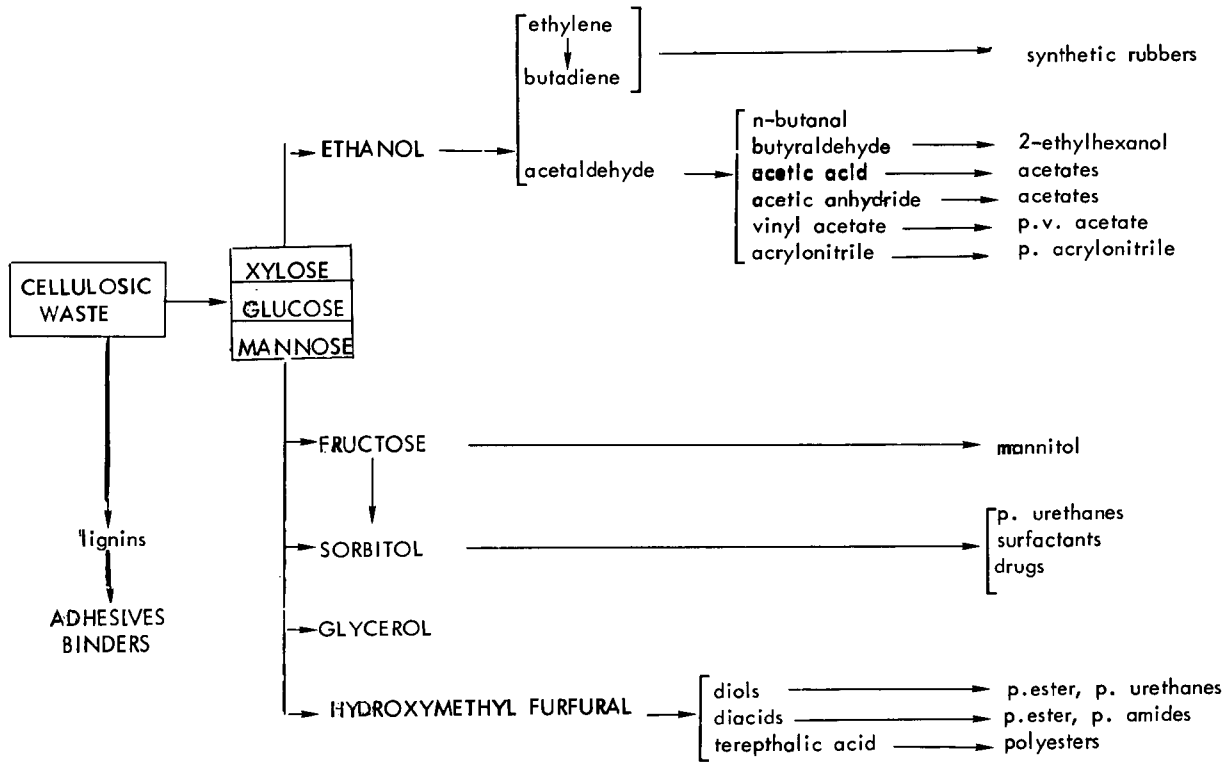


Fig. 2: Possible routes to petrochemicals from cellulosic wastes

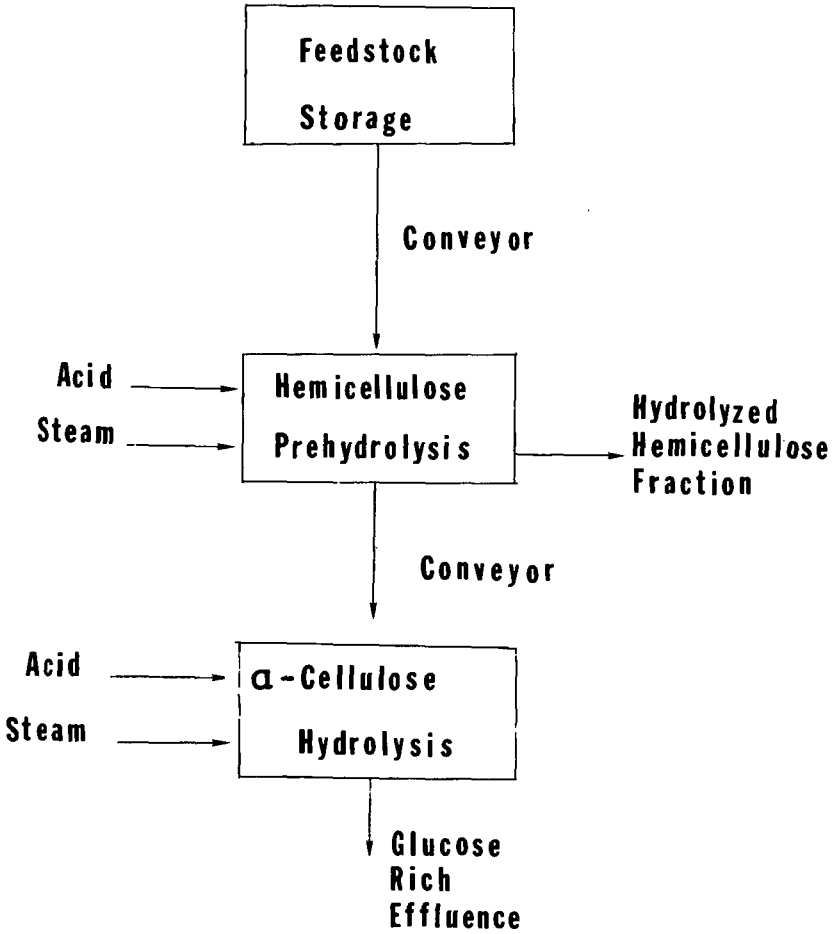
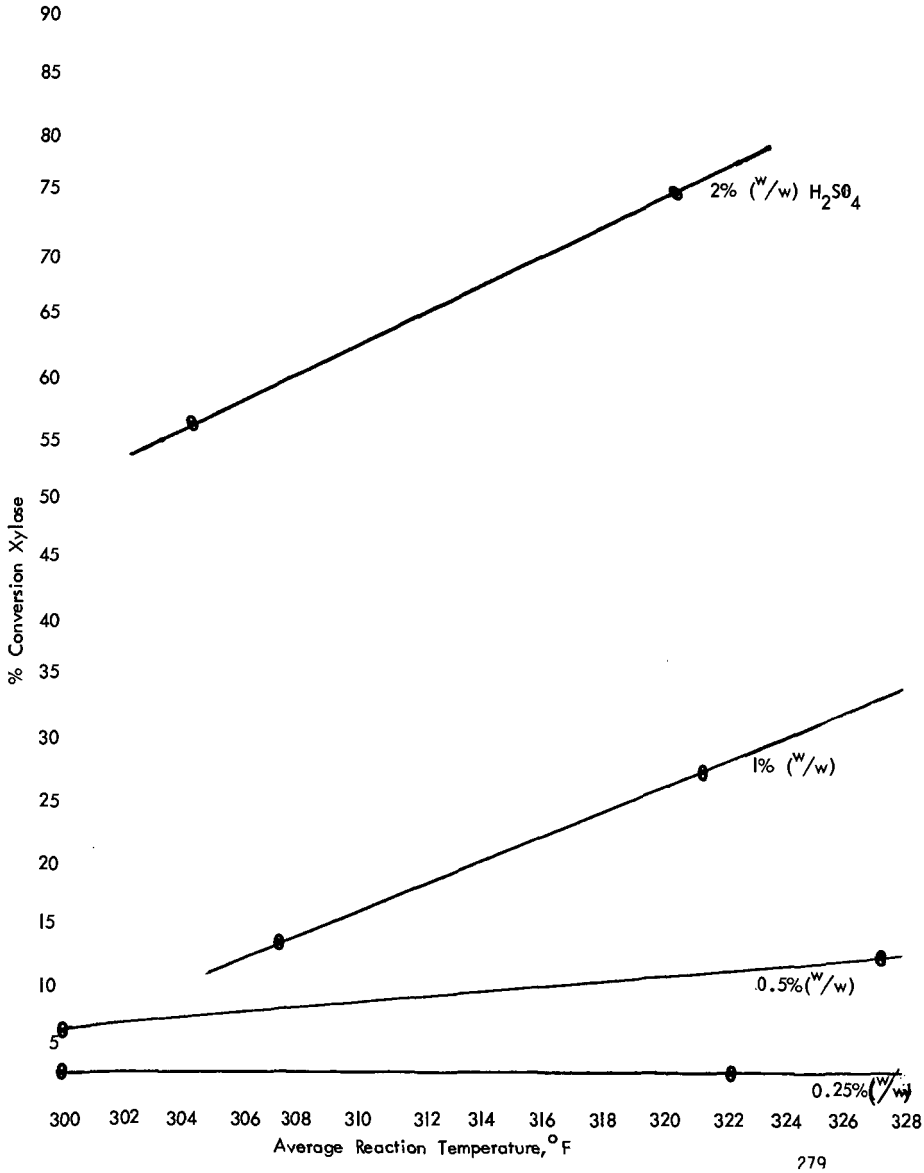
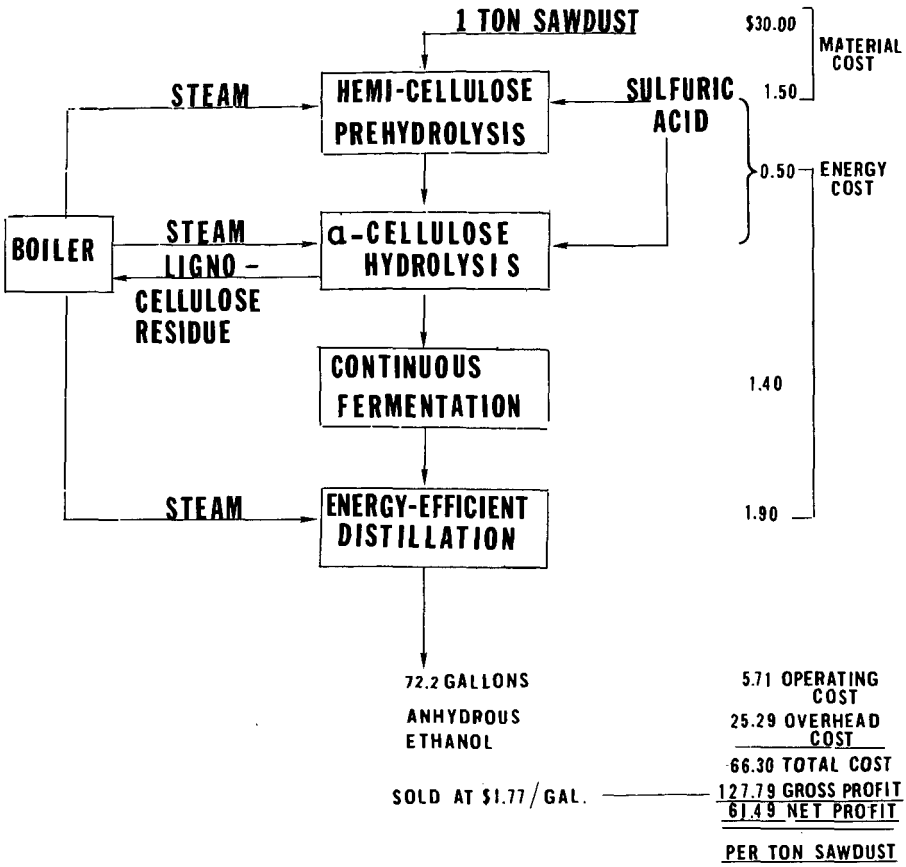


Fig.3: Schematic of continuous acid hydrolysis with hemicellulose utilization

PRELIMINARY DATA ON THE EFFECTS OF ACID CONCENTRATION AND TEMPERATURE ON THE CONVERSION OF HEMICELLULOSE TO XYLOSE IN HARDWOOD SAWDUST

Fig. 4





2,000 TON PER DAY PLANT

Total plant cost (1980):	$75 million
Conversion of hemi-cellulose to xylose:	80%
Conversion of α-cellulose to glucose:	60%
Conversion of sugars to ethanol:	45%

NET PROFIT: $122,980 per day, $40.8 million per year @ 91% capacity factor

PRODUCTION: 48 million gallons anhydrous ethanol per year from 666,000 tons sawdust

FIG.5: PRELIMINARY ECONOMICS OF CONTINUOUS PREHYDROLYSIS ACID HYDROLYSIS, FERMENTATION AND DISTILLATION