

DILUTE ACID HYDROLYSIS OF WOOD IN A TWO-STAGE
CONTINUOUS FLOW PROCESS: HIGH SOLIDS TESTING

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SUMMARY

Research at the Solar Energy Research Institute (SERI) has shown that dilute acid hydrolysis of wood using plug flow reactor technology has significant promise for the production of fermentable sugars for fuel-grade ethanol. However, analysis has shown that several key areas of technical uncertainty remain. For example, the concentration of the sugars produced has a significant effect on process economics. Slurries of 20% solids by weight must be processed to produce economical concentrations. Current research at SERI, described in this paper, is addressing these questions in engineering-scale experiments to provide a foundation for further development.

Keywords: acid hydrolysis, wood hydrolysis, plug flow reactor, ethanol

INTRODUCTION

The hydrolysis of cellulose for the production of fermentable sugars has been studied extensively by a number of researchers. Work on dilute acid

hydrolysis was widespread during World War II in the U. S. and elsewhere. The process produces sugars and their degradation products, depending on acid concentration, reaction temperature and reaction time. The reaction theory was reviewed in a previous paper (1).

Most of the early work was based on percolation reactors which generally have long residence times and produce a dilute sugar stream. Several researchers have investigated continuous slurry flow systems which can operate at higher temperatures and shorter reaction times, producing higher yields (2-4). These projects, however, used dilute wood slurries, because of the difficulties inherent in processing high solids slurries. This results in a dilute sugar stream that is uneconomic to recover. Two projects did address high solids processing (5,6), but neither produced an economic process because of expensive equipment or operating problems.

The current SERI experiment is based on work performed over the last several years at Dartmouth College and Badger Engineers, Inc., using plug flow reactor technology (3,7). The plug flow reactor has several potential advantages over other processes. First, the reactor can operate with short residence times and high temperatures to produce relatively high product yields. In addition, because of the short residence time, the reactor can be smaller and less expensive than percolation reactors or extruders. Finally, the conditions required for high glucose yield produce furfural as a degradation product of xylose. Furfural is a valuable byproduct which may provide a significant cash flow for a near-term wood-to-ethanol plant.

The experiment at SERI is designed to hydrolyze concentrated wood slurries (20%) at an engineering scale using a two-stage process. In the first stage, wood flour is prehydrolyzed, degrading the hemicellulose and producing a

slurry resistant to plugging, dewatering and bridging. The slurry is then pumped to the hydrolysis reactor where the reaction is completed. In this manner, more concentrated slurries can be processed than was previously possible.

The experiment has taken place in two phases. The first phase involved a single stage hydrolysis process with low solids slurries (10%) to replicate Dartmouth's data at a larger scale and to provide a baseline for later work. This phase was completed in May 1986 and documented in a SERI report (8). During the second phase, now underway, the equipment was modified for the two-stage process, and experiments were begun to determine the feasibility of high-solids processing.

BACKGROUND

Research sponsored by SERI on high-temperature, dilute sulfuric acid hydrolysis of wood began several years ago at the Thayer School of Engineering at Dartmouth College. During the first few years, kinetic studies of biomass hydrolysis were conducted using glass ampules (9). When yield data from these experiments showed promise, research at Dartmouth was expanded to examine yields from continuous flow reactors. These experiments were conducted with reactors made of various lengths of 1.3-cm (0.5-in.) tubing. Using these reactors, Kwarteng developed kinetic parameters for glucose, xylose and furfural yields, and achieved glucose yields from hardwood flour as high as 55% (4).

In 1983, an engineering analysis was begun at Badger Engineers, Inc., to determine the technical and economic feasibility of producing ethanol on a

commercial scale with the plug flow reactor technology developed at Dartmouth (7). Badger developed conceptual designs for ethanol-production plants with capacities of 19×10^6 L/yr (5.0×10^6 gal/yr) and 95×10^6 L/yr (25×10^6 gal/yr). They addressed a variety of issues, such as feedstock availability and cost, process design, equipment selection, product yield and recovery, and capital and operating costs.

The larger plant would require about 1800 metric tons of wood chips per day. The Badger study concluded that waste wood from logging, lumber mills, and forest thinning operations is available in most forested areas to supply this quantity at a reasonable cost. The process design calls for the wood chips to be reduced in size to -20 mesh prior to hydrolysis.

The design of the hydrolysis reactor was based on the Dartmouth research. Operating conditions of 265°C and 5.5 seconds residence time were selected to provide high yields of both glucose and furfural. The hydrolyzate is then neutralized and the liquids and solids separated in preparation for fermentation. A continuous fixed bed is used for fermentation with yeast immobilized on resin beads.

The Badger economic analysis showed that the concentration of the sugar stream has a major effect on the cost of downstream processing equipment and operating costs. While the Dartmouth work was conducted with 10% solid slurries, the Badger design is based on mixtures of 20% solids. To make this mixture pumpable in their continuous flow process, Badger recommended a preliminary hydrolysis of the wood at 167°C with 1% acid for five minutes. At these conditions, the wood is partially hydrolyzed and forms a slurry resistant to the dewatering and bridging evidenced by a 20% raw wood mixture.

Based on this design, Badger performed an economic analysis to determine

the selling price of the ethanol product. The analysis included the capital and operating costs for the process and allowed credits for the furfural by-product and excess electricity generated. The selling price for ethanol from the larger plant ranged as low as \$0.32/L (\$1.23/gal) depending on byproduct credits and economic assumptions.

Although the ethanol selling price is very promising, the Badger analysis pointed out several areas of technical uncertainty critical to the eventual success of the technology. First, the pumpability of 20% wood slurries has not been demonstrated other than Badger's laboratory-scale prehydrolysis tests. Second, most of the Dartmouth work used hardwood flour (-60 mesh), not the larger particles recommended by Badger (-20 mesh). Third, fermentation tests of actual wood hydrolyzates have been limited; real hydrolyzates contain organics which may be toxic to yeasts. Fourth, preliminary tests by Badger at the Dartmouth labs showed that separation of the liquids and solids in the hydrolyzate may be a difficult operation. And finally, all of the work to date has taken place at a laboratory scale which gives little information about the ultimate yields and operability of a commercial-scale plant. The study therefore recommended that the above issues be addressed at an engineering-scale to reduce the technical uncertainty in the process.

The research currently underway at SERI is designed to resolve several of the uncertainties raised by the Badger study. An engineering-scale experiment has been designed based on the two-stage hydrolysis process. Using this equipment, tests are being conducted to determine the pumpability of 20% wood slurries. Initial tests will use the same hardwood flour studied at Dartmouth, but later tests will examine the larger particle size. In addition, the hydrolysis reactor used in the SERI experiments is an order or

magnitude larger than that used at Dartmouth, and it should therefore provide useful operating experience. Finally, hydrolyzates made by the SERI system can be used to study fermentation and separation. SERI hydrolyzates are now being used in fermentation tests at the Tennessee Valley Authority labs in Muscle Shoals, Alabama, under subcontract to SERI. The results of all of these tests should reduce the level of uncertainty surrounding the technology and could then lead to industrial involvement and a larger demonstration plant.

DESIGN OF THE SERI EXPERIMENT

SERI's plug flow acid hydrolysis experiment is designed to determine the feasibility of hydrolyzing high solids wood slurries at an engineering scale using dilute sulfuric acid. Wherever possible, standard chemical processing equipment was selected to maximize the relevance of our results to an industrial application. A simplified process flow schematic of the process is shown in Figure 1.

The hydrolysis reaction takes place in two steps. In the first, wood flour, hot water and sulfuric acid are fed into the prehydrolysis reactor (PHRX) continuously to achieve the desired solids and acid concentrations. The PHRX operates at temperatures of 140-170°C and residence times of 5-10 min. The resultant slurry is then pressurized by a progressing cavity pump to 4.6 MPa (650 psig), and flows to the plug flow hydrolysis reactor (HRX). In this reactor the hydrolysis reaction is completed at temperatures of 240-260°C and residence times of 4-10 sec. The products of the reaction are flashed to 415 kPa (75 psig), and the vapor and liquid phases are separated, cooled,

collected and analyzed.

The system is divided into four subsystems: the prehydrolysis equipment, the hydrolysis equipment, the flash vapor recovery equipment and the hydrolyzate recovery equipment. This section describes each subsystem in more detail.

Prehydrolysis Subsystem

The prehydrolysis section consists of a 190-L (50-gal) reactor and the associated equipment for feeding wood flour, water, steam and acid at the rates required to achieve desired solids and acid concentrations, reactor temperature and residence time.

The heart of the prehydrolysis subsystem is the continuous stirred tank reactor, shown in Figure 2, which was designed by and fabricated for SERI from 316L stainless steel. The reactor is jacketed and has numerous penetrations for material addition and instrumentation. A hydraulic turbine agitator is installed in the head of the reactor to ensure thorough mixing of the wood slurry. The reactor is mounted on three BLH (5 kN) load cells which are used to determine the level of the contents of the reactor.

Water is pumped from a tank to the prehydrolysis reactor (PHRX) by a Gould 3333 14-stage centrifugal pump. The water is heated to 140-160°C by a HydroHeater M101 mixing valve which adds 1.5 MPa (200 psig) steam to achieve the desired temperature. The flow rate of the hot water is controlled by a loop consisting of a MicroMotion D40 mass flow meter, a Foxboro 760 self-tuning controller, and a Research Control Valve.

Just prior to the PHRX, concentrated sulfuric acid (93%) is metered into a mixing tee in the water line by a Durcometer B1060 double diaphragm metering pump. The 40-L (10-gal) acid storage tank is suspended from a BLH load cell to monitor acid flow rate. The acid-water mixture then enters the reactor through a dip-tube which projects to the bottom of the reactor and is penetrated by several sets of holes.

Wood flour is added to the PHRX by a VibraScrew loss-in-weight feeder with a 0.6 m³ (20 ft³) hopper. At the bottom of the hopper, two rotating blades supply wood at a constant bulk density to the main feed screw. The speed of the screw is controlled automatically to feed the appropriate mass flow rate, as measured by a load cell. Since the wood flour in the hopper tends to form bridges, ratholes and chimneys, a bridge-breaking device was installed to ensure continuous flow to the blades. The device is based on an invention developed and patented at SERI by Diebold and Scahill (10).

The wood flows from the feeder, through a plexiglass boot, and into an airlock mounted on the top of the prehydrolysis reactor. The airlock, designed and fabricated at SERI, allows wood to be added to the reactor without bleeding down the reactor pressure or allowing steam to escape into the wood supply. The airlock consists of two 6-inch pneumatically actuated knife gate valves, a 6-inch pipe hopper in between, and the valves and controls required to cycle the knife valves and pressurize the intermediate chamber. During a typical cycle, the top knife valve opens, wood drops into the chamber and the top valve closes. The chamber is then pressurized with inert gas to a pressure slightly higher than reactor pressure. The bottom valve opens and the wood drops into the reactor. Smooth flow of the wood is ensured by the injection of inert gas at several points above both knife

valves. The airlock system is controlled by the computer which runs the data acquisition program, described in a later section. The design of the airlock is described in more detail by Schell (11).

The flow rates of the wood and hot water inlet streams are controlled by a Foxboro 760 controller to provide the desired solids concentration and the prehydrolysis residence time. The controller actually seeks to regulate the level of the reactor contents, sensed by the reactor load cells, thereby controlling residence time. The ratio output feature of the level controller supplies remote set points to both the wood feed rate controller and the water flow rate controller to regulate the input streams in the correct proportion.

The PHRX pressure is controlled by a Fisher 98-H pressure relief valve, designed to bleed off the inerts introduced through the airlock and maintain a constant reactor pressure. The bleed stream, which contains some steam, is cooled, condensed and collected for later analysis.

Hydrolysis Subsystem

The hydrolysis subsystem is designed to bring the prehydrolyzed slurry to the desired hydrolysis conditions and provide the correct residence time for the reaction to be completed.

The prehydrolysis reactor is directly coupled to a hydraulically driven Moyno 9P4 progressing cavity pump with a viton stator and an undersized stainless steel rotor. The viton stator swells due to the temperature of the slurry; this swelling provides the clearances required to achieve the output pressure of 4.6 MPa (650 psig).

Just downstream of the pump, the flow rate of the slurry is measured by a Polysonics UF84 ultrasonic flowmeter. This flowrate is controlled by a Fisher analog controller which regulates Moyno pump speed by varying the hydraulic flow rate to the motor through a Worcester electrically actuated ball-type control valve. The prehydrolyzed slurry flows from the pump to the hydrolysis reactor, a pipe reactor shown in Figure 3. The reactor is 3.8 cm (1.5 in.) in diameter and 1.2 m (4 ft) long, and is fabricated from Schedule 80 Hastelloy C-276 pipe and fittings. The reactor is mounted vertically to prevent buildup of pockets of uncondensed steam. The slurry is introduced to the reactor through a long-radius elbow at the head of the reactor to induce swirling. High pressure steam (5.6 MPa, 800 psig) is injected at the elbow through a full cone Hastelloy spray nozzle, consisting of twenty 0.13-cm (0.05-in.) holes drilled at angles up to 45° to the flow. The flow of steam is regulated by a Fisher analog controller to control temperature within the reactor as measured by a thermocouple in the flow path downstream of the reactor entrance.

At the reactor discharge, the products flow through a globe-type pressure letdown valve, made by Masonelian, the purpose of which is two-fold. First, the valve serves to control the reactor pressure, sensed by a Foxboro 821GH pressure transmitter near the end of the reactor. Second, the rapid pressure and temperature drop through the valve quench the reaction, preventing degradation of the products.

The products flow through the pressure letdown valve into the flash separator, a 0.3-m (1.0-ft) diameter vessel designed by and fabricated for SERI from schedule 40 stainless steel 316L pipe and fittings. The separator is 1.4 m (4.5 ft) tall and is equipped with a 15-cm (6-in.) thick Fleximesh

mist eliminator pad near the top. The liquid level in this tank is maintained by a control loop consisting of a diaphragm type Foxboro 823DP differential pressure transmitter, a Fisher analog controller, and a flow control valve, described below in the Hydrolyzate Recovery Section.

Flash Vapor Recovery Subsystem

The vapor stream exiting the flash separator consists of steam, with small amounts of furfural, acetic acid, and some noncondensables. The flow rate of the vapor stream is controlled by a Taylor back-pressure regulator which controls separator pressure to about 415 kPa (75 psig). The stream flows through a Micromotion D100 mass flowmeter which determines mass flow directly based on the Coriolis effect.

The vapor stream then flows to a condenser, a conventional shell and tube heat exchanger supplied by American Standard (Model SSCF-8036). The level of condensate is regulated by a level control loop based on a Foxboro 823DP differential pressure transmitter. Condenser pressure is regulated by a Nupro pressure relief valve which bleeds off noncondensables. The condensate is stored in a 1100-L (300-gal) cross-linked polyethylene tank.

Hydrolyzate Recovery Subsystem

The liquid phase leaving the flash separator contains sugars, other hydrolysis products, sulfuric acid and some unreacted solids. The flow of the hydrolyzate is regulated by the level control loop on the separator, as described earlier, to ensure that the hydrolyzate leg runs liquid full. A Red

Valve 0.5-in. air-operated pinch valve is used to minimize plugging. The hydrolyzate is cooled in an American Standard SSCF-8078 four-pass horizontal shell and tube heat exchanger, and then flows through an Exac EX120 mass flow meter. The stream is stored in a 3800-L (1000-gal) polyethylene tank.

EXPERIMENTAL PROCEDURES

Product yields from the two-stage plug flow experiment can be predicted using Saeman's model (12) with kinetic parameters developed by Kwarteng at Dartmouth (4) for hardwood flour. These parameters are shown in Table 1. Using the parameters in Table 1, graphs of the product yields were prepared and are shown in Figures 4 and 5. Figure 4 shows the extent of the reaction at typical prehydrolysis conditions. As can be seen, there is little cellulose hydrolysis at these conditions. In Figure 5, hydrolysis conditions for maximum glucose yield are shown. From this graph it is evident that glucose yields above 50% should be attainable with residence times of about 5 to 8 sec at 255°C. At these conditions, the remaining hemicellulose hydrolyzes rapidly to xylose, which then degrades to furfural.

A number of experiments are planned using the two-stage hydrolysis system. Initially, the PHRX will be operated independently to examine the pumpability of a 20% slurry of hardwood flour. The prehydrolysis product will be analyzed for sugar content to determine optimum operating conditions. This will then lead to tests of the whole system with the 20% flour slurries. When these experiments are complete, tests of larger particle sizes will take place. Throughout these experiments, yields will be determined and operability of the

system will be assessed.

Each experiment is begun by bringing the equipment up to reaction conditions on water, acid and steam. Water is heated to the desired temperature, mixed with acid, and added to the prehydrolysis reactor. Steam flows to the reactor jacket. Slowly, the reactor temperature, pressure and level come to the desired conditions. The Moyno pump is started up at a speed selected to provide the approximate desired flow rate. As the viton stator in the pump swells from the hot water, the hydrolysis reactor pressure control valve can be closed to achieve the desired pressure. At this point, high pressure steam is introduced into the hydrolysis reactor to bring its temperature to the desired level. The remainder of the product separation and collection equipment is brought on line as the temperature rises. Finally, when all the equipment and control loops are operating smoothly at the desired conditions, the wood feeder is turned on to begin feeding wood to the prehydrolysis reactor.

During each experiment, the process streams are sampled at a range of conditions. Product concentrations in the samples are then determined by high performance liquid chromatography (HPLC) analysis. Data from the pressure, temperature, mass flow, level and weight instruments are recorded continuously by the data acquisition system. In addition, residence time for the hydrolysis reaction is calculated for each run based on the measured flow rate and the internal reactor volume. These data are combined with the product concentrations to determine product yields.

RESEARCH ISSUES

The experiments planned for the two-stage system will provide a more thorough understanding of the plug flow hydrolysis process. Technical issues such as the pumpability of concentrated slurries and the effect of larger particle sizes will be resolved. In addition, by analyzing the hydrolyzates and comparing the product yields to predicted results, it will be determined if the high yields obtained in laboratory research and with low solids slurries can be maintained in the two-stage process.

In addition to these issues, a variety of questions regarding operability of the process will be addressed. An important one is the buildup of solid deposits in the hydrolysis reactor and elsewhere. These deposits, believed to be a product of lignin and furfural decomposition products, caused operating problems in experiments at both SERI and Dartmouth. At severe hydrolysis conditions, the deposits buildup rapidly, eventually plugging the reactor. At high yield conditions during the low solids tests at SERI, the reactor could plug within a couple of hours. Even if the reactor doesn't plug, the decrease in internal reactor volume due to the deposits complicates the determination of residence time for an accurate characterization of reaction conditions. This problem will be investigated further during the upcoming tests to see if the rate of buildup changes with the higher solids concentration.

We'll also gain valuable lessons about equipment and material selection. High-temperature, dilute sulfuric acid is an extremely corrosive environment which necessitated special attention to materials of construction. Alloys such as Hastelloy C-276 and Carpenter 20 were used in some areas where service was particularly severe. Stainless steel 316 and 316L were used where

conditions were more moderate. Where an elastomer was required, viton was selected. All equipment will be checked periodically throughout the experiments to identify any effects of corrosion and to confirm the suitability of these materials for the conditions.

Other equipment issues will also be examined. For example, a hydraulic turbine agitator is installed on the PHRX to mix the wood slurry. We'll check for adequacy of mixing during tests. We'll also determine the success of the airlock in feeding wood to the PHRX without affecting reactor pressure. In addition, the plug flow hydrolysis process presents a number of difficult instrumentation requirements. Very few instruments are built for the combination of high temperature, high pressure, sulfuric acid and wood slurries. Flow measurement is a particular problem. We've got a variety of instruments for several different process variables throughout the system and we'll assess the suitability of these instruments for the application. Finally, identification of a slurry pump to handle the acidity, temperature and pressure was a difficult task. We believe the progressing cavity pump will do the job, but it may not be the best pump for a commercial application. We'll examine its performance and determine its suitability for larger-scale systems.

As a result of the experiments we should gain quantitative information about the product yields and concentrations and qualitative information about the operability of the system. These results will then allow us to draw conclusions about the future potential of this technology. Although questions may still remain about the scale-up to larger sizes and incorporation of the product recovery and fermentation steps, the information will exist to evaluate further development efforts.

CONCLUSIONS

Research and analysis on the plug flow reactor technology for the production of ethanol has shown significant promise, although several areas of technical uncertainty remain. Through experiments at SERI, we expect to answer several of these questions. First, is processing 20% hardwood flour slurries in a continuous flow process feasible? Second, does the use of larger particle sizes affect product yield or system operability? And finally, can an engineering-scale plug flow reactor be operated stably with high yields?

The answers to these questions will provide the foundation for further commercial development.

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Table I. Kinetic Parameters for Dilute-Acid Hydrolysis

i	Reaction	k_i (min ⁻¹)	n_i	E_i (cal/mol)
1	Crystalline cellulose --->glucose	1.44×10^{15}	1.16	33717
2	Glucose --->HMF	3.84×10^9	0.57	20988
3	Xylan --->xylose	6.17×10^{13}	1.17	27827
4	Xylose --->intermediate	2.33×10^{12}	0.69	27130
6	Furfural --->degradation products	5.55×10^5	0.58	15279
8	Furfural --->other products	4.11×10^{11}	0.52	23943

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Figure 1. Process Flow Schematic of Two-Stage Acid Hydrolysis System

Figure 2. Prehydrolysis Reactor

Figure 3. Hydrolysis Reactor

Figure 4. Product yields at Prehydrolysis Conditions
167°C, 1% H₂SO₄

Figure 5. Product yields at Hydrolysis Conditions
255°C, 1% H₂SO₄

Figure 1

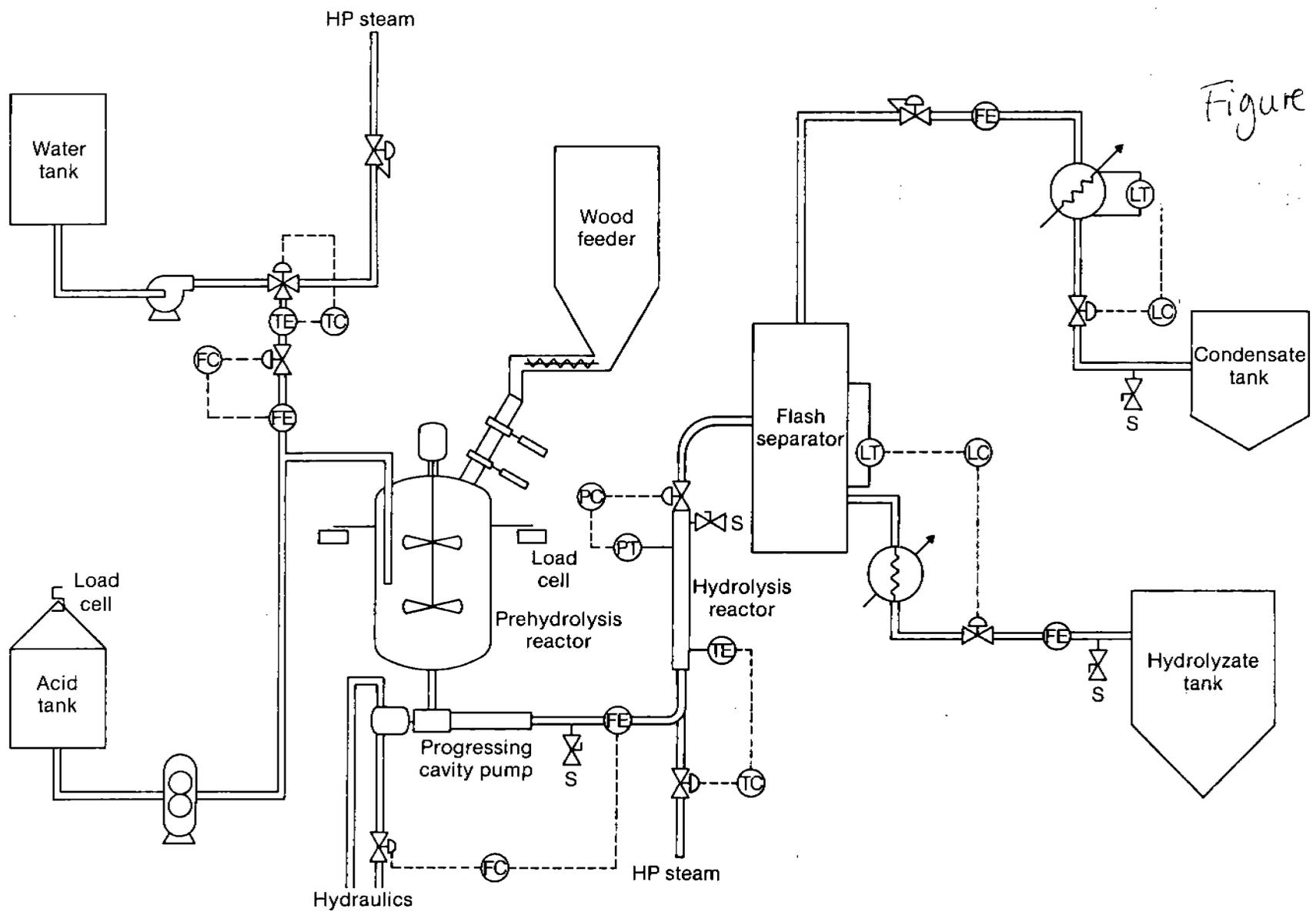


Figure 3

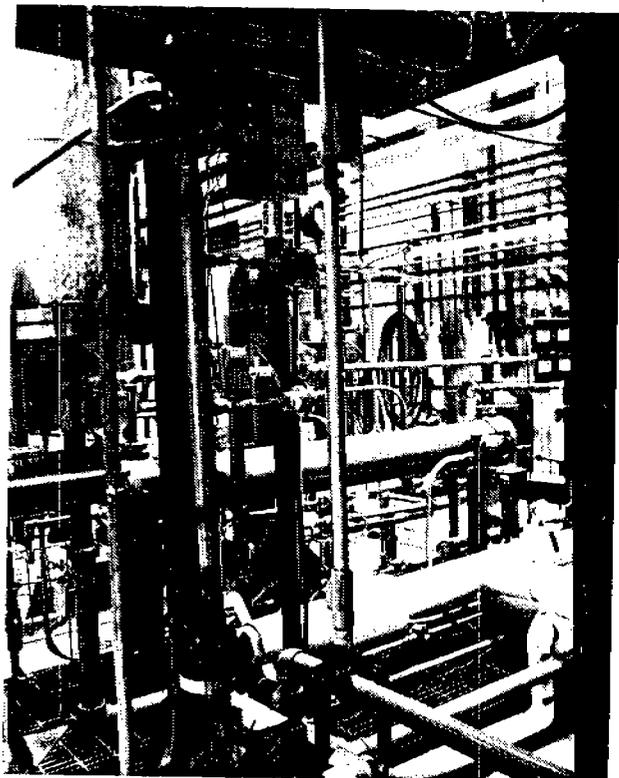


Figure 2

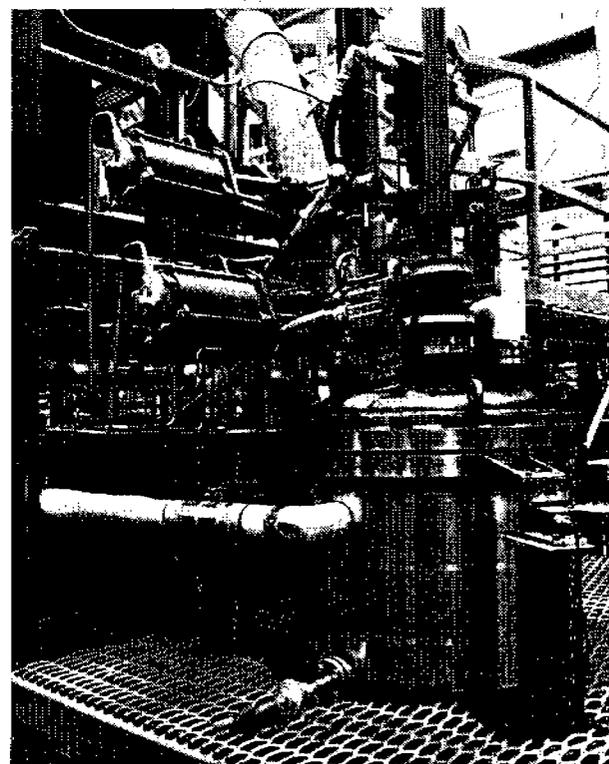


Figure 4

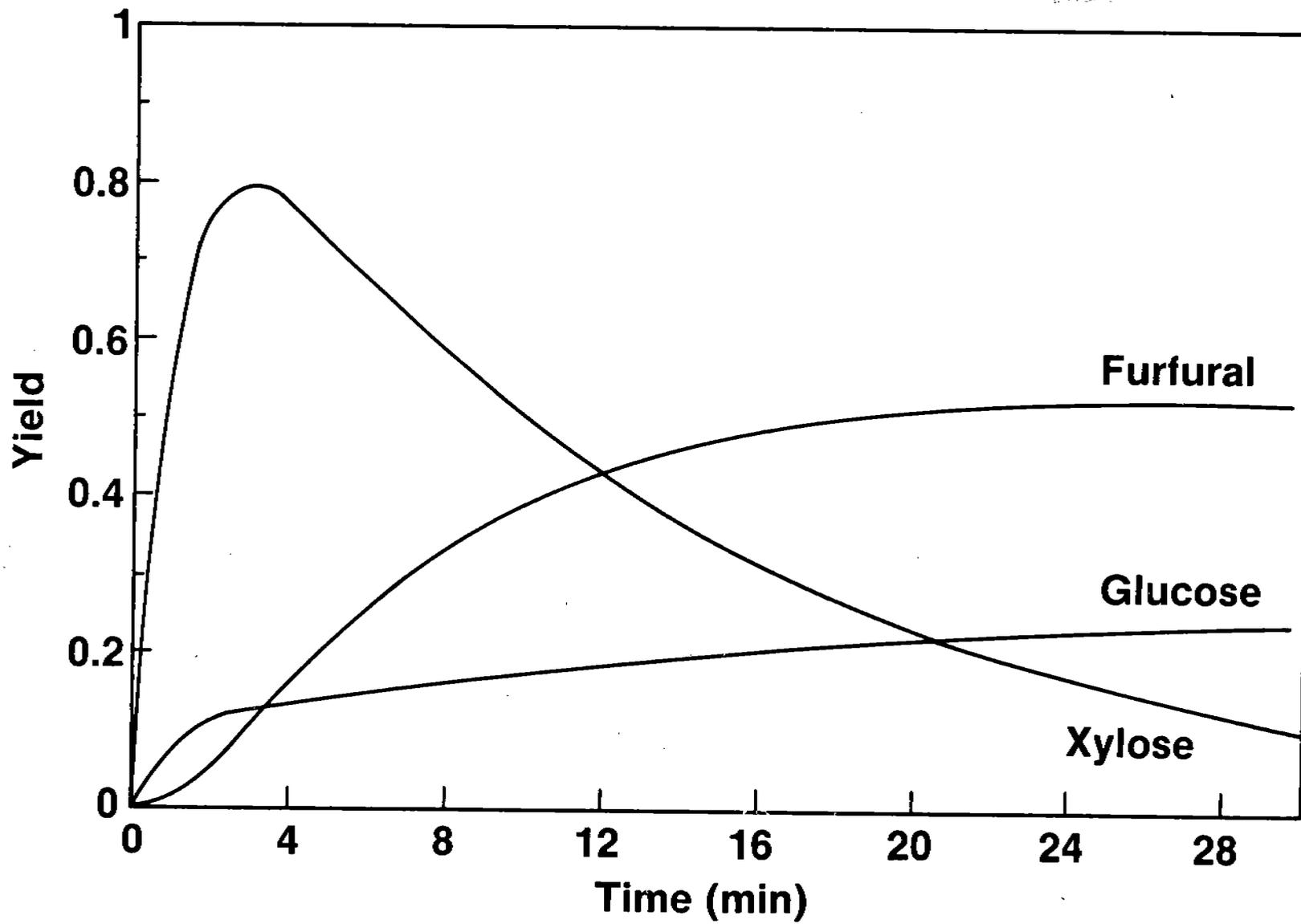


Fig 5

