DSE-3060-T3

# DESIGN, FABRICATION AND OPERATION OF A BIOMASS FERMENTATION FACILITY

Technical Progress Report No. 3, April 1—July 31, 1979

By
Daniel J. O'Neil
Alton R. Colcord
Mahendra K. Bery
Ronnie S. Roberts
Dalip K. Sondhi
Bryan C. Robb
Ronald R. Williams
Alfred A. Cook
J. J. Nachowiak
J. D. Crider

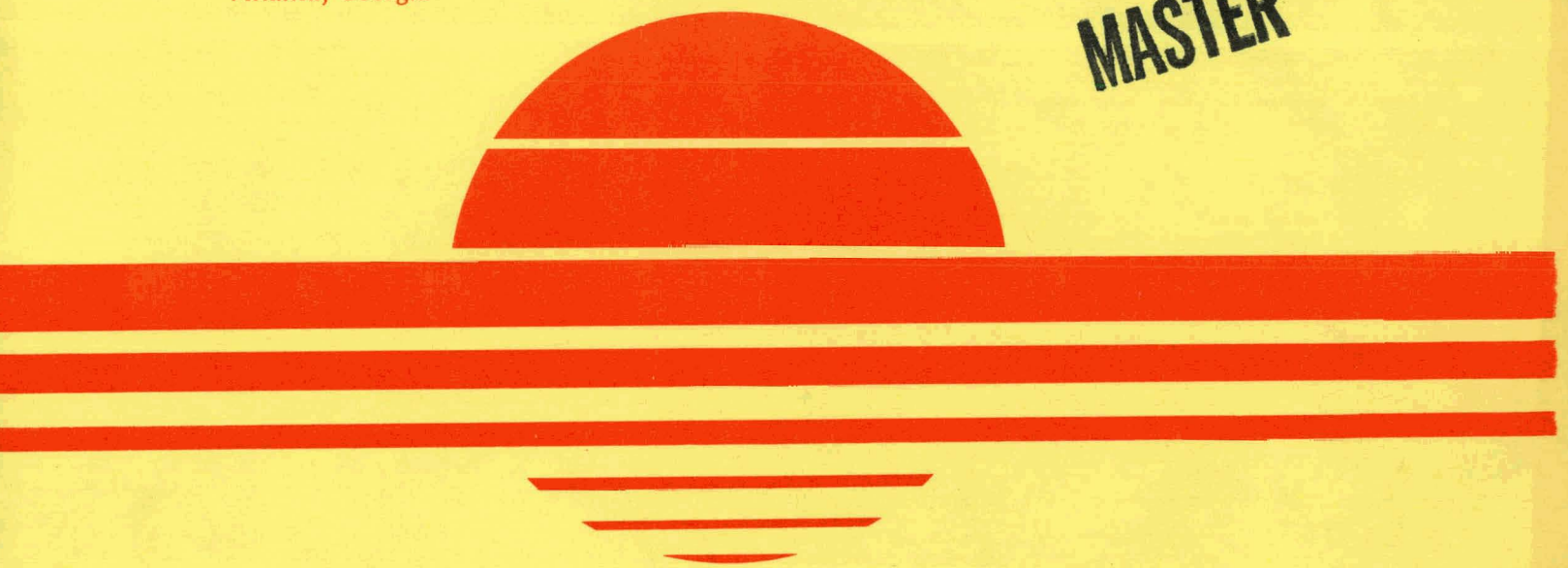
August 1979

Work Performed Under Contract No. ET-78-C-01-3060

Georgia Institute of Technology
Engineering Experiment Station
Atlanta, Georgia

Sverdrup and Parcel and Associates, Inc.
St. Louis, Missouri





U.S. Department of Energy

2071

Solar Energy

## DISCLAIMER

## DISCLAIMER



Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy $6.00
Microfiche $3.50

DSE-3060-T3
Distribution Category UC-61

# DESIGN, FABRICATION AND OPERATION OF A BIOMASS FERMENTATION FACILITY

Technical Progress Report No. 3

April 1, 1979 - July 31, 1979

Daniel J. O'Neil
Alton R. Colcord
Mahendra K. Bery
Ronnie S. Roberts
Dalip K. Sondhi

GEORGIA INSTITUTE OF TECHNOLOGY

and

Bryan C. Robb
Ronald R. Williams
Alfred A. Cook
J.J. Nachowiak
J.D. Crider

SVERDRUP AND PARCEL AND ASSOCIATES, INC.

Contract No. ET-78-C-01-3060
U.S. DEPARTMENT OF ENERGY

TABLE OF CONTENTS

## LIST OF FIGURES

## LIST OF TABLES

## 1.0 INTRODUCTION

Management of this USDOE contract was transferred from the U.S. Department of Energy in Washington to the Solar Energy Research Institute (SERI) in Golden, Colorado. Technical reviews were held in Washington in April for the USDOE, in Atlanta on May 9, 1979 for SERI, in Golden on May 27, 1979 and on June 8, 1979 for SERI. Approval for the conceptual design was received at the latter meeting. A reorientation of the design philosophy for the three oven dry ton per day process development unit resulted. The approved conceptual design is described in Section 3.0 of this report.

Further studies on process economics and optimization for hexose production from wood by dilute acid hydrolysis were conducted. In the previous report, detailed studies on process economics and optimization of hexose production were undertaken for a continuously stirred reactor (CSTR) and a plug flow reactor (PFR). These studies were based on Saeman's kinetics for a Douglas fir substrate. The studies in this report are based on Fagan's kinetics for a Kraft paper substrate. Application to a plug flow reactor and to a fixed bed reactor (FBR) have been undertaken. The initial results, as predicted in an earlier report, indicate that the FBR is at least comparable to a PFR in terms of process economics. Results of these studies are presented in Section 2.0.

Section 4.0 describes the progress which has been achieved under Task 2 of this contract, "Detailed Engineering Design," which had been interrupted by the unanticipated revisions, and concomitant delay, experienced in obtaining final approval of the conceptual design for the process development unit.

## 2.0 PROCESS ECONOMICS

### 2.1 Further Studies on Process Economics and Optimization for Hexose Production by Dilute Acid Hydrolysis in a Plug Flow Reactor

In a previous report (1) an optimization study on hexose production by the acid hydrolysis of cellulose was discussed. The study was based on a CSTR/PFR system with a recycle of the unreacted cellulose. It was shown that an optimized PFR recycle system could produce hexose for less than 5.7¢/lb.

The hydrolysis of cellulose is considered to follow the reaction sequence:

$$\text{Cellulose} \xrightarrow{k_1} \text{Hexose} \xrightarrow{k_2} \text{Degradation products} \qquad (2.1)$$

Where the rate constants are functions of acid concentration $C_A$ and temperature T:

$$k_1 = k_{10}\, C_A^m \exp\,(-E_1/RT) \qquad (2.2)$$

and

$$k_2 = k_{20}\, C_A^n \exp\,(-E_2/RT) \qquad (2.3)$$

The previously reported study used Saeman's values for the parameters $k_{10}$, $k_{20}$, m, n, $E_1$ and $E_2$ (2). These values are indicated for a Douglas Fir substrate. Fagan *et al.* (3) reported different values of these parameters for a Kraft Paper substrate. Both sets of parameter values are summarized in Table 2-1. Table 2-2 shows a comparison of the rate constants $k_1$ and $k_2$ calculated from the two sets of parameter values shown in Table 2-1. The acid concentration is assumed to be one weight percent for the comparison. Some preliminary calculations have been made with the Fagan parameters to determine their impact on conclusions reached in the previous study. All the results reported here were obtained using essentially the same computer program of the previous work (1). The system parameters used here are shown in Table 2-3.

Table 2-1 Summary of Values of the Kinetic Parameters of Saeman (2) and Fagan et al. (3) for the Acid Hydrolysis of Cellulose

| Parameter | Units | Saeman Values for Douglas Fir | Fagan et al. Values for Kraft Paper |
|---|---|---|---|
| $k_{10}$ | $min^{-1}$ | $1.73 \times 10^{19}$ | $2.80 \times 10^{20}$ |
| $k_{20}$ | $min^{-1}$ | $2.38 \times 10^{14}$ | $4.90 \times 10^{14}$ |
| m | - | 1.34 | 1.78 |
| n | - | 1.02 | 0.55 |
| $E_1$ | cal/gm mole | 42,900 | 45,100 |
| $E_2$ | cal/gm mole | 32,870 | 32,800 |

Table 2-2 Comparison of the Rate Constants of Cellulose Hydrolysis Calculated from Saeman (2) and Fagan (3) Parameters for Various Temperatures and 1 Weight Percent Sulfuric Acid

| Temperature °C | $k_1$, $hr^{-1}$ | | $k_2$, $hr^{-1}$ | |
|---|---|---|---|---|
| | Saeman | Fagan | Saeman | Fagan |
| 170 | 0.71 | 0.95 | 0.87 | 1.94 |
| 180 | 2.09 | 2.93 | 1.98 | 4.41 |
| 190 | 5.84 | 8.65 | 4.36 | 9.68 |
| 200 | 15.7 | 24.4 | 9.28 | 20.6 |
| 210 | 40.3 | 65.9 | 19.1 | 42.4 |
| 220 | 99.7 | 171 | 38.3 | 84.8 |

Table 2-3 Recycle System Parameters for Fagan et al. Kinetics (3)

| Parameter | Value | Remarks |
|---|---|---|
| $C'_{co}$ | 115 kg equivalent hexose per $m^3$ | cellulose feed concentration equivalent to 10 wt% cellulose |
| $C_A$ | 3 wt percent | concentration of sulfuric acid |
| $\$_c$ | \$0.066/kg equivalent hexose | cost of cellulose assuming cellulose is 45% of wood and the cost of wood is \$30 per oven-dry ton |
| $\$_A$ | \$0.088/kg | cost of sulfuric acid at \$60/ton and the equivalent lime for neutralization at \$35/ton |
| $\$_{recycle}$ | \$0.0055/kg equivalent hexose | cost of recycling unreacted cellulose |
| $\$_R$ | \$0.40/$m^3$-hr | cost of reactor |
| $\$_{conc}$ | \$1.39/$m^3$ evaporated | cost of concentrating hexose solution. Based on five-effect evaporator with energy costing \$2/MM BTU |
| $C^*_g$ | 135.0 kg hexose/$m^3$ | desired hexose concentration, equivalent to 13 wt % hexose solution |
| T | 463K | temperature equivalent to 190° C |
| $\theta$ | 0.9 kg cellulose recycled/kg cellulose unreacted | fraction of unreacted cellulose recovered |

Figure 2.1 shows the sensitivity of the optimum hexose production cost to acid concentration for a PFR at 170°C and 190°C. An optimum acid concentration of approximately three percent is indicated. Table 2-4 shows the sensitivity of the optimum hexose production cost and the optimum residence time to temperature for three percent by weight sulfuric acid. Convergence problems were encountered in the computations above 200°C. However, it appears that at temperatures above 200°C optimum residence times will become too small (i.e., below 30 seconds) for proper operation of the reactor. A residence time of at least one minute is considered desirable to allow for sufficient mixing time of the feed materials in the reactor. At 190°C the minimized hexose production cost results in a slightly higher figure than 5.7¢/lb. Table 2-5 summarizes a comparison of optimized results based on Saeman's and Fagan's kinetic parameters. It is to be noted that the Saeman parameters showed an optimum acid concentration around one percent whereas the Fagan parameters indicate three percent acid. The Fagan kinetic parameters were developed using acid concentrations of 0.2, 0.5 and 1.0 percent. The use of the equations at three percent acid then represents a considerable extrapolation of these data. It is also important to note that Fagan *et al*. did not directly measure the degradation rate of the glucose. Their data consisted of simultaneous cellulose concentration and glucose concentration versus time profiles. A least square error approach was then used to fit the model parameters to these data. Fagan's parameters for the degradation of glucose in particular is not in agreement with Saeman's parameters. Under the conditions shown in Table 2-2, Fagan's $k_2$ is more than twice the $k_2$ reported by Saeman. Saeman directly measured the degradation of glucose in a cellulose-free system. The difference in the two could be the result of increased glucose degradation in relatively stagnant regions such as the interstices in the cellulose. The difference could also be due simply to the data fitting technique.

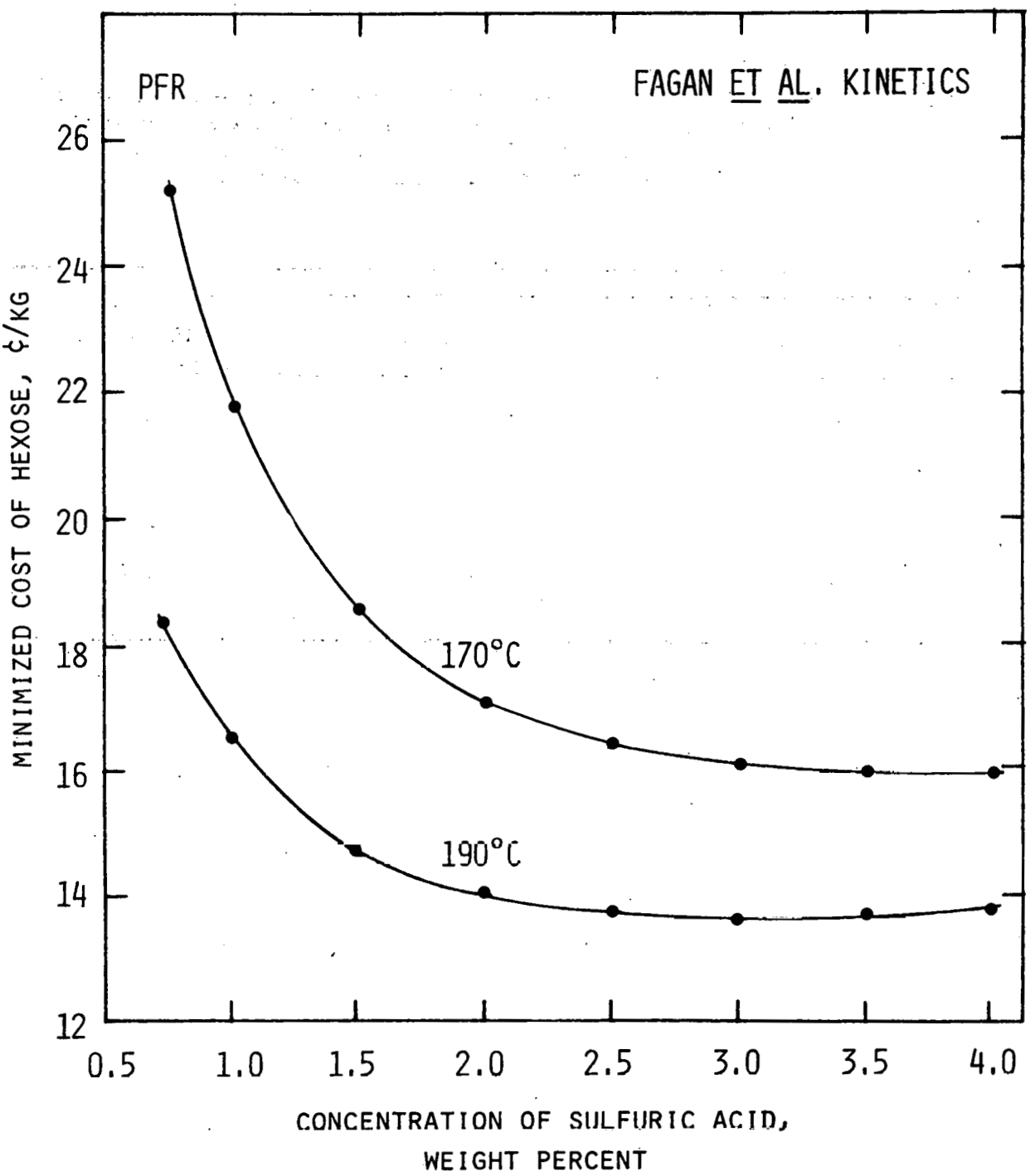



Figure 2.1. Effect of Sulfuric Acid Concentration on The Minimized Cost of Producing a 13% Hexose Solution in a PFR System (See Table 2-3 for Other Operating Conditions)

Table 2-4 Sensitivity of the Optimum Residence Time and the Minimized Cost of Hexose to Temperature in a PFR Recycle System at 3% Sulfuric Acid and 10% Cellulose Slurry Concentration (See Table 2-3 for other operating conditions)

| Temperature °C | Optimum Residence Time, Minutes | Minimized Hexose Cost, ¢/kg |
|---|---|---|
| 170 | 8.9 | 16.1 |
| 180 | 3.3 | 14.6 |
| 190 | 1.3 | 13.6 |
| 200 | 0.51 | 12.7 |

In summary, the kinetic parameters of Saeman and Fagan et al. result in different sets of operating conditions in an optimized PFR recycle system as can be seen in Table 2-5. In particular, the Fagan parameters indicate a lower operating temperature of 190°C and a higher acid concentration of three weight percent. The latter condition involves a considerable extrapolation of the kinetic data of Fagan et al. Also, Fagan's kinetic parameter, $k_2$, is not the result of a direct measurement of the degradation of glucose and is in considerable disagreement with Saeman's value. In spite of these drawbacks, it is important to note that both the lower temperature and higher acid concentration can be achieved in the existing conceptual design of the PDU without modifications. In order to realize a satisfactory hexose production cost, it will be necessary to operate at cellulose-slurry concentrations higher than ten weight percent.

## 2.2. OPTIMIZATION: FIXED BED REACTOR

Minimum cost functions for the production of hexose by a continuous stirred tank reactor (CSTR) and a plug flow reactor (PFR) have been previously reported (1). A similar minimum cost function can be developed for a fixed bed reactor (FBR). A generalized process to produce a hexose solution of given concentration by dilute acid hydrolysis is shown in Figure 2.2. The assumptions made in conducting the model process are presented in Table 2.6. The model parameters to be investigated for the process are given in Table 2.7. The major cost elements of producing hexose by this process can be given as:

$$\begin{aligned}\text{cost/kg hexose} = (&\text{cost of cellulose consumed}\\ &+ \text{cost of acid-lime}\\ &+ \text{cost of reactor}\\ &+ \text{concentrator cost})/\text{kg hexose}\end{aligned} \qquad (2.4)$$

In order to minimize the cost of hexose a model of the FBR was developed. The kinetics for the saccharification of cellulose and the degradation of glucose reported by Saeman (2) were used to model the reaction (2.1). The FBR is shown in Figure 2.3.

Table 2-5 Optimized Hexose Production in a PFR Using Saeman (2) Kinetic Parameters and Fagan (3) Kinetic Parameters

| PFR System Condition | Saeman Parameters | | Fagan Parameters | |
|---|---|---|---|---|
| | 10%* | 20%* | 10 %* | 20%* |
| Temperature, °C | 210 | 210 | 190 | 190 |
| Optimum Res. Time, Min. | 1.4 | 1.3 | 1.3 | 1.1 |
| Optimum Acid Concn, wt% | 1.0 | 1.0 | 3.0 | 3.0 |
| Minimized Hexose Cost, ¢/kg | 12.5 | 10.3 | 13.6 | 10.4 |
| Cellulose Converted to Hexose, wt% | 77.4 | 79.7 | 79.9 | 82.2 |

* concentration of the cellulose slurry

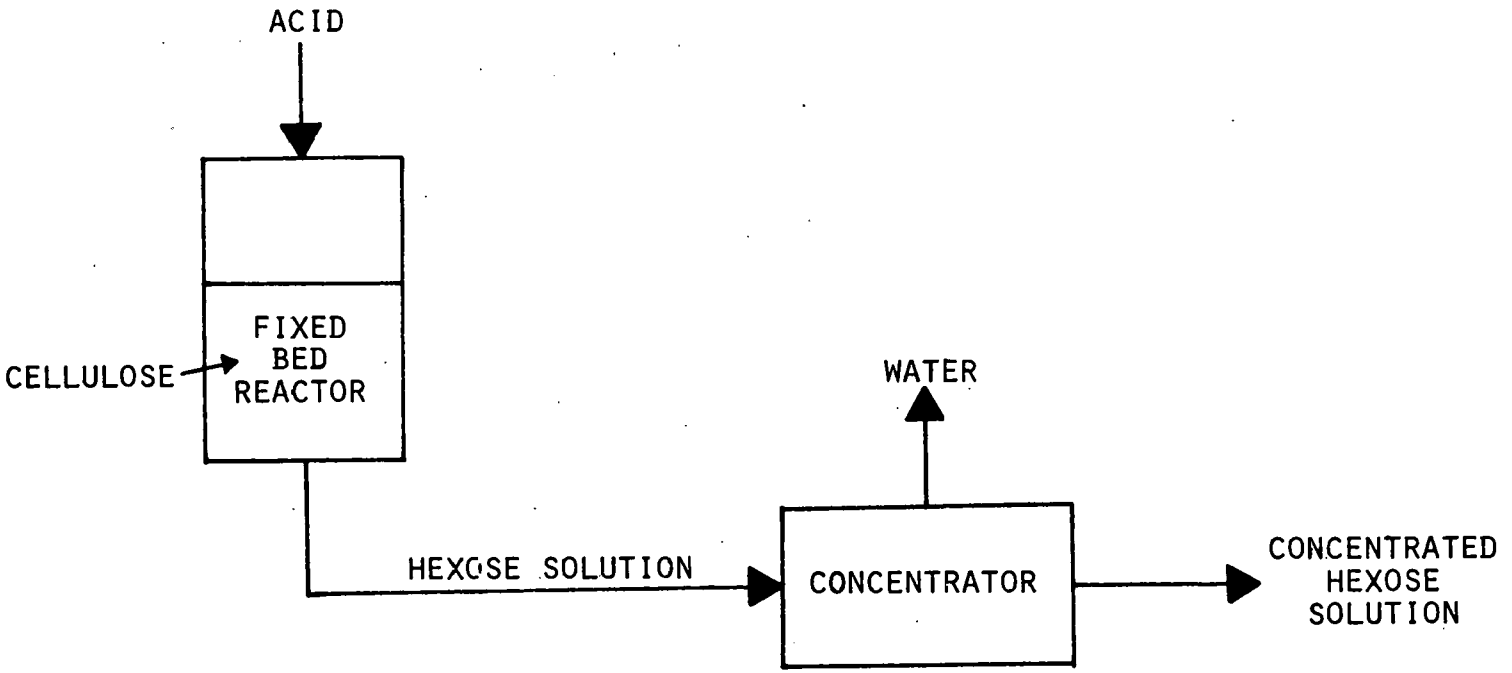



Figure 2.2 Process to Produce a Hexose Solution by Dilute Acid Hydrolysis of Cellulose

Table 2.6 Process Assumptions

| |
|---|
| 1. Cellulose feed free of hemicellulose and lignin |
| 2. Douglas fir kinetics (Saeman) |
| 3. Cost of cellulose based on wood cost at 45% cellulose content |
| 4. No credit for lignin or hemicellulose |
| 5. The cellulose concentration is constant |
| 6. The flowrate of the acid is varied with time to give a constant residence time |
| 7. Lime neutralization of hydrolysis acid solution |
| 8. Multiple-effect evaporation to concentrate hexose solution |
| 9. 13% final hexose concentration |

Table 2.7 Model Parameters

| |
|---|
| 1. Cost of cellulose |
| 2. Concentration of cellulose |
| 3. Concentration of sulfuric acid |
| 4. Temperature |
| 5. Cost of reactor |
| 6. Cost of sulfuric acid and the equivalent lime for neutralization |
| 7. Cost of concentrating hexose solution |
| 8. Concentration of final hexose solution |

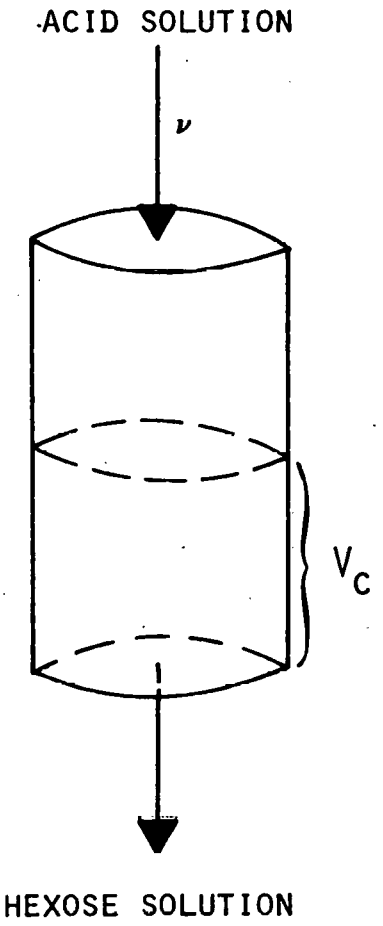



Figure 2.3 Fixed Bed Reactor

Initially the reactor contains only cellulose. At time zero, acid is introduced into the reactor. Plug flow of the acid is assumed. The reaction of the cellulose is first order with respect to cellulose (2). Assuming that the bulk density of the cellulose is constant, the volume of the reactor occupied by the cellulose decreases with time. The residence time, $\tau$, decreases with time if the flowrate of the acid remains constant. A constant $\tau$ is preferable since the yield of hexose tends to dominate the cost function. The flowrate of acid must then decrease with time for $\tau$ to remain constant.

$$\tau = \text{constant} = V_c/\nu \tag{2.5}$$

where $\tau$ = residence time

and $V_c$ = volume of reactor which contains cellulose

Therefore $\nu = V_c/\tau$ (2.6)

The rate at which the cellulose disappears in the presence of acid is

$$-C_c' \frac{dV_c}{dt} = k_1 C_c' V_c \tag{2.7}$$

where $C_c'$ = concentration of cellulose expressed as equivalent hexose

The initial acid into the reactor will contact cellulose of volume $V_c$ and take time $\tau$ to pass through the cellulose. The volume of cellulose contacted by the acid exiting the reactor at any time t will be

$$\int_{V_{co}}^{V_c} dV_c/V_c = -k_1 \int_0^{t-\tau} dt \tag{2.8}$$

or $$V_c = V_{co} e^{-\alpha} \tag{2.9}$$

where $\alpha = k_1 (t-\tau)$

$V_{co}$ = volume of reactor which contains cellulose initially

$k_1$ = rate constant for the saccharification of cellulose

and $t$ = elapsed time since acid was introduced into the reactor

Note that $t$ must exceed $\tau$ for acid to exit the reactor.

The volumetric flowrate of acid leaving the reactor for constant $\tau$ assuming an approximately constant density process would be

$$\nu = V_c/\tau = V_{co}\, e^{-\alpha}/\tau \qquad (2.10)$$

The concentration of hexose leaving the reactor will be a function of the residence time. Assuming that the initial concentration of hexose is zero and that the density of the aqueous phase is approximately constant,

$$\frac{dC_g}{d\tau} = k_1 C_c' - k_2 C_g \qquad (2.11)$$

where $C_g$ = concentration of hexose

and $k_2$ = rate constant for the degradation of hexose

Therefore,
$$\int_0^{C_g} dC_g (k_1 C_c' - k_2 C_g)^{-1} = \int_0^{\tau} d\tau \qquad (2.12)$$

or
$$C_g = (k_1 C_c'/k_2)(1-e^{-\beta}) \qquad (2.13)$$

where $\beta = k_2\tau$

A complete reactor cycle of the FBR would consist of:

(1) Introducing acid for time $(t-\tau)$ into the cellulose;

(2) Draining acid from the cellulose for time $\tau$; and

(3) Time, $t_d$, for introducing fresh cellulose into the reactor including turnaround time.

The total time per batch would be:

$$t_t = (t-\tau) + \tau + t_d = t + t_d \qquad (2.14)$$

where $t_t$ = total time per batch cycle

Neglecting the hexose remaining with the cellulose. The production of hexose per cycle of the reactor will be

$$Q_g = \int_{\tau}^{t} C_g \nu dt \qquad (2.15)$$

Integration upon insertion of equations (2.10) and (2.13) gives

$$Q_g = (V_{co} C_c'/\beta)\ (1-e^{-\beta})\ (1-e^{-\alpha}) \qquad (2.16)$$

The consumption of the acid per reactor cycle is

$$Q_A = \int_{\tau}^{t} C_A \nu dt \qquad (2.17)$$

$$\text{or } Q_A = (V_{co} C_A/\gamma)\ (1-e^{-\alpha}) \qquad (2.18)$$

where $C_A$ = concentration of the acid

and $\gamma = k_1\tau$

The consumption of cellulose per cycle of the reactor is

$$Q_c = \rho_c (V_{co} - V_c) \qquad (2.19)$$

$$\text{or } Q_c = \rho_c V_{co} (1-e^{-\alpha}) \qquad (2.20)$$

where $\rho_c$ = bulk density of the cellulose

The cost function (2.4) can now be written as

$$f(t,\tau) = (f_1 f_3/f_2) + f_4 \tag{2.21}$$

In equation (2.21) above

$f$ = cost/kg hexose

$f_1$ = (cost of cellulose consumed + cost of acid-lime + cost of reactor) per cycle

$$= \$_c Q_c + \$_A Q_A + \$_R V_{co}$$

$$= \$_c V_{co} \rho_c (1-e^{-\alpha}) + (\$_A V_{co} C_A/\gamma)(1-e^{-\alpha}) + \$_R V_{co} \tag{2.22}$$

$f_2 = Q_g$, production of hexose per cycle as given by equation (2.16) (2.23)

$f_3$ = total cycle time, $t_t = t + t_d$ (2.24)

$f_4$ = concentrator cost = $\$_{conc}(1/C_g - 1/C_g^*)$

$$= \$_{conc}\left[\{k_2/(k_1 C_c')\}/(1-e^{-\beta}) - 1/C_g^*\right] \tag{2.25}$$

where $\$_c$ = cost of cellulose

$\$_A$ = cost of acid and equivalent lime for neutralization

$\$_R$ = cost of reactor

$\$_{conc}$ = cost of concentrating the hexose solution to the desired value

$C_g^*$ = desired hexose concentration

Extreme points and inflection points can be determined using the minima-maxima principle:

$$\frac{\partial f}{\partial \tau} = 0 \tag{2.26}$$

and $$\frac{\partial f}{\partial t} = 0 \qquad (2.27)$$

If t and $\tau$ are, in general, denoted by x, then differentiation of f gives

$$\frac{\partial f}{\partial x} = \frac{\partial}{\partial x}\left[(f_1 f_3/f_2) + f_4\right]$$

$$= \left[f_1\frac{\partial f_3}{\partial x} + f_3\frac{\partial f_1}{\partial x} - (f_1 f_3/f_2)\frac{\partial f_2}{\partial x}\right]/f_2 + \frac{\partial f_4}{\partial x} \qquad (2.28)$$

Differentiation of equations (2.22), (2.23), (2.24), and (2.25) with respect to $\tau$ gives:

$$\frac{\partial f_1}{\partial \tau} = -\left[\$_c \rho_c V_{co} k_1 e^{-\alpha}\right] + \left[\$_A C_A V_{co}/(\gamma\tau)\right]\left[(1-\gamma)e^{-\alpha}-1\right] \qquad (2.29)$$

$$\frac{\partial f_2}{\partial \tau} = \left[V_{co} C_c'/(\beta\tau)\right]\left[(1-\gamma)e^{-\alpha} + (1+\beta)\, e^{-\beta} - (1+\beta-\gamma)e^{-(\alpha+\beta)} - 1\right] \qquad (2.30)$$

$$\frac{\partial f_3}{\partial \tau} = 0 \qquad (2.31)$$

$$\frac{\partial f_4}{\partial \tau} = -\left[\$_{conc} k_2^2/(k_1 C_c')\right]\left[e^{-\beta}/(1-e^{-\beta})^2\right] \qquad (2.32)$$

Differentiation of equations (2.22), (2.23), (2.24), and (2.25) with respect to t gives:

$$\frac{\partial f_1}{\partial t} = k_1 V_{co} e^{-\alpha}(\$_c \rho_c + \$_A C_A/\gamma) \qquad (2.33)$$

$$\frac{\partial f_2}{\partial t} = (k_1 V_{co} C_c'/\beta)\ (1-e^{-\beta})e^{-\alpha} \qquad (2.34)$$

$$\frac{\partial f_3}{\partial t} = 1 \tag{2.35}$$

$$\frac{\partial f_4}{\partial t} = 0 \tag{2.36}$$

Extreme points and inflection points can now be determined by substituting the $f_i$'s and the $\left(\frac{\partial f_i}{\partial x}\right)$'s into equation (2.28) and setting the expression equal to zero. The two resulting non-linear equations can be solved for values of t and $\tau$. A computer program is being completed to obtain these values for the FBR. The FBR results will be presented in the next quarterly report.

## REFERENCES


1. O'Neil, D.J., et al., "Design, Fabrication and Operation of a Biomass Fermentation Facility," April 1979, GIT/EES Project No. A-2256-000, Technical Progress Report No. 1 (USDOE Contract No. ET-78-C-01-3060).

2. Saeman, J.F., "Kinetics of Wood Saccharification," Industrial and Engineering Chemistry, 1945, 37, VI, 43.

3. Fagan, R.D., et al., "Kinetics of the Acid Hydrolysis of Cellulose Found in Paper Refuse," Environmental Science and Technology, June 1971, 5, No. 6, 545.

## 3.0 DESIGN FOR PDU

### 3.1 Approved Conceptual Design

On June 8, 1979 representatives of SERI, Georgia Tech and Sverdrup and Parcel met and approved the conceptual design of the PDU as shown in block diagram form in Figure 3.1. As shown in this figure the "mainline" process includes the hydrothermal decompression pretreatment, prehydrolysis, dilute acid hydrolysis, (batch) fermentation and alcohol recovery. Since azeotropic distillation is presently the only viable process for producing anhydrous alcohol and since the technology is well developed, it was agreed not to include the production of 100% alcohol in the PDU at this time. A product containing 60 to 85% ethanol will be produced. However, the PDU will be prepared to investigate new separation techniques as they become available in the future. Several optional processes have been included in the conceptual design and will be included in the detailed engineering design but will not be constructed initially with the mainline system.

Dilute acid hydrolysis using a plug flow reactor will be included in the P and I diagrams and the detailed design. Enzymatic hydrolysis, simultaneous saccharification and fermentation, continuous fermentation with recycle and continuous tower fermentation processes are options which are included in the P and I diagrams but will not be included in the detailed engineering design.

### 3.2 PROCESS P & I DIAGRAMS

#### 3.2.1 Mainline System

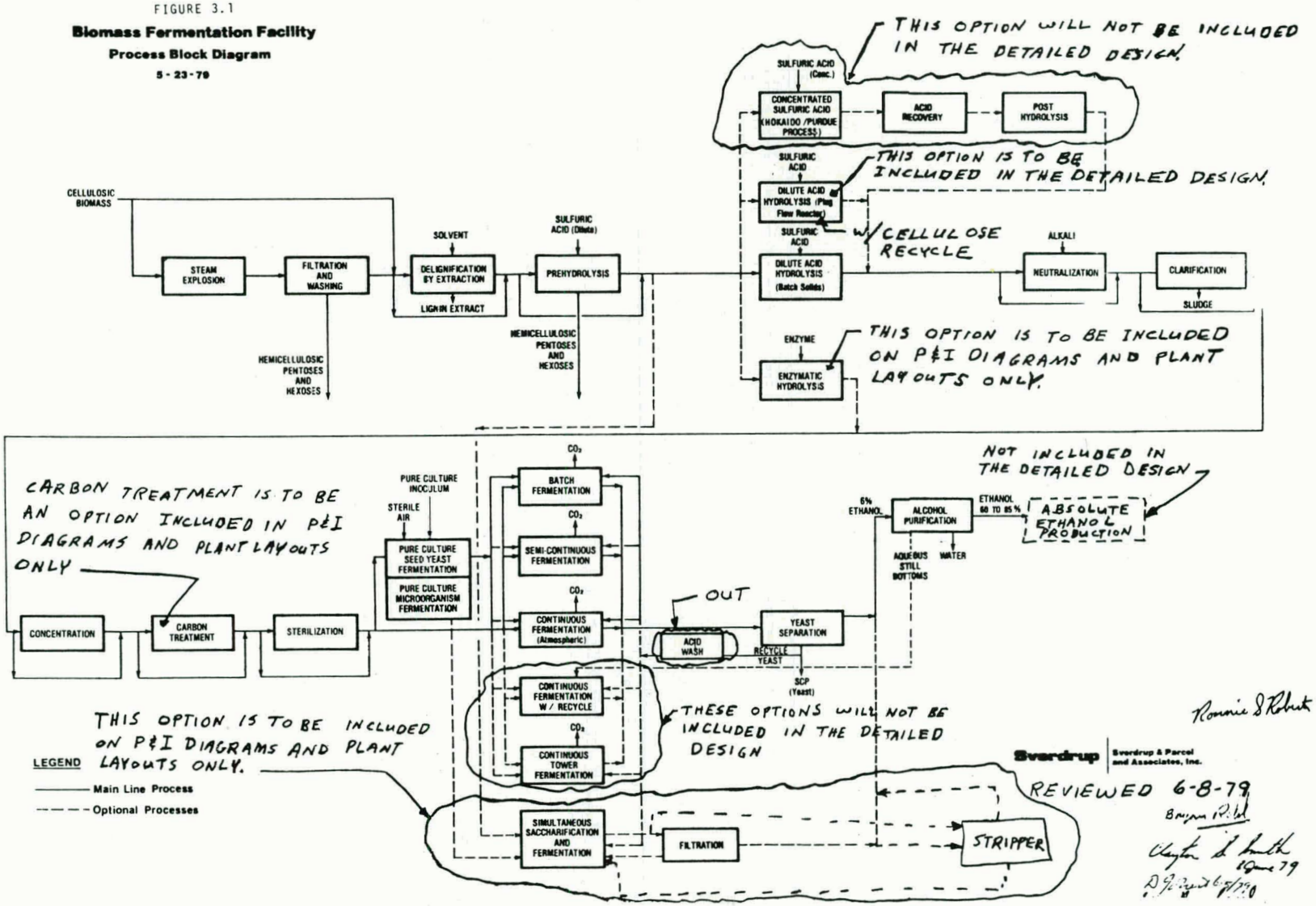
The mainline PDU consists of the following systems: pretreatment, hydrolysis (including prehydrolysis), neutralization and concentration, fermentation and alcohol recovery. The pretreatment system P & I diagram is shown in Figure 3.2. Referring to this diagram the biomass (wood chips) is first processed through a hammermill to reduce the chip size preparatory to hydrothermal decompression. The hammermilled wood is then conveyed to a feed hopper which feeds a "gun". After the "gun" is loaded with wood chips, saturated steam is introduced at a pressure between 500 and 1000 psi. The wood

FIGURE 3.1

**Biomass Fermentation Facility**

**Process Block Diagram**

**5-23-79**




Ronnie S Robert

Sverdrup | Sverdrup & Parcel and Associates, Inc.

REVIEWED 6-8-79

Bryan P. Lee

Clayton L Smith 8 June 79

D. J. Reed 6/7/79

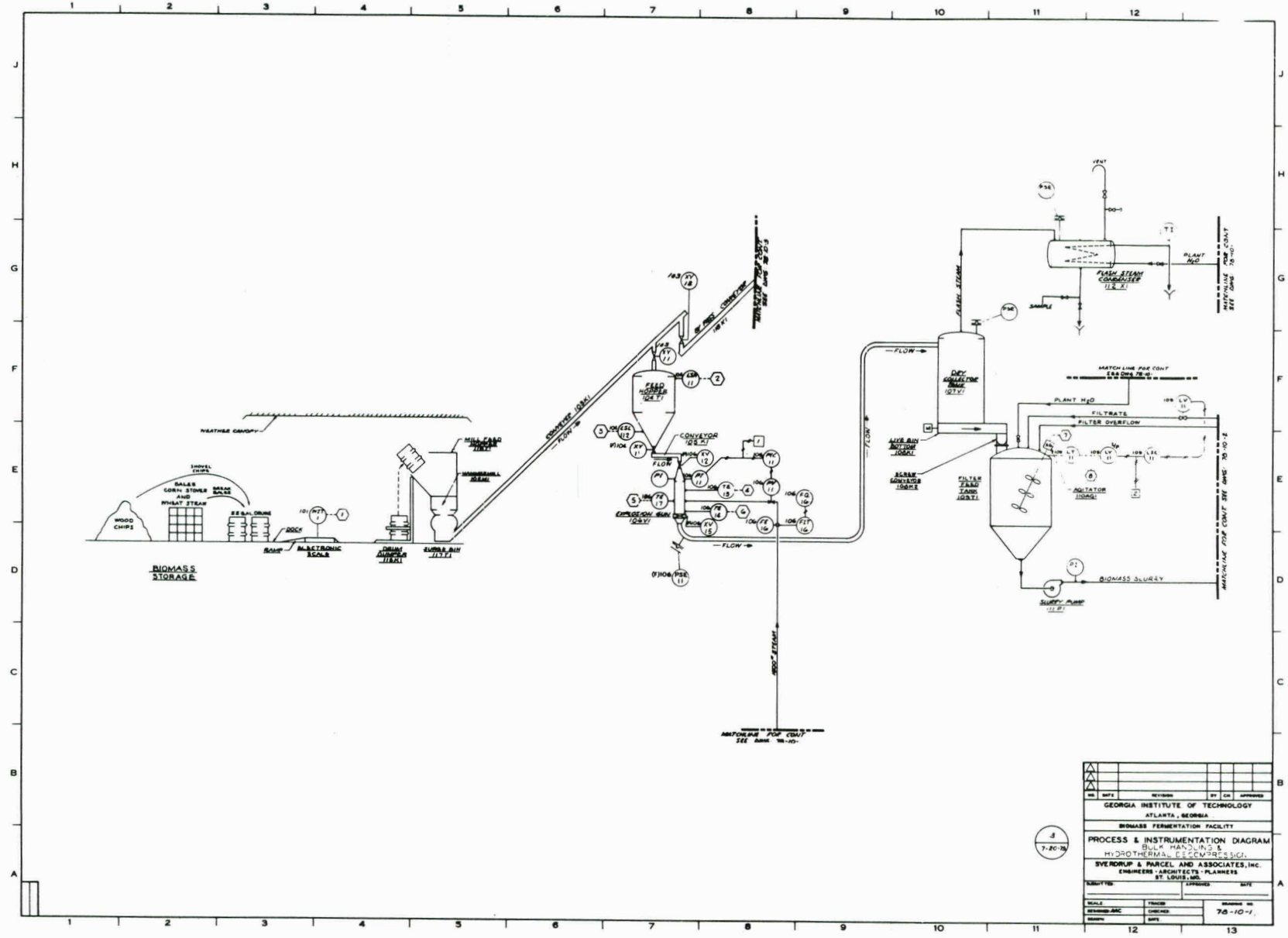



FIGURE 3.2 PRETREATMENT

is soaked at this pressure for the required time and then discharged through a quick opening valve and nozzle. The effect is to explosively decompress the wood separating the lignin from the biomass thus permitting the lignin to be easily extracted. The exploded biomass is then washed to extract the water solubles by slurring and processing through the rotary vacuum filter which is shown in Figure 3.3 The filtrate is either sampled and monitored or pumped to storage tanks. The washed filter cake is conveyed to the solids storage bin for delignification and subsequent hydrolysis. The deliginification of the biomass filter cake take place in the extraction unit shown in Figure 3.4. After the extraction vessel is filled with the biomass, ethanol or other suitable solvent and removed from the holocellulose. The solvent containing the lignin is transported to a solvent recovery unit where the solvent is recovery and recycled and the lignin is monitored and collected.

The extracted biomass is steam purged to remove residual solvent and then subjected to a mild acid prehydrolysis (0.5% $H_2SO_4$ at 150°C) to remove the remaining hemicellulose. The prehydrolysis liquor is then pumped to the prehydrolyzate holding tanks and held for subsequent processing or disposal. The remaining solid biomass which is essentially cellulose is fed into the fixed bed reactor where it is treated with dilute sulfuric acid at relatively high temperature (190°C) compared to the prehydrolysis. The hydrolyzate liquor is pumped from the reactor through a flash tank to reduce the temperature and pressure and then stored in the hydrolyzate storage tanks prior to further processing.

The ethanol (or solvent) lignin solution is fed to a system shown in Figure 3.5 where the lignin and ethanol are separated and the ethanol is recovered for reuse. The solution is pumped continuously to a vacuum stripping column where the lignin is removed from the bottom as a lignin water slurry and the overhead consists of essentially ethanol and water. The ethanol water solution is fed into the ethanol recovery still where the approximately 95% ethanol product from the still overhead is returned to the ethanol storage tank. The bottoms from this still is essentially water and is monitored and discarded.

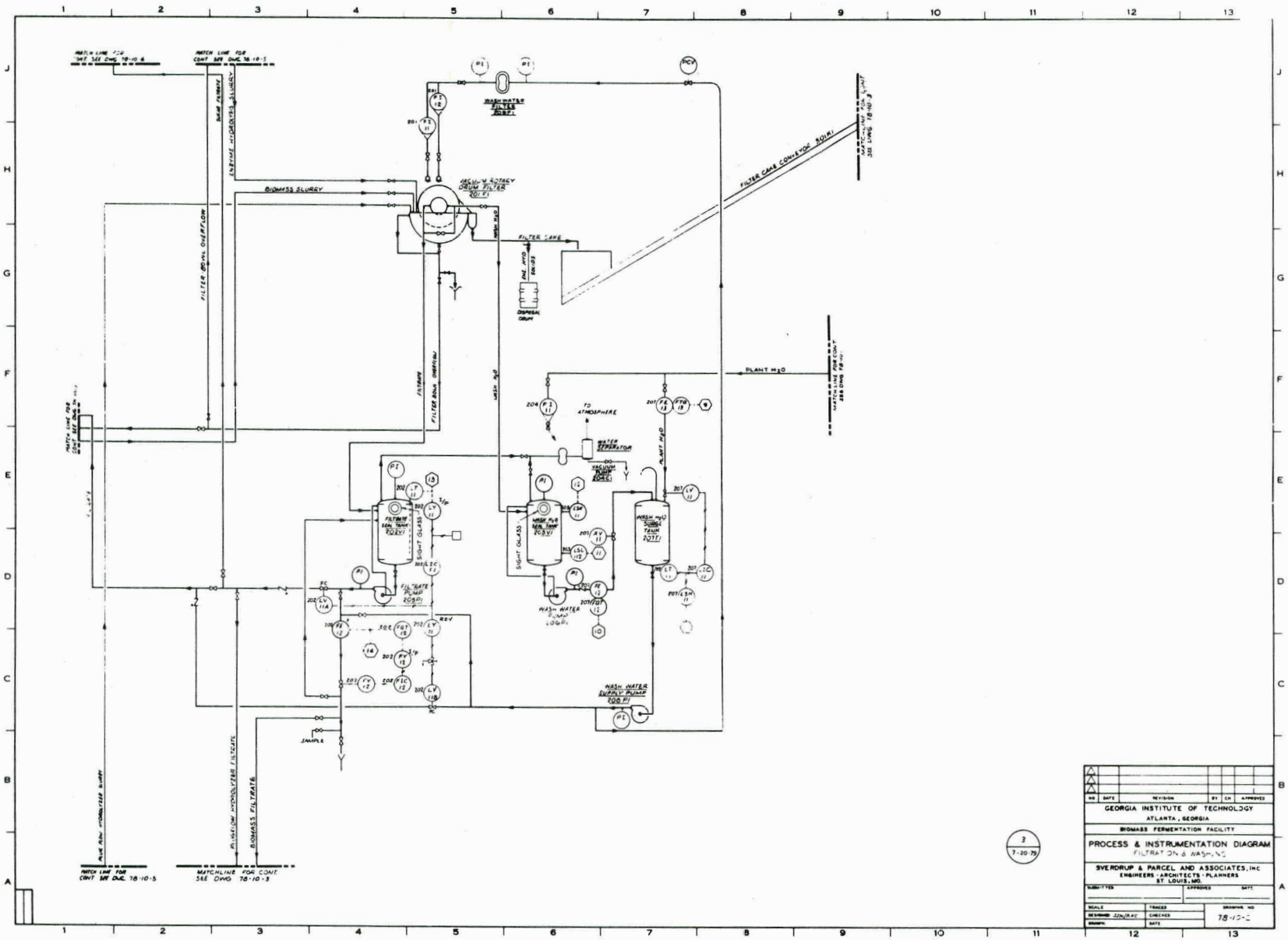



FIGURE 3.3 FILTRATION AND WASHING

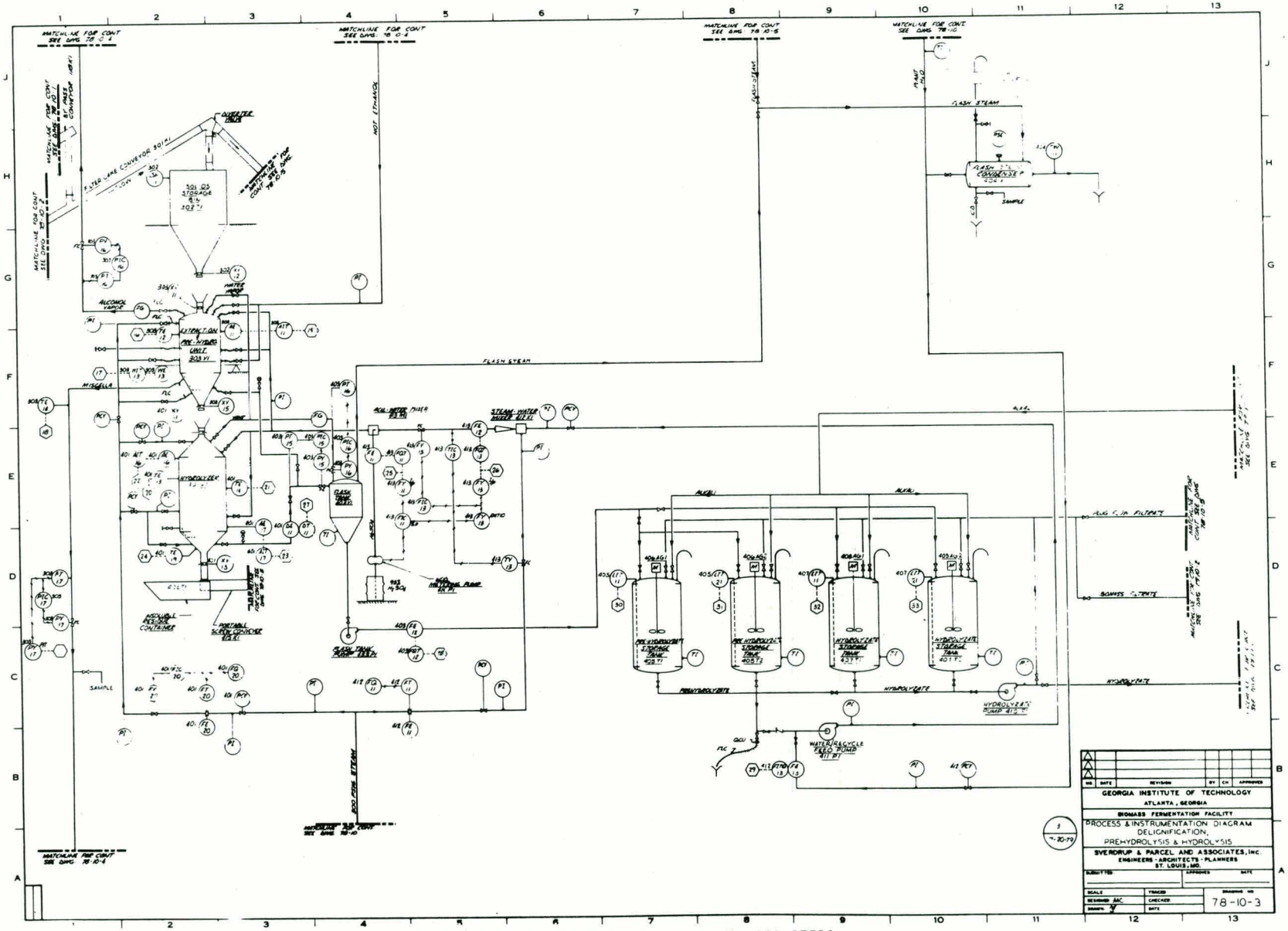



FIGURE 3.4 DELIGNIFICATION AND HYDROLYSIS STEPS

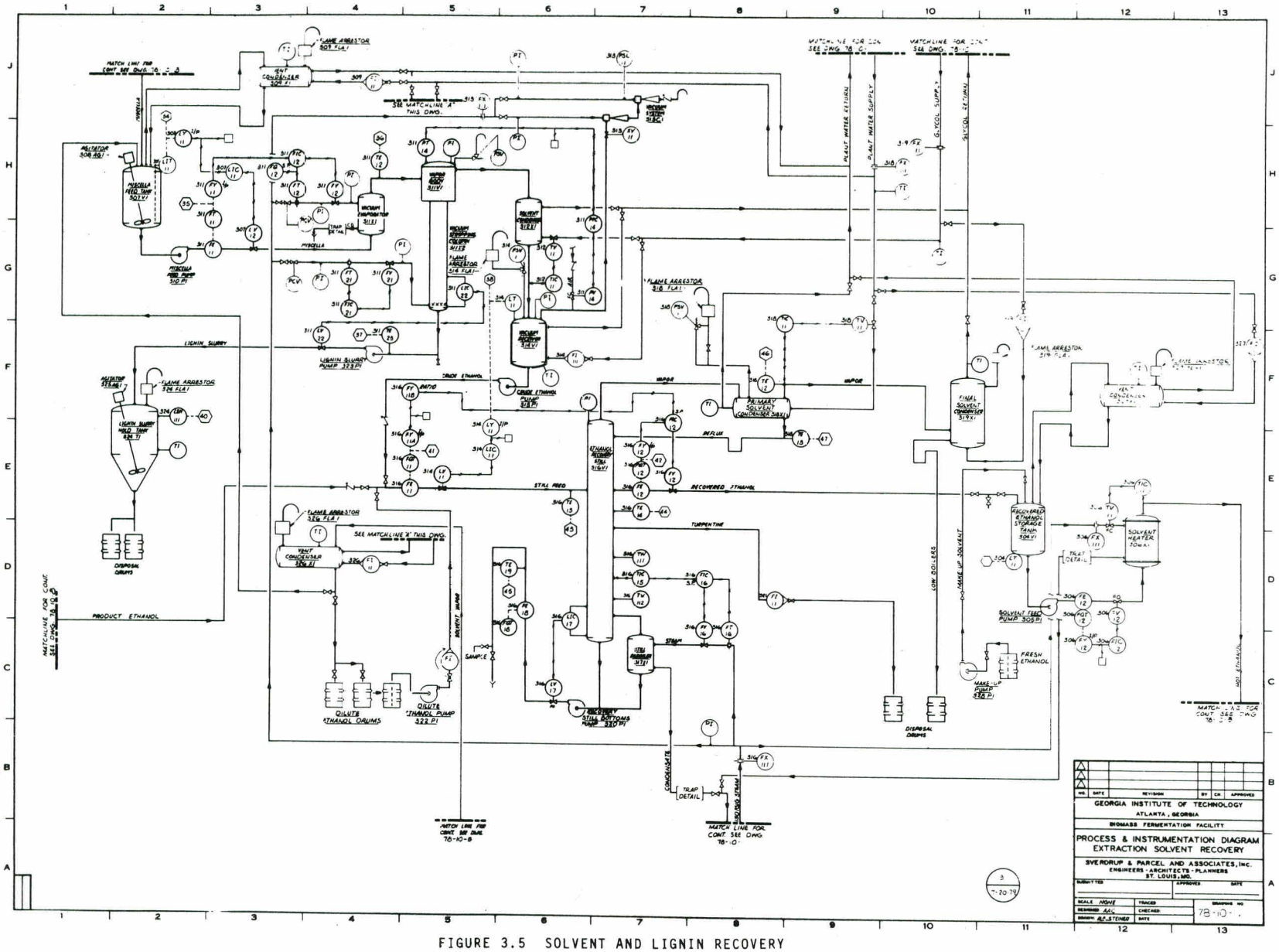



FIGURE 3.5 SOLVENT AND LIGNIN RECOVERY

The stages for the neutralization of hydrolyzate and concentration of the sugar solution are shown in Figure 3.6. The hydrolyzate is pumped to the neutralizer tank where suitable alkali (calcium hydroxide) is added to neutralize the sulfuric acid. The neutralized solution is then filtered to remove the calcium sulfate and any other solids which might be present. The clarified solution containing approximately 5% sugar is concentrated to 13-20% depending on the requirement by passing through an evaporator (under vacuum). The concentrated sugar solution is then passed through a plate and frame type continuous sterilizer to the sterile storage tank. The sterilized sugar syrup is then passed through a cooler. Now it is ready to be used in the fermentation medium as shown in Figure 3.7 The fermentation stage consists of two fermenters. The first is 300 liters and the second is of 1500 liters capacity. The fermenters are interconnected so that these can either be operated independently or in a series. In the mainline process, the sterilized growth medium is fermented continuously in a two stage system.

The first stage of the fermentation is carried out in the 300 liter fermenter which is operated partially under aerobic conditions to maintain the constant growth of the yeast culture. The broth is then fed continuously to the second stage (1500 liter vessel) kept under strict anaerobic conditions for the production of ethanol. The "beer" from the second stage is fed to a settler to separate the yeast. The separated yeast can be recycled to the first stage of the fermentation. The clear beer containing 6-8% ethanol is sent to the beer still feed tank. The ethanol is recovered from the beer by distilling it in a packed column. The final ethanol concentration in the overheads is between 60 to 85%. The bottoms of the still containing the remainder of the ethanol will be monitored to conduct exact material balances and discarded. The P & I diagram for the ethanol recovery system is given in Figure 3.8.

The important features of the proposed "Process Development Unit" are that it is a very flexible system. The various steps involved in the main line system can by by-passed. This would enable us to evaluate the impor-

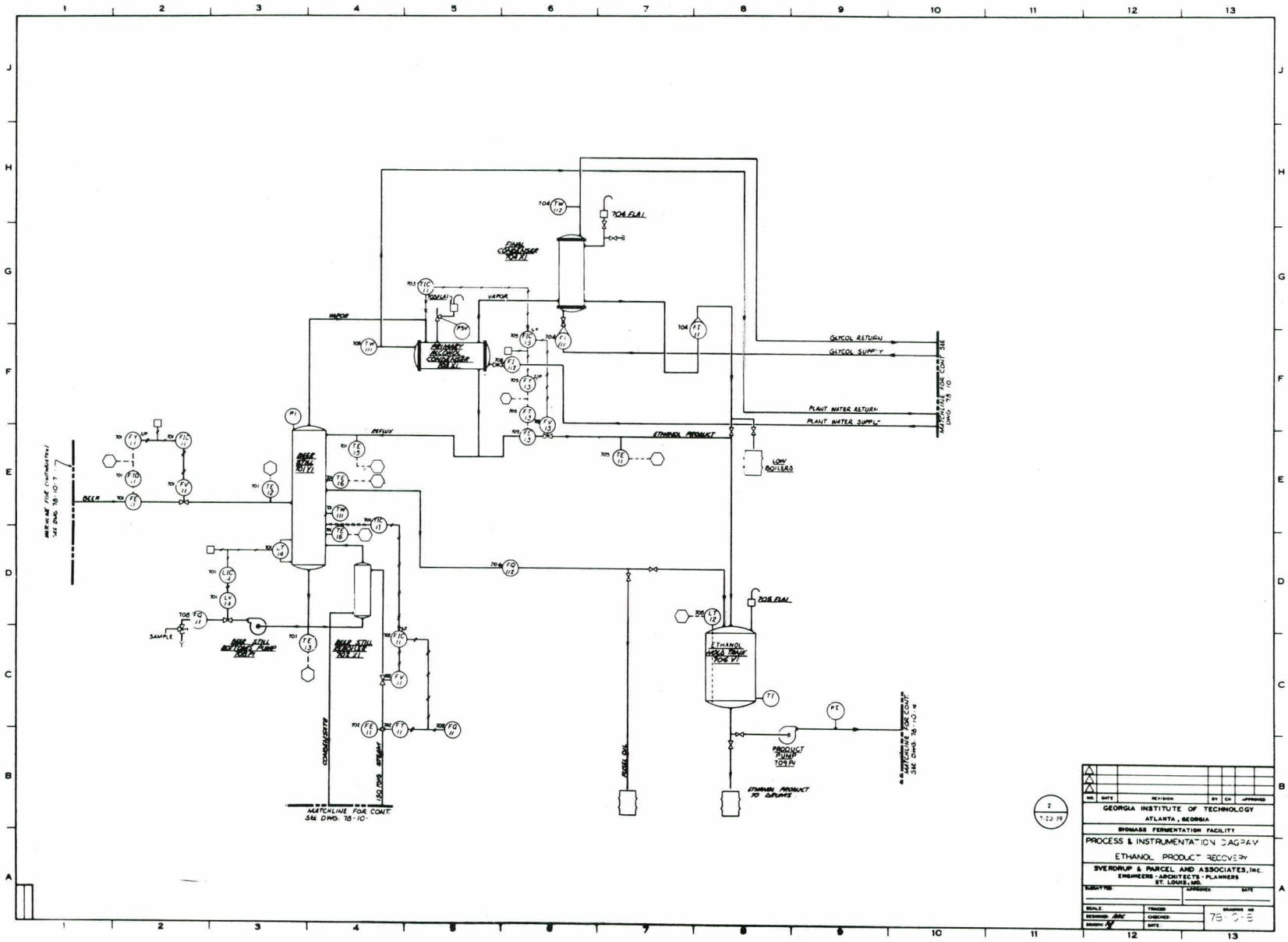



FIGURE 3.8 ETHANOL PRODUCT RECOVERY

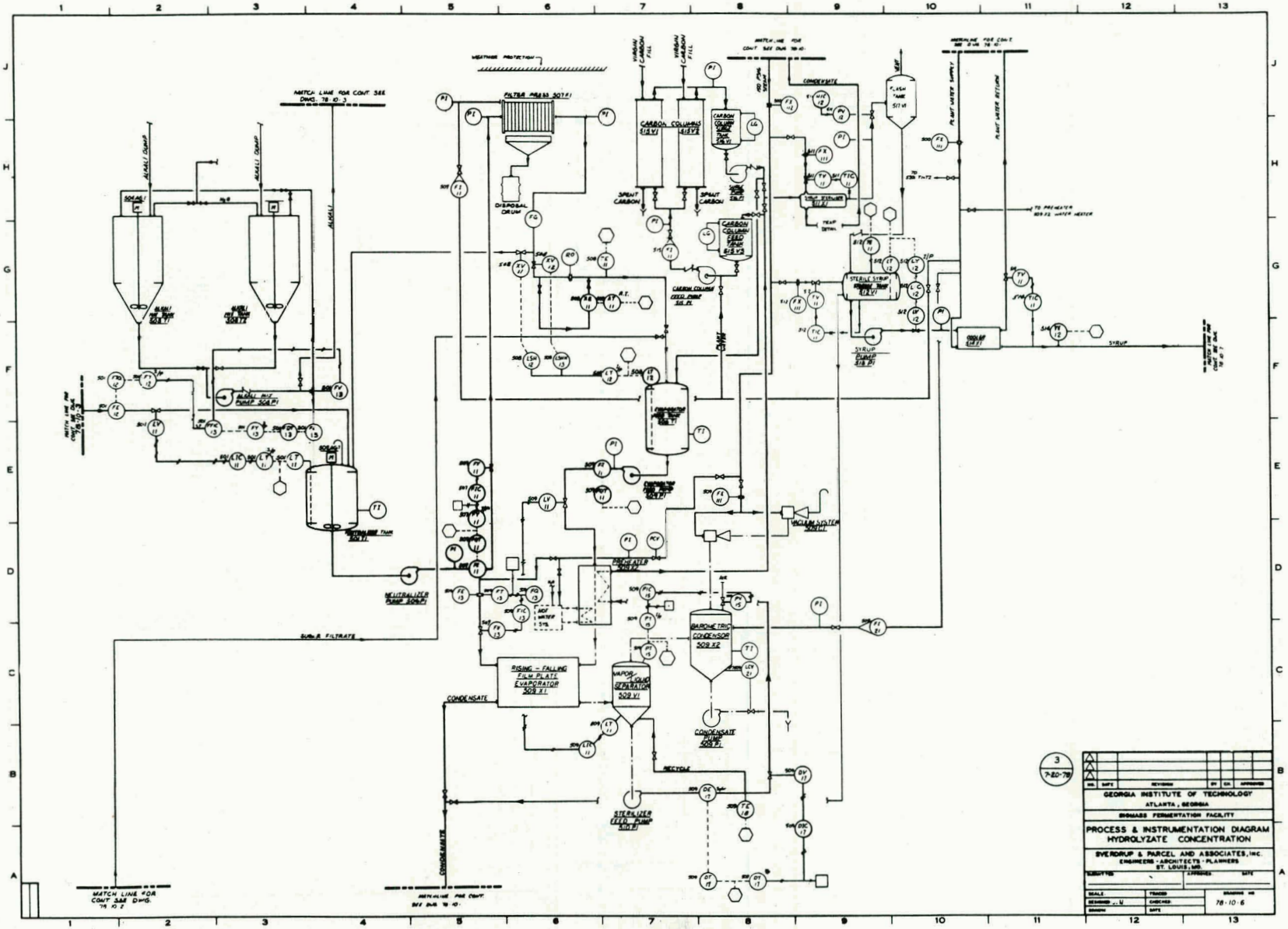



FIGURE 3.6 HYDROLYZATE CONCENTRATION

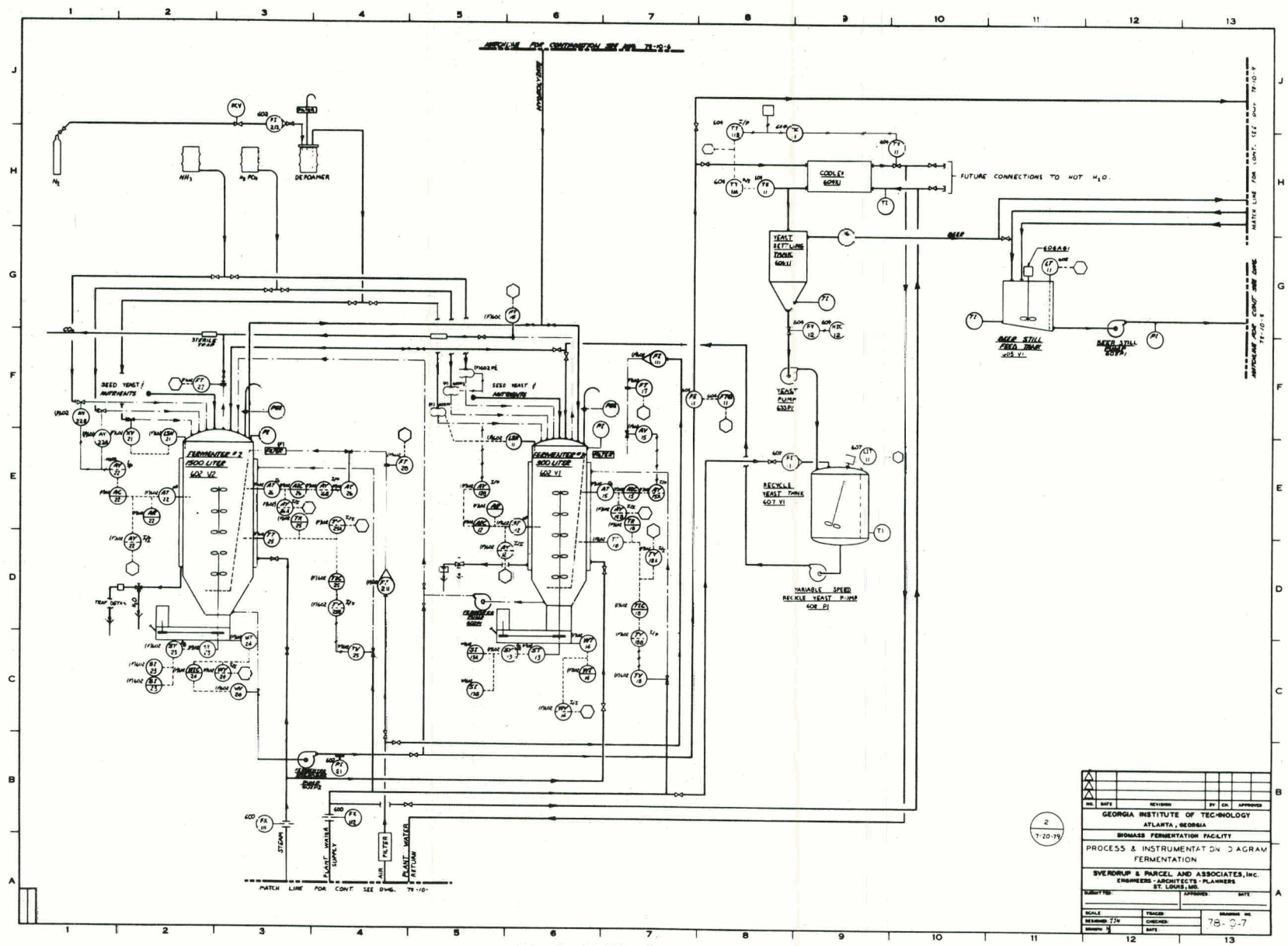



FIGURE 3.7 FERMENTATION

tance of each step. The steps that can be by-passed are given below:

1. Steam explosion of wood
2. Delignification
3. Prehydrolysis
4. Detoxification of sugar syrup
5. Sterilization of sugar syrup

The above flexibility of the operation would add to the data base to be collected by operating the PDU as discussed previously.

### 3.2.2 OPTIONAL SYSTEMS

A very interesting hydrolysis process which is included in the P & I diagrams, and which will be a part of the detailed engineering design but will not be a part of the initially constructed PDU, is plug flow with solids recycled. Figure 3.9 shows process flow and instrumentation for a plug flow reactor. Biomass which has been dilignified and prehydrolyzed (essentially pure cellulose) is fed into the plug flow mix tank where the solids concentration is adjusted to the required value (between 10%-30%), acid is added and the slurry is heated. From the mix tank the slurry is pumped through a preheater at high pressure and the steam is introduced to heat the slurry to the required reaction temperature. The reacted material is discharged through an orifice into a flash tank to reduce temperature and pressure, thereby quenching the reaction. The hydrolyzate is pumped into the vacuum filter, Figure 3.3 where the sugar solution is separated from the unreacted cellulose which is recycled to the plug flow reactor.

Another system option is continuous enzymatic hydrolysis. The present design plans would, with minor modification, permit the operation of enzymatic hydrolysis on a batch basis. In order to operate enzymatic hydrolysis continuously, additional equipment will be necessary. The P & I diagram for continuous enzymatic hydrolysis system is also shown in Figure 3.9. The biomass is fed into the enzyme reactors, one of which also serves as the plug flow mix tank. Enzymes from the enzyme mix tank are added. The two tanks are alternately filled and emptied to give semi-continuous operation.

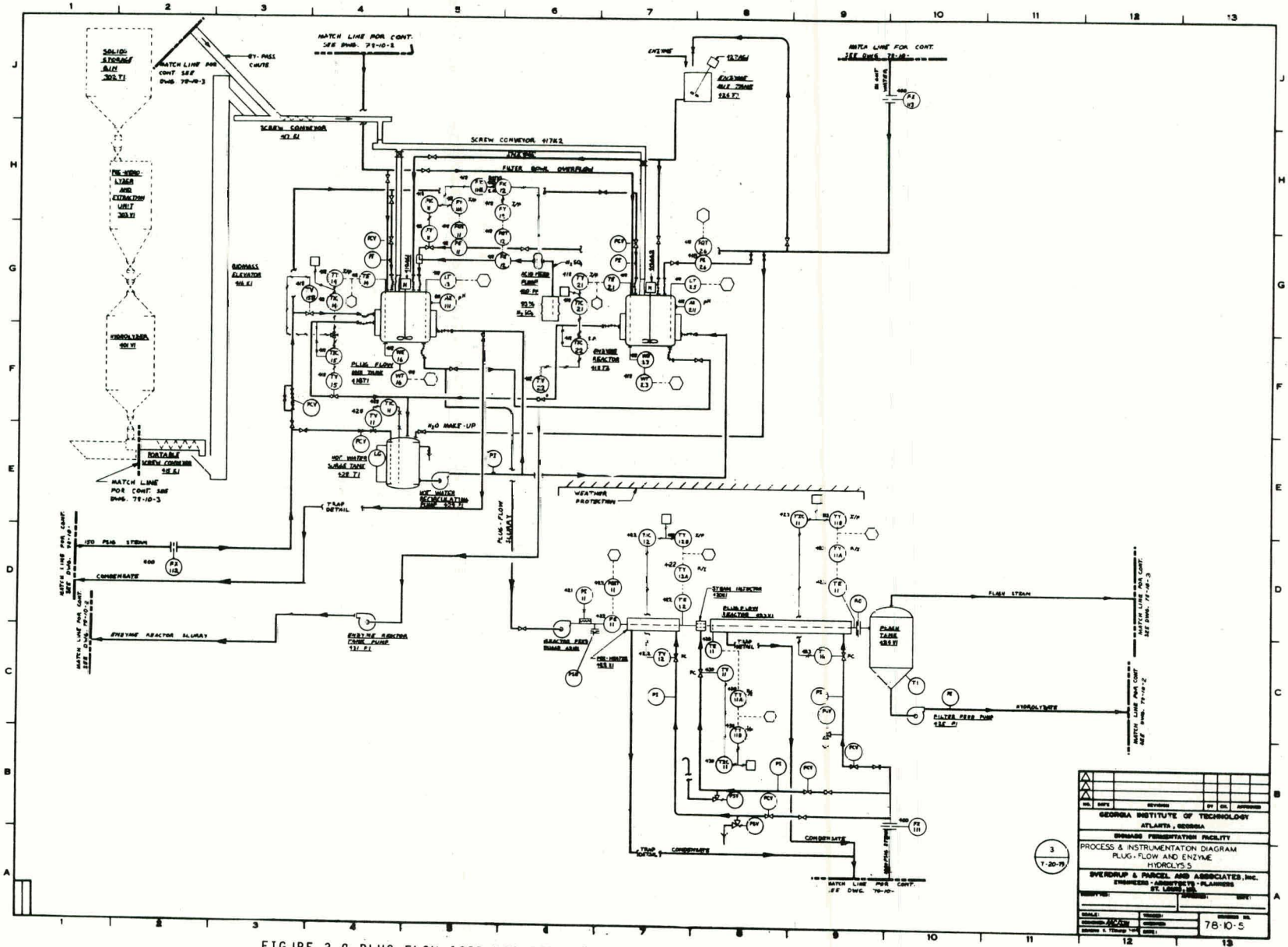



FIGURE 3.9 PLUG FLOW ACID REACTOR AND ENZYMATIC HYDROLYSIS REACTOR

The enzymatic hydrolysis slurry is pumped to the vacuum filter where the sugar solution is separated from the unreacted cellulose. The cellulose is either recycled to the enzyme reactors or sent to the waste disposal. The filtrate containing the sugars is then concentrated and sent to the fermenter for conversion into ethanol.

Simultaneous saccharification and fermentation is another interesting option. In this operation the slurry of the delignified biomass and enzyme solution is fed to a well mixed fermenter. Here a mixed microflora or a mixed enzyme system may be used to hydrolyze cellulose into glucose which then simultaneously can be fermented into ethanol; the broth is then sent to the yeast settling tank where most of the floating solid particles are separated and can be recycled. The beer is then preheated and passed through an ethanol stripper under vacuum. The ethanol vapors are condensed and can further be sent to the distillation column depending upon the final ethanol concentration. The bottoms of the vacuum stripper can be recycled.

## 4.0 PROGRESS IN DETAILED ENGINEERING DESIGN

Resumption of work on the detailed engineering design followed SERI approval of the conceptual design on June 8, 1979. Drafting work for the "P & I" flow diagrams and for the equipment layout drawings was resumed. Layouts were based upon assumed physical sizes of equipment in the absence of quotations for physical sizes.

Process and Instrumentation flow diagrams (Reference number SK6 138-11, 12, 13, 14, 15, 16, 17 and 18) were updated and renewed at the "90% Conceptual Review" meeting of June 29, 1979. Also prepared and reviewed were diagram nos. SK6 138-20 and 21 which show "Equipment location-Northwest and Northeast" for the facility site.

Detailed equipment lists were being developed to reflect the layout sizing assumptions and cost estimate bases to be consistent with the engineering drawings under review. A second "90% Conceptual Review" meeting was held in July. Process and Instrumentation Flow Diagrams were further updated or prepared for an August "90% Conceptual Review" meeting.

Liquid stream design flows were determined and added to in-house reproducible points of P & I Diagrams 78-10-1 and 78-10-3 to serve as a bases for sizing of piping, pumps, and associated pipeline specialities and valving. The information will be utilized in the preparation of process equipment specifications. Work on the design flow determination continues.

## 4.1. EQUIPMENT SPECIFICATIONS - OVERALL PDU (meeting)

MEETING DATES: July 9, 10 and 11, 1979

LOCATION: Georgia Institute of Technology
Engineering Experiment Station
Atlanta, Georgia

| PARTICIPANTS: | Georgia Tech | Sverdrup & Parcel |
|---|---|---|
| | M.K. Bery | A.A. Cook |
| | A. Colcord | J.D. Crider |
| | R.S. Roberts | J.J. Nachowiak |
| | D. Sondhi | B.C. Robb |
| | D.J. O'Neil | |

This was a process mechanical, 90% conceptual review meeting. The review drawings transmitted to Georgia Tech, attention Mr. Alton Colcord, June 29, 1979, via first class mail, were not received before or during this review meeting. The review proceeded using sepia reproducible prints ("red lines") of the same review drawings.

The following drawings were reviewed and signed off by Georgia Tech and Sverdrup and Parcel personnel with comments and corrections noted thereon:

| Drawing No. | Dated | Title | Status | Signed-Off |
|---|---|---|---|---|
| Biomass Fermentation Facility - Process and Instrumentation Diagrams: | | | | |
| SK6138-11 | 6/29/79 | Bulk Handling and Steam Explosion | 90% Conceptual Review | 7/11/79 |
| SK6138-12 | 6/29/79 | Filtration and Washing | 90% Conceptual Review | 7/11/79 |
| SK6138-13 | 6/29/79 | Delignification, Prehydrolysis and Hydrolysis | 90% Conceptual Review | 7/11/79 |
| SK6138-14 | 6/29/79 | Extraction Solvent Recovery | 90% Conceptual Review | 7/11/79 |
| SK6138-15 | 6/29/79 | Plug Flow Hydrolysis | 90% Conceptual Review | 7/11/79 |
| SK6138-16 | 6/29/79 | Hydrolyzate Concentration | 90% Conceptual Review | 7/11/79 |
| SK6138-17 | 6/29/79 | Fermentation | 90% Conceptual Review | 7/11/79 |
| SK6138-18 | 6/29/79 | Ethanol Product Recovery | 90% Conceptual Review | 7/11/79 |
| 8 1/2 x 11 Sketch (no no.) | 7/3/79 | Block Diagram - SSF | 60% Conceptual Review | 7/11/79 |
| SK6138-20 | 6/29/79 | Equipment Location Northwest | 60% Conceptual Review | 7/11/79 |
| SK6138-21 | 6/29/79 | Equipment Location Northeast | 60% Conceptual Review | 7/11/79 |

Five blueline prints of each of the above signed-off sepias were made and mailed to Georgia Tech. July 12, 1979, Sverdrup & Parcel File No. 6138-P13 transmittal.

The following comments on the signed-off drawings apply to mechanical equipment specification and may or may not appear on future P & I diagrams or layout drawings, but should be used when specifying equipment.

| Drawing No. | Comment |
|---|---|
| SK6138-11 | Hammermill 102M1: Use 1" screen per GIT. See quote. |
| | Conveyor 103K1: Size to match hammermill or provide surge capacity under mill. |
| | Explosion Gun 106V1: Review size in view of surge capacity elimination. (Refers to surge capacity of collector tank 107V1). |
| | Dry Collector Tank 107V1: Inquire about non-stick coating. |
| | Belt Feed 108K1: Provide variable speed multiple screw live bottom in lieu of belt feed, then short screw conveyor to filter feed tank. |
| | Filter Feed Tank 109T1: Make 50 cubic feet in size. Safety interlock manway to explosion gun required. |
| | Drum Dumper: Provide 55 gallon drum dumper (in lieu of elevated drum weighing and charging platform). |
| SK6138-12 | Vacuum Rotary Drums Filter 201F1: Position adjustment for (washing) heads required. Delete weighing system. Provide solid supports. |

| Drawing No. | Comment |
|---|---|
| SK6138-13 | Solids Storage Bin 302T1: Size 1.25 times extraction/ prehydrolysis vessel. Remote control solids outlet valve. |
| | Extraction Unit 303V1: Change to extractor/prehydrolyzer. Reduce extraction unit size to meet these schedules: 1 hour extraction time, 15 minutes prehydrolysis time at (design) temperature. 2 hours (solids) holdup, extraction/ prehydrolysis. Manway required. Remote control solids inlet valve. Segmented (removable) screen for 303V1 is required. (Not welded in). |
| | Hydrolyzer 401V1: Batch final hydrolysis only. Reduce hydrolysis unit size to meet this schedule: 30 minutes hydrolysis time. Hydrolyzer size to be same size as extraction/prehydrolysis unit. Prehydrolysis will be performed in extractor unit 303V1, not in hydrolyzer. Manway required. Provide for screen replacement. Segmented screens for 401V1 required. (Not welded in). Provide for fines removal: 401V1 - provide tangential backwash connection to assist solids removal with nozzle for injecting liquid in cone vicinity (per diagram); external connection to be by GIT. |
| | Acid Metering Pump 414P1: Review need for throttling bypass. |
| | Flash Tank 403V1: Locate near hydrolyzer. |
| | Flash Tank Pump: Provide (not shown). |
| | Pre-Hydrolyzate Pump 409P1: Review need. |
| | Cold Trap 404X2: (With flash steam condenser). Delete. |
| SK6138-14 | Miscella Feed Tank 307V1: Check out operation under pressure. |
| | Turpentine Wash Column 321L1: Deleted. |
| | Dilute Ethanol Pump 322P1: (From 321L1) Deleted. |
| | Vent Condenser 326X1: Review effect of water in miscella feed tank. |

| Drawing No. | Comment |
|---|---|
| SK6138-15 | Preheater 422X1: 170°C for less than one minute. |
| | Steam Injector 430X1: Operational design to be for 210°C (effluent). |
| | Plug Flow Reactor 423X1: 113 lb cellulose per hour, 10% slurry. Design: 2 minutes retention (time) at 210°C. Range: 30 seconds to 8 minutes. 2-3/4" to 3" I.D. requested by G.I.T. Eliminate bends between steam injector and flash tank. |
| SK6138-16 | Carbon Columns 515V1 and V2: "Discuss tank and pumps." (After carbon columns.) |
| | Enzyme Reactor 418T1: Change name to Plug Flow Mix Tank. |
| | Biomass Conveyor 417K1: Changed to two conveyors: 417K1 and 417K2. |
| SK6138-17 | Seed Yeast Tank 601V1 and Seed Yeast Pump 601P1: Both deleted. |
| | Fermenter No. 1-300 Liter 602V1<br>Fermenter No. 2-1500 Liter 602V2<br>(and associated equipment): Subject to review of Chemapec proposal by G.I.T. |
| | Recycle Yeast Tank 607V1: Added. |
| SK6138-18 | Fusel Oil Wash Column 706L1: Deleted. |
| | Wash Column Bottoms Pump 707P1: Deleted. |
| | Product Pump (709P1): Added. Returns product to feed Ethanol Recovery Still 316V1, SK6138-14. |
| 8-1/2 x 11<br>Block Diagram-SSF | Microorganism Fermenter 610V1: Deleted. To be provided by G.I.T. |
| | Filters 613F1 and F2: Deleted. Replace with gravity separator. |
| | Filter (Not shown): Add. Required for clarifying beer to Feed Tank 605V1. |
| | Sterilizer (Not shown): Add. |

| Drawing No. | Comment |
|---|---|
| SK6138-20 | 423X1, 2, 3 - Plug Flow Reactor: Will be shorter than shown, per P & I diagram. |
| SK6138-21 | 507F1 Filter Press: (Not circular). |

Other results of this review meeting were as follows:

G.I.T. furnished a quotation for Hammermill 102M1 dated June 29, 1979 from Sedberry Industries, Inc.

Feed Hopper 104T1 (by Iotech) is to have 4 hours minimum capacity. Iotech sizing is preferred if larger than this.

A phone call was made to Iotech Corporation, Ltd. to clarify certain questions about the steam explosion equipment on July 9, 1979, at 2:30 P.M. Their proposal will be $117,000 for the chip feed hopper, chip feeder, gun, cyclone, chutes, interconnecting piping, bends and instrument connection provisions, complete with structural stand. The collector (Item 107V1) is "just a cyclone" with no storage capacity. There is no way to sample dry material after steam explosion. Sampling is "not that practical". Their quote will assume the cyclone discharges directly to a reslurry tank. Sampling at the reslurry tank was suggested. Unslurried steam exploded wood is "very difficult to handle". It is "not free flowing and tends to stick". "Cyclone cleaning is a problem". A three hour capacity for the chip feed hopper was mentioned. The piping from the explosion gun to the cyclone is "thick", not thin wall tubing.

Vacuum Rotary Drum Filter 201F1 should be specified with both precoat and wash water separation features. Bridges in filter valve will be changed for the two modes of operation.

Extraction/Prehydrolysis Unit 303V1 and Hydrolyzer 401V1: Platforms will be provided at both levels (near top of 303V1 and near top of 401V1). Each platform will be 180° segments of annuli. Access will be by permanent ladders.

The goal for minimizing ethanol losses from extraction, solvent recovery, and ethanol product recovery will be 4 lb/hour combined total.

Fermenter Beer Cooler 604X1: Coolant piping shall be shown on piping physicals. Piping shall be shown schematically on flow diagrams for alternative heating, but heating piping will not be shown on piping physicals except for tee-in points.

Fermenters 602VI and 602V2: Fermenters shall be valved to permit either fermenter to operate independently.

An Equipment List (6-29-79 Layout Basis) dated July 3, 1979, 13 pages, intended for 90% Conceptual Review was presented to this meeting but was not reviewed. A copy was left for G.I.T. to review themselves.

4.2 ENZYMATIC HYDROLYSIS

Representatives (R.J. Malley and L.H. Posorske) of Novo Laboratories, Inc. met with Georgia Tech and Sverdrup and Parcel engineers on July 10, 1979.

Novo is a Danish firm specializing in enzymes and biochemistry. They produce the enzymes for manufacture of high fructose corn syrup, corn syrup, dextrose, detergents, cheese, and wine. They are staffed in the U.S. with 40 research and development people.

They manufacture cellulase, an enzyme suitable for the hydrolysis of wood derived cellulose to glucose, from a trichoderma viride strain organism. Their strain was developed from Natick Laboratories microbes. The Miles Laboratories cellulase has a higher activity than Novo's. Ten cellulases are commercially available from various manufacturers. Seven of these are from Japanese firms.

Novo has obtained 60% conversion of steam exploded wood in one pass. Glucose yield was determined by hexokinase assay of glucose and reducing sugars. They have not tested conversion of recycled cellulose after a single pass conversion. They find a large variation in steam exploded wood samples with respect to enzyme hydrolysis.

Novo's cellulose hydrolysis enzymes are all water soluble. Novo can recover their enzymes from the glucose hydrolysis product by ultrafiltration, precipitation with ammonium salts or reverse osmosis.

All commercially available cellulases are deficient in betaglucosidase. Therefore, Novo adds additional cellobiase enzyme to their cellulase enzyme. (Cellobiase causes hydrolysis to glucose, $C_6H_{12}O_6$, of the cellobiase, $C_{12}H_{22}O_{11}$, beta-glucoside fragments of the incomplete hydrolysis of cellulose by cellulase or acid.) Novo also indicated that the glucose (product) formed inhibits the conversion of cellulose to cellobiose to glucose.

It was asked what the starting concentration of cellulose could be. 12% cellulose slurry has been converted. Municipal waste from a hydropulper, 4 to 6% cellulose, has also been converted. At 6% concentration, stirring problems occur for the first 1/2 to 3/4 hour.

Novo stated that enzyme conversion of cellulose has not yet proven to be more economical than acid hydrolysis. More developmental work is still needed. Novo cannot make cellulase enzyme in Denmark because it is available only as a solution and has a short shelf life.

Enzyme hydrolysis of cellulose is performed at 4 to 6 pH and at ambient to 55°-58°C temperatures. Above 55°C these enzymes begin to denature (deteriorate). Severe denaturing occurs at 60° to 65°C.

Novo mentioned that the Iotech steam exploded wood that they received contained 10 to 20% water soluble material before enzyme hydrolysis.

Simultaneous saccharification and fermentation was discussed (S.S.F). Typical operating temperatures are about 36°C (98.8°F).

Questions were asked about viscosity and stirring problems. Some viscosity increase and water absorption of slurry components is possible but no obvious stirring problems occurred during Novo's testing. For a 24 to 48 hour conversion, viscosities of 1 to 3 cp occur 1/2 to 1 hour after beginning.

Sterilization before straight enzyme saccharification (conversion, hydrolysis) may not be necessary. The temperature during the saccharification is the important governing factor. For saccharification at 40°C, sterilizamay be important.

With regard to enzyme testing, future plans would be arranged between Dr. Bery of G.I.T. and Dr. Posorske of Novo.

## 4.3 FERMENTATION/EVAPORATION/YEAST ISOLATION/DISTILLATION

A meeting with representatives of the A.P.V. Company, Inc. was held at the Sverdrup and Parcel offices on June 13, 1979 to discuss tower fermentation, evaporation, yeast decantation, and distillation. Detailed quotations dated June 25, 1979 for beer and solvent distillation were provided by A.P.V.

In the former case, quotations were based on a requirement to produce an 85% by weight ethyl alcohol product for a feed consisting of 1316 lbs/hr of water and 84 lbs/hr of ethyl alcohol together with dissolved solids. The product from the bottom is to contain 0.1% w/w or less of ethyl alcohol. A tray distillation column, 16-inch diameter, with a total of 24 valve trays cartridge-type construction is recommended. The column height would be approximately 32 feet and 300 lbs/hr of steam is required for column operation. A complete system, less instrumentation or control valves, would include a thermosyphon reboiler, condenser, vent condenser, bottom pumps, product pump, reflux tank, vapor ducting, and necessary piping and valves. Experience has demonstrated that trays do not foul as seriously as does packing. All equipment in contact with process fluid should be manufactured in 304 stainless steel or better.

In the case of ethanol recovery a 90% w/w ethanol recovery was specified from a feed consisting of 900 lbs/hr of ethanol and 300 lbs/hr of water with the possibility of traces of acetic acid, methanol, and turpentine. The bottom product is to contain 0.5% w/w or less of ethanol. For this application a two foot diameter column manufactured in carbon steel was recommended. A total of twenty-four valve trays, of cartridge type construction, is recommended. Steam at 1000 lb/hr is required for column operation. The total package would include a thermosyphon reboiler, condenser, vent condenser, bottoms pump, product pumps, reflux tank, vapor ducting, as well as the necessary piping and valves. Most of this equipment would be manufactured in carbon steel.

## 4.4 ACID HYDROLYSIS

Huntington Alloys (International Nickel Co.) performed corrosion testing by autoclaving with 0.5% sulfuric acid at 375°F for 48 hours on potential materials of construction. Samples tested included Alloy G, Inconel Alloy 625, Monel Alloy 400, Incoloy Alloy 825, and Carpenter Cb-3. The testing conditions simulate those in batch dilute acid hydrolysis. Duplicate samples were run. The results are given in Table 4.1.

TABLE 4-1

Corrosion Testing of Alloys in Dilute Sulfuric Acid

| Alloy | Test 1 | Test 2 | Avg. |
|---|---|---|---|
| Alloy G | 1.3 MPY | 4.7 MPY | 3.0 MPY |
| Inconel Alloy 625 | 10.5 | 18.8 | 14.6 |
| Monel Alloy 400 | 137.0 | 69.3 | 103.2 |
| Incoloy Alloy 825 | 151.2 | 106.2 | 128.7 |
| Carpenter 20 Cb-3 | - | 123.8 | 123.8 |

The results for Alloy G, Monel 400, and Carpenter 20 Cb-3 are comparable to results previously reported by Cabot's Stellite Division.

## 5.0 FUTURE WORK

Completion of work on Phase I during the following period will entail the following tasks:

(a) Completion of the process economics and optimization study for hexose production in a fixed bed reactor (FBR).

(b) Completion of mass and energy balances for a commercial-scale plant of 1,000-ODT/DAY capacity.

(c) Completion of cost estimates for a commercial-scale (1000 ODT/DAY) wood-to ethanol plant.

(d) Completion of detailed engineering costs for a three oven-dry ton per day process development unit (PDU)

(e) Completion of the detailed engineering design for a three oven-dry ton per day process development unit (PDU)

☆ U.S. GOVERNMENT PRINTING OFFICE: 1980—640-258/2071