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DESIGN, FABRICATION AND OPERATION OF A BIOMASS
FERMENTATION FACILITY

Technical Progress Report No. 2, January 1—March 31, 1979

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Georgia Institute of Technology
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Atlanta, Georgia

U.S. Department of Energy

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GEORGIA INSTITUTE OF TECHNOLOGY

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ABSTRACT

The conceptual design for a three oven-dry ton per day biomass fermentation facility is presented. Based on a detailed evaluation of emerging technologies and improved modifications of current technology, a mainstream process and optional unit operation and sub-systems have been selected which offer the greatest probability of success for an economic and technically feasible process for production of ethanol from lignocellulosic biomass (hardwoods, wheat straw, corn stover, etc.).

The design is intentionally flexible as stipulated in the contractual objectives. Recommendations of equipment is premised on its versatility for multi-functional application, thus enabling investigation to assess a number of process configurations while adhering to a cost-effective capital investment in the process development unit. A specific criterion in selection has been to facilitate the generation of engineering data based on the application of the results of research contractors of the U.S. Department of Energy.

The design for a total system includes the facility for evaluation of three pretreatment options, for isolation of by-product streams, for evaluation of acid and enzymatic hydrolysis, sugar concentration, alternative fermentation technologies and alcohol recovery for production of absolute ethanol. In order to maintain capital costs for the PDU within reasonable limits monitoring of by-product streams will be undertaken and, for unit operation with high potential (such as membrane concentration of ethanol) but which are in early stages of development smaller-scale equipment and/or plumbing taps for late addition of full-scale (i.e., PDU-scale) equipment is recommended.

The rationale, and process economics, upon which the recommendations are based is detailed, as is a study of biomass feedstock availability.

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1.0. INTRODUCTION

This report summarizes the first six months of activity accomplished under a Phase I contract for the "Design, Fabrication, and Operation of a Biomass Fermentation Facility". The Phase I contract is being performed in two major parts:

I. Conceptual Design

II. Detailed Engineering Design

This report presents recommendations for the conceptual design of a three oven-dry ton per day process development unit (PDU) which is to evaluate high potential processes for the production of ethanol from lignocellulosic biomass residues (e.g., hardwoods, corn stover, and wheat straw). An exhaustive analysis of emerging and modified technologies for achieving economic and technically feasible production processes was undertaken.

The report begins with a survey of biomass availability which concerns itself with both the availability of supplies of biomass for operation of the PDU and also with regional and national projections, and costs, of biomass which are available for production of ethyl alcohol.

The reader is introduced in Section 3.0., on the basis of an "overview" to the recommended system for a three oven-dry ton per day PDU. A so-called "main stream" process is presented which effectively forms a baseline process for alcohol production. Amplification of the PDU system is accomplished by a discussion of alternative unit operations and sub-systems which should ideally be incorporated into the PDU for purposes of maximizing the probability of developing an optimum process. Material balances for all process options are presented.

The following section develops in greater details the logic employed in

the decision-making regarding the construction of the conceptual design.

The emphasis on flexibility, cost-effective PDU construction and operation, and the critical selection-elimination process is examined in greater depth for each unit operation.

An intensive sensitivity analysis for the optimization of the process for hexose production from cellulose via acid hydrolysis is presented. Both continuously stirred tank reactor (CSTR) and plug flow reactor (PFR) configurations have been considered, with the latter showing excellent production cost projections.

The benefits and disadvantages of enzymatic hydrolysis are also considered based on currently available data.

2.0. BIOMASS FEEDSTOCKS

2.1. Biomass Availability

This report is an update of the biomass Feedstock section of Technical Progress Report No. 1. Included are estimates of the amount of agricultural and woody biomass that are potentially available as feedstock for biomass fermentation facilities. First, regional and national estimates were made for the amount of agricultural and woody biomass that would be available on an annual basis as feedstocks for fermentation facilities. It should be noted that agricultural residues herein mentioned refer only to crop residues and do not include animal manure. From these figures estimates were made as to the total theoretical plant capacity that could exist in each region. This information was also displayed as the number of 1,000 oven dry ton per day (ODTPD) plants, or 2,000 ODTPD plants, or 5,000 ODTPD plants that could be annually sustained by the calculated biomass. This same type of analysis was then undertaken for the state of Georgia. The analysis included herein for the state of Georgia supercedes the analysis previously done in Technical Report Number 1 in regards to the amount of woody biomass available. All other data included on woody biomass in Technical Report No. 1 is still correct. (e.g. the land requirements and economic data). An analysis was also made as to the amount of land needed to provide the agricultural residues for a 1,000 ODTPD facility based on various crops. Finally a comparison was made between the Georgia Tech calculations of biomass availability and those done by SRI International which were based on various price levels for the biomass.

2.1.1. Regional and National Biomass Availability

The approach used to estimate the amount of agricultural biomass available by region of the country was based on work done by

the Stanford Research Institute in 1976 entitled "Crop, Forestry and Manure Inventory - Continental United States". In the report regional totals were given for crop biomass as to the amounts that were sold, fed, used for fuel, returned to the soil as fertilizer and wasted. It was assumed that the amounts sold, used as feed, and used for fuel would not be available for use as feedstock for a fermentation facility. However, it was stated in the SRI report that on the average only half of the biomass amount returned to the soil need be returned as fertilizer. Therefore, the agricultural biomass estimates calculated are based on the assumption that 50% of the returned biomass and 50% of the wasted was assumed to be recovered to reflect the fact that not all waste is recoverable and also to reflect a conservative bias in the estimates.

The amount of woody biomass available on an annual basis was based on a 5% recovery of wood in the following categories: annual excess growth, annual other removals, annual plant residue, annual logging residue, annual unused plant residue, rough wood, rotten wood, annual mortality, and less than 5 inch diameter breast height (d.b.h.) wood. Though it is quite possible to recover more than 5% per year of the wood in some of those categories it is not true in all. The less than 5 inch d.b.h. wood comprises a very large portion of the total biomass available and an assumption of any more than 5% recovery of this type of wood would be seen as potentially hazardous in the maintenance of future growing stock. The recovery of rough and rotten trees at a pace faster than 5% a year is probably economically unfeasible and perhaps environmentally unwise. This 5% recovery approach maintains a moderately conservative but realistic bias in the estimate.

Table 2.1. contains the biomass tonnage for six regions of the country and the U.S. total. The regions and the states included in these regions are:

Northeast	- Me., N.H., Vt., Mass., Conn., R.I., N.Y., N.J., Pa., Md., Del., W. Va.
Southeast	- Va., N.C., S.C., Ga., Fla.
South Central	- Tenn., Miss., Ala., Ark., La., Okla., Tex.
North Central	- N. Dak., S. Dak., Minn., Wis., Mich., Nebr., Iowa, Ill., Ind., Ohio, Kan., Mo., Ky.
Mountains	- Mont., Idaho, Wyo., Nev., Utah, Colo., Ariz., N. Mex.
Pacific	- Wash., Oreg., Calif., (Alaska and Hawaii agricultural biomass was not included though some woody biomass was.)

The following subsections describe the amount of biomass produced and the number of ethanol plants that could be sustained by this biomass in the U.S. and each region. The data used in the subsections description are displayed in Tables 2.1. through 2.5. Table 2.1. gives the national and regional totals of the agricultural and woody biomass tonnage recoverable; Table 2.2. breaks this tonnage information into percentages reflecting the percentage of the residue total available in each region by residue type. Table 2.3. shows total ethanol plant capacity in ODTDP that could be sustained by the biomass and also the number of 1,000 or 2,000 or 5,000 ODTDP plants that could be sustained by the biomass. Table 2.4. shows the same type information for only recoverable agricultural biomass and Table 2.5. shows this information for only recoverable woody biomass. Please note in Tables 2.1., 2.3., 2.4., and 2.5. the biomass for use as a feedstock in ethanol plants is represented as 100%, 50%, 33%, and 10% of the recoverable amount. This is to reflect a range because even if all the

Regional and National Biomass Potentially Available on an
Annual Basis Based Upon 1975 - 1977 Data
(Dry Weight Tons)

Table 2.1.

Biomass Region	Percentages of Maximum Recoverable Biomass			
	<u>100%</u>	<u>50%</u>	<u>33%</u>	<u>10%</u>
<u>Northeast</u>				
Agricultural	719,339	359,670	239,780	71,934
Woody	<u>34,319,250</u>	<u>17,159,625</u>	<u>11,439,748</u>	<u>3,431,925</u>
Total	35,038,589	17,519,295	11,679,528	3,503,859
<u>Southeast</u>				
Agricultural	4,898,983	2,449,492	1,632,994	489,899
Woody	<u>38,293,500</u>	<u>19,146,750</u>	<u>12,764,500</u>	<u>3,829,350</u>
Total	43,192,483	21,596,242	14,397,494	4,319,248
<u>North Central</u>				
Agricultural	64,980,361	32,490,180	21,660,120	6,498,036
Woody	<u>33,013,050</u>	<u>16,506,525</u>	<u>11,004,350</u>	<u>3,301,305</u>
Total	97,993,411	48,996,705	32,664,470	9,799,311
<u>South Central</u>				
Agricultural	14,267,042	7,133,521	4,755,681	1,426,704
Woody	<u>46,567,150</u>	<u>23,283,575</u>	<u>15,522,383</u>	<u>4,656,715</u>
Total	60,834,192	30,417,096	20,278,064	6,083,419
<u>Mountain</u>				
Agricultural	10,411,475	5,205,738	3,470,492	1,041,148
Woody	<u>15,136,800</u>	<u>7,568,400</u>	<u>5,045,600</u>	<u>1,513,680</u>
Total	25,548,275	12,774,138	8,516,092	2,554,828
<u>Pacific</u>				
Agricultural	9,928,794	4,964,397	3,309,598	992,879
Woody	<u>32,608,100</u>	<u>16,304,050</u>	<u>10,869,365</u>	<u>3,260,810</u>
Total	42,536,894	21,268,447	14,178,963	4,253,689
<u>U.S. Total</u>				
Agricultural	105,205,994	52,602,997	35,068,665	10,520,599
Woody	<u>199,937,850</u>	<u>99,968,925</u>	<u>66,645,950</u>	<u>19,993,785</u>
Total	305,143,844	152,571,922	101,714,615	30,514,384

Table 2.2.

Percentage Share of Regional and National
Biomass Totals By Region and Biomass Type

<u>Biomass Region</u>	<u>Regional % of Regional Total</u>	<u>Regional Agricultural % of National Agricultural Total</u>	<u>Regional Woody % of National Woody Total</u>	<u>Regional % of U.S. Total</u>
<u>Northeast</u>				
Agricultural	2.1	.7	-	.3
Woody	97.9	-	17.2	11.2
Total	100.0	-	-	11.5
<u>Southeast</u>				
Agricultural	11.3	4.7	-	1.6
Woody	88.7	-	19.2	12.6
Total	100.0	-	-	14.2
<u>North Central</u>				
Agricultural	66.3	61.8	-	21.3
Woody	33.7	-	16.5	10.8
Total	100.0	-	-	32.1
<u>South Central</u>				
Agricultural	23.5	13.6	-	4.7
Woody	76.5	-	23.3	15.3
Total	100.0	-	-	20.0
<u>Mountain</u>				
Agricultural	40.8	9.9	-	3.4
Woody	59.2	-	7.6	5.0
Total	100.0	-	-	8.4
<u>Pacific</u>				
Agricultural	23.3	9.4	-	3.3
Woody	76.7	-	16.3	10.6
Total	100.0	-	-	13.9
<u>U.S. Total</u>				
Agricultural	(see last	100	-	34.5
Woody	column)	-	100	65.5
Total		-	-	100.0

Table 2.3.

Regional and National Potential Plant Capacity and
Number of 1,000, 2,000 and 5,000 ODTPD* Plants
Sustainable by Agricultural and Woody Biomass Based on
Percentage of the Maximum Recoverable

Biomass Region	Percentage of Maximum Recoverable Agricultural and Woody Biomass			
	<u>100%</u>	<u>50%</u>	<u>33%</u>	<u>10%</u>
<u>Northeast</u>				
Total Capacity (ODTPD)	100,110	50,055	33,370	10,011
Number of 1,000 ODTPD Plants	100	50	33	10
Number of 2,000 ODTPD Plants	50	25	16	5
Number of 5,000 ODTPD Plants	20	10	6	2
<u>Southeast</u>				
Total Capacity (ODTPD)	123,407	61,704	41,136	12,341
Number of 1,000 ODTPD Plants	123	61	41	12
Number of 2,000 ODTPD Plants	61	30	20	6
Number of 5,000 ODTPD Plants	24	12	8	2
<u>North Central</u>				
Total Capacity (ODTPD)	279,981	139,990	93,327	27,998
Number of 1,000 ODTPD Plants	279	139	93	27
Number of 2,000 ODTPD Plants	139	69	46	13
Number of 5,000 ODTPD Plants	55	27	18	5
<u>South Central</u>				
Total Capacity (ODTPD)	173,012	86,906	57,937	17,381
Number of 1,000 ODTPD Plants	173	86	57	17
Number of 2,000 ODTPD Plants	86	43	28	8
Number of 5,000 ODTPD Plants	34	17	11	3
<u>Mountain</u>				
Total Capacity (ODTPD)	72,995	36,498	24,332	7,300
Number of 1,000 ODTPD Plants	72	36	24	7
Number of 2,000 ODTPD Plants	36	18	12	3
Number of 5,000 ODTPD Plants	14	7	4	1

Table 2.3 (Continued)

	<u>100%</u>	<u>50%</u>	<u>33%</u>	<u>10%</u>
<u>Pacific</u>				
Total Capacity (ODTPD)	121,534	60,767	40,511	12,153
Number of 1,000 ODTPD Plants	121	60	40	12
Number of 2,000 ODTPD Plants	60	30	20	6
Number of 5,000 ODTPD Plants	24	12	8	2
<u>U.S. Total</u>				
Total Capacity (ODTPD)	871,839	435,920	290,613	87,184
Number of 1,000 ODTPD Plants	871	435	290	87
Number of 2,000 ODTPD Plants	435	217	145	43
Number of 5,000 ODTPD Plants	174	87	58	17

*ODTPD = oven dry tons per day

NOTE: All numbers were truncated when calculating the number of plants

Table 2.4.

Regional and National Potential Plant Capacity and
Number of 1,000, 2,000 and 5,000 ODTPD* Plants
Sustainable by Agricultural Biomass Based on
Percentages of the Maximum Recoverable

Biomass Region	Percentages of Maximum Recoverable Agricultural Biomass			
	100%	50%	33%	10%
<u>Northeast</u>				
Total Capacity (ODTPD)	2,055	1,023	685	205
Number of 1,000 ODTPD Plants	2	1	0	0
Number of 2,000 ODTPD Plants	1	0	0	0
Number of 5,000 ODTPD Plants	0	0	0	0
<u>Southeast</u>				
Total Capacity (ODTPD)	13,997	6,999	4,666	1,400
Number of 1,000 ODTPD Plants	14	7	4	1
Number of 2,000 ODTPD Plants	7	3	2	0
Number of 5,000 ODTPD Plants	2	1	0	0
<u>North Central</u>				
Total Capacity (ODTPD)	185,658	92,829	61,886	18,566
Number of 1,000 ODTPD Plants	185	92	61	18
Number of 2,000 ODTPD Plants	92	46	30	9
Number of 5,000 ODTPD Plants	37	18	12	3
<u>South Central</u>				
Total Capacity (ODTPD)	40,763	20,381	13,586	4,076
Number of 1,000 ODTPD Plants	40	20	13	4
Number of 2,000 ODTPD Plants	20	10	6	2
Number of 5,000 ODTPD Plants	8	4	2	0
<u>Mountain</u>				
Total Capacity (ODTPD)	29,747	14,874	9,916	2,975
Number of 1,000 ODTPD Plants	29	14	9	2
Number of 2,000 ODTPD Plants	14	7	4	1
Number of 5,000 ODTPD Plants	5	2	1	0

Table 2.4. (Continued)

	<u>100%</u>	<u>50%</u>	<u>33%</u>	<u>10%</u>
<u>Pacific</u>				
Total Capacity (ODTPD)	28,368	14,184	9,456	2,837
Number of 1,000 ODTPD Plants	28	14	9	2
Number of 2,000 ODTPD Plants	14	7	4	1
Number of 5,000 ODTPD Plants	5	2	1	0
<u>U.S. Total</u>				
Total Capacity (ODTPD)	300,588	150,294	100,196	30,059
Number of 1,000 ODTPD Plants	300	150	100	30
Number of 2,000 ODTPD Plants	150	75	50	15
Number of 5,000 ODTPD Plants	60	30	20	6

*ODTPD=oven dry tons per day

NOTE: All numbers were truncated when calculating the number of plants

Table 2.5:

Regional and National Potential Plant Capacity and
Number of 1,000, 2,000 and 5,000 ODTPD Plants
Sustainable by Woody Biomass Based on Percentage
of the Maximum Recoverable

Biomass Region	Percentage of Maximum Recoverable Woody Biomass			
	<u>100%</u>	<u>50%</u>	<u>33%</u>	<u>10%</u>
<u>Northeast</u>				
Total Capacity (ODTPD)	98,055	49,028	32,685	9,806
Number of 1,000 ODTPD Plants	98	49	32	9
Number of 2,000 ODTPD Plants	49	24	16	4
Number of 5,000 ODTPD Plants	19	9	6	1
<u>Southeast</u>				
Total Capacity (ODTPD)	109,410	54,705	36,470	10,941
Number of 1,000 ODTPD Plants	109	54	36	10
Number of 2,000 ODTPD Plants	54	27	18	5
Number of 5,000 ODTPD Plants	21	10	7	2
<u>North Central</u>				
Total Capacity (ODTPD)	94,323	47,162	31,441	9,432
Number of 1,000 ODTPD Plants	94	47	31	9
Number of 2,000 ODTPD Plants	47	23	15	4
Number of 5,000 ODTPD Plants	18	9	6	1
<u>South Central</u>				
Total Capacity (ODTPD)	133,049	66,524	44,350	13,305
Number of 1,000 ODTPD Plants	133	66	44	13
Number of 2,000 ODTPD Plants	66	33	22	6
Number of 5,000 ODTPD Plants	26	13	8	2
<u>Mountain</u>				
Total Capacity (ODTPD)	43,248	21,624	14,416	4,325
Number of 1,000 ODTPD Plants	43	21	14	4
Number of 2,000 ODTPD Plants	21	10	7	2
Number of 5,000 ODTPD Plants	8	4	2	0
<u>Pacific</u>				
Total Capacity (ODTPD)	93,166	46,583	31,055	9,317
Number of 1,000 ODTPD Plants	93	46	31	9
Number of 2,000 ODTPD Plants	46	23	15	4
Number of 5,000 ODTPD Plants	18	9	6	1

Table 2.5. (Continued)

	<u>100%</u>	<u>50%</u>	<u>33%</u>	<u>10%</u>
<u>U.S. Total</u>				
Total Capacity (ODTPD)	571,251	285,626	190,417	57,125
Number of 1,000 ODTPD Plants	571	285	190	57
Number of 2,000 ODTPD Plants	285	142	95	28
Number of 5,000 ODTPD Plants	114	57	38	11

* ODTPD = oven dry tons per day

NOTE: All numbers were truncated when calculating the number of plants

the recoverable biomass was collected not all would be used as feedstock for ethanol plants. It is believed that the estimates in the 33% - 10% recoverable range will more likely reflect the amount available for use by ethanol production plants. Woody biomass will have competing end uses as an energy source for alternative conversion technologies (e.g., gasification, combustion, methanol production, etc.).

2.1.1.1. U.S. Totals

The total biomass potential estimated as annually recoverable is over 305 million dry tons, of which agricultural residues represent 34.5% and woody biomass 65.5% of the total. Assuming 10%-33% useage of this maximum recoverable, 30.5 - 101.7 million tons is available as feedstock. This translates to 87 - 290 1,000 ODTPD plants that can be sustained in perpetuity nationwide (excluding economic considerations). Woody biomass could sustain 57-190 1,000 ODTPD plants while agricultural biomass could sustain 30-100 1,000 ODTPD plants. Realistically many fermentation facilities would likely use a combination of woody and agricultural feedstocks rather than rely soley on one type.

2.1.1.2. Northeast

The total biomass potential estimated as annually recoverable in the Northeast is over 35 million oven dry tons of which agricultural residues represent 2.1% and woody biomass 97.9% of the regional total. The region itself represents only 11.5% of the total U.S. biomass available, next to the last in biomass quantity among the six regions. The agricultural contribution is very small, not enough to sustain even one 1,000 ODTPD plant at the 33% recovery level. The

woody biomass can sustain 9-32 1,000 ODTDP plants in the region at the 10%-33% recovery level. Obviously wood is the preferred feedstock for this region. The agricultural and woody biomass tonnage available at the 10-33% recovery level is 3.5-11.7 million tons, enough to sustain 5-16 1,000 ODTDP plants.

2.1.1.3. Southeast

The total biomass potential estimated as annually recovered in the Southeast is over 43 million dry tons, of which 11.3% is agricultural and 88.7% is woody. Assuming 10%-33% is recoverable for fermentation facilities 4.3-14.4 tons is available as feedstocks. This translates to 12-41 sustainable 1,000 ODTDP plants in the region. The region represents 14.2% of the national biomass total, third largest of the regions. The agricultural biomass could sustain 1-4 1,000 ODTDP at the 10%-33% recovery level and the woody biomass could sustain 10-36 1,000 ODTDP plants at the same levels of recovery. The Southeast has the second largest amount of woody biomass of the six regions and it would be the more plentiful feedstock. However, agricultural production does supply enough residue to contribute as feedstock if the production is concentrated in certain areas of the region rather than dispersed.

2.1.1.4. North Central

The total biomass potential estimated as annually recoverable in the North Central region is almost 98 million tons. This is 32.1% of the national biomass total, the largest contribution of any of the six regions. Of this total 66.3% is agricultural residue and 33.7% is woody biomass. This region is the only one containing more

agricultural than woody biomass. It contains 61.8% of all the agricultural biomass available in the U.S. The agricultural biomass at the 10%-33% recovery level is 6.5-21.7 million dry tons, enough to sustain 18-61 1,000 ODTPD fermentation plants. The woody biomass at the 10-33% recovery level equals 3.3-11 dry tons, enough to sustain 9-31 1,000 ODTPD plants. Total biomass at 10-33% recovery equals 18.6-61.9 million dry tons, enough tonnage to annually sustain 27-93 1,000 ODTPD plants. Wood is fairly evenly distributed in five of the six regions whereas agricultural residue is primarily concentrated in this region, therefore both agricultural and woody biomass can contribute significantly in the North Central region as feedstocks. But if agricultural biomass is counted on nationally to contribute heavily as a fermentation feedstock then intense usage of it must occur in this region.

2.1.1.5. South Central

The South Central region contains over 60 million dry weight tons of biomass, of which 23.5% is agricultural and 76.5% is woody. At the 10%-33% recovery level there is 17.4-57.9 million tons of biomass available, enough to annually sustain 17-57 1,000 ODTPD fermentation plants. The agricultural portion of the biomass total at the 10%-33% recovery level could sustain 4-13 1,000 ODTPD plants at those recovery levels. The South Central region is the second largest biomass contributor of the six regions contributing 20% of the U.S. total. It is the largest contributor of woody biomass containing 23.3% of all the woody biomass available and the second largest contributor of agricultural biomass containing 13.6% of all the agricultural

biomass available. Timber is obviously the more abundant feedstock though agricultural residue could be used to some extent.

2.1.1.6. Mountain

The Mountain region contains a potential of over 25 million dry tons of biomass, of which 40.8% is agricultural and 59.2% is woody. At the 10%-33% recovery level this region could sustain 7-24 1,000 ODTPD fermentation plants. At the 10%-33% recovery level agricultural residue could supply 2-9 1,000 ODTPD fermentation plants and woody biomass could supply 4-14 1,000 ODTPD plants. This region contains the smallest quantity of total biomass though it has the third largest amount of agricultural biomass available, 9.9% of the U.S. agricultural biomass total. It has the smallest quantity of timber available only 7.6% of the U.S. woody biomass total. However, there is still more woody on a tonnage basis available than agricultural residue. The use of biomass in this region would be largely determined by the density of the biomass (is it centralized in certain regions or dispersed) and how this impacts the economics of fermentation facilities.

2.1.1.7. Pacific

The Pacific region contains over 42 million dry tons of biomass potentially available of which 23.3% is agricultural and 76.7% is woody. This region ranks fourth out of the six regions in quantity of biomass available. At the 10%-33% recovery level this equals 3.3-10.9 million tons, enough to sustain 12-40 1,000 ODTPD fermentation plants. This region has the fourth lowest agricultural biomass available and at the 10%-33% agricultural residue could supply

2-9 1,000 ODTDP plants annually. The region has the fifth lowest woody biomass total and at the 10%-33% recovery could annually supply with woody biomass 9-31 1,000 ODTDP fermentation plants.

2.1.1.8. Conclusion

Woody biomass is roughly more available than agricultural biomass by a 2 to 1 ratio nationwide. If the economics favor wood as a feedstock for the fermentation plants then the South Central, Southeast, and Northeast regions will be the areas where these fermentation plants are most likely to locate. If the economics favor agricultural residue as a feedstock then the North Central, South Central, and Mountain areas would be the more favorable regions for a number of fermentation plants to locate. If the economics are such that both woody and agricultural biomass cost the same as feedstocks then the North Central and South Central regions and to a lesser degree Southeast and Pacific regions would be the favored regions in which to locate a number of fermentation facilities. These are generalizations and are not meant to imply that plants could not locate in any region using either or both feedstocks. Local supply conditions, especially transportation costs and the density of the desired biomass type will be most important factors in determining the economic feasibility of locating a plant in a given area.

2.1.2. Georgia Tech and SRI International Estimates

SRI International recently completed a study "Mission Analysis for the Federal Fuels from Biomass Program, Volume III; Feedstock Availability", January 1979. This report gave estimates of the amounts of various types of biomass that are collectable at various

prices for 1975 and various years in the future. Table 2.6 displays the information for their estimates of agricultural residue (just crop, manure has been deleted) and woody biomass for various prices for various years. The Georgia Tech estimate for the amount of woody and agricultural biomass potentially recoverable based on 1975 data equals over 305 million dry tons. This compares favorably with the 1975 total in Table 2.6 at \$30/dry ton of 378 million tons. However the SRI total shows a roughly 2 to 1 ratio of agricultural biomass to woody biomass, exactly the opposite of the Georgia Tech calculation which showed woody biomass as being twice as much as agricultural. The Georgia Tech calculation includes wood that is not included in the SRI estimate, most notably trees less than 5 inches in diameter at breast height. This could account for some of the discrepancy in woody biomass availability (199.9×10^6 tons estimated by Georgia Tech vs. 143×10^6 tons for SRI). The \$30/dry ton price is at present a reasonable delivery price for a ton of wood chips. Also at this \$30/ton price assuming .6 lb/Hexose/lb. cellulose the cost of ethanol (95%) can be held under \$1.20/gal.

In order to produce 95% ethanol at under \$1.20/gal. and assuming .6 lb. of hexose/lb. cellulose, then wheat straw must cost no more than roughly \$23/ton and corn stover no more than \$27.50/ton. Based on that information the agricultural biomass available based on the SRI data assuming \$25/ton would equal 191 million tons. This is higher than the Georgia Tech non-price based estimated of 105 million tons. SRI assumes a certain substitution of agricultural residue that is being used for other purposes for use as a fuel/feedstock as the

Table 2.6.

SRI International Summary of Residue Availability in 1975, 1985, and 2,000 For the U.S. By Type of Residue and Price

<u>Year</u>	<u>Price Per Dry Ton Delivered</u>		<u>Millions of Dry Tons Delivered</u>		
	<u>\$/10⁶ BTU</u>	<u>\$/ton</u>	<u>Agricultural</u>	<u>Woody**</u>	<u>Total</u>
1975	.67	10	40	60	138
	1.34	20	147	79	226
	2.00	30	235	143	378
	2.66	40	289	189	478
	3.33	50	328	220	548
	4.00	60	340	253	593
	4.66	70	*356	283	639
1985	.67	10	35	68	103
	1.34	20	101	88	189
	2.00	30	190	154	344
	2.66	40	259	202	461
	3.33	50	287	240	527
	4.00	60	357	276	633
	4.66	70	373	308	681
2000	.67	10	43	73	116
	1.34	20	125	94	219
	2.00	30	233	114	347
	2.66	40	322	164	486
	3.33	50	388	217	605
	4.00	60	423	286	709
	4.66	70	456	318	774

* a portion of this total may not be economically collectable due to factors such as stubble left, after harvesting or dispersion of residues even though at the given price the residue is theoretically counted as recoverable.

** includes base case standing vegetation added into base case woody biomass.

SOURCE: SRI International, "Mission analysis For the Federal Fuels From Biomass Program, Volume III: Feedstock Availability," (January 1979) pp. 27,28,29,32,65,66,67.

price gets higher. However, real world data indicates that the price of wheat straw delivered in Georgia averages \$70/ton with a range of \$40-90/ton (see Technical Report No. 1 of this project, Appendix A for verification). Also information in a letter from R.M. Ford of the U.S. Department of Agriculture, Agricultural Research, North Central Region, Peoria, Illinois, indicates prices for various types of agricultural biomass in his region for February 1979 as follows:

Hay, alfalfa, heavy grass mixed, U.S. Grade No. 2	-	\$61.70/ton
Straw, (oat or wheat) U.S. Grade No. 1	-	\$79.75/ton
Corn Stover	-	no information

This data indicates that present prices for agricultural residues do not make them economically attractive as a feedstock for fermentation facilities.

The SRI data indicates that at present if there was a large enough demand for agricultural biomass at \$70/ton almost 356 million tons would be available. In 1985 they estimate 373 million tons would be available at that price and in the year 2000 456 million tons would be available at that price, also. What is hard to understand about this data is that in the 1976 report of SRI, "Crop, Forestry, and Manure Residue Inventory - Continental United States" the total amount of crop residue produced at that time is given as 277.561 million tons. How could more than that be available in 1975 or even a good deal more be available in 1985 and 2000? Crop production would have to expand tremendously to produce that much more residue above 277 million tons.

The debate about which estimate of available residue is

more appropriate maybe a moot point in light of the cost of residue in the \$60-80/ton range. Unless agricultural residue is in the \$20-\$30/dry ton delivered cost range as is wood it will not be a desirable feedstock for fermentation. Therefore no matter how much potential is out there at \$70/ton, it will not likely be used as a feedstock for a fermentation facility.

Based on the above information it appears the regions where wood is an abundant feedstock will be the ones more likely to develop these large fermentation facilities unless it becomes more economical to sell an agricultural product, such as corn, as an energy feedstock rather than as a food source. In that case the large agricultural production regions, especially the North Central, would still be desirable regions in which to locate the fermentation plants. For example corn at \$2.50/bushel (\$83/ton) will yield ethanol at \$1.20/gal. (assuming cost of hexose at \$.057/lb.). Corn at prices of \$2.30/bushel or less does occur but grain prices are subject to fairly severe fluctuations from year to year and a somewhat consistent price over a number of years would be hard to anticipate. Wood prices on the other hand do not tend to fluctuate as badly as crop prices, especially pulpwood. Pulpwood quality or even non-commercial quality wood is the type that would be used in these fermentation plants. The price for this type of wood is low especially for hardwood. Pulpwood prices are expected to rise only 1% per year (above inflation) for the next 20 years. Softwood pulpwood in Georgia is about 13.60/dry ton prior to harvest and delivery. These costs should be under \$30/dry ton delivered.

In summary, agricultural residue though abundant in certain regions doesn't look appealing as feedstock at current prices. Agricultural products, such as corn do look appealing when they reach certain price levels but they will fluctuate at times to uneconomical levels. Wood seems to be the most abundant and consistently cheapest potential feedstock.

2.1.3. Land Requirements for Agricultural Residue Production

In Technical Progress Report No. 1 estimates were given for the amount of land required to annually sustain a 1,000 ODTPD facility on wood in perpetuity. For softwood this amount is 233,333 acres (365 square miles) which is equivalent to a 10.8 mile radius around the plant of nothing but softwood forest. For hardwood 466,667 acres (729 square miles) is the amount needed which is equivalent to a 15.2 mile radius around the plant of nothing but hardwood forest.

The same type of estimates have been made for various agricultural residues and are contained in Table 2.7. Rice provides the largest amount of residue per acre and requires even less land to sustain a 1,000 ODTPD facility than softwood if the assumption is made that all the residue produced would be used by the fermentation plant. In that case 165,406 acres or a 9.1 mile radius would be required. However, if only 30% of the total residue produced is recovered then 551,353 acres are required or a 16.6 mile radius. The 30% estimate of residue recovery is based on the approach developed earlier to estimate regional and national agricultural residue totals. This approach was to assume residues used as feed, fuel, or sold would continue to be used in that manner and that half of the returned and

Table 2.7.

The Amount of Land Required to Produce the Agricultural
Residue Necessary to Sustain a 1000 Oven Dry Ton Per Day
Ethanol Production Plant

Crop	<u>All Residues Produced Are Used</u>			<u>30% of Residues Produced Are</u>		
	Acres	Square Miles	Radius* (Miles)	Acres	Square Miles	Radius (Miles)
Rice	165,406	258	9.1	551,353	861	16.6
Soybeans	237,547	371	10.9	791,823	1237	19.8
Corn	243,646	381	11.0	812,153	1269	20.1
Irish Potatoes	254,545	398	11.3	848,483	1326	20.5
Wheat	267,388	418	11.5	891,293	1393	21.1
Peanuts	270,062	422	11.6	900,207	1407	21.2
Barley	331,108	517	12.8	1,103,693	1725	23.4
Rye	394,571	617	14.0	1,315,237	2055	25.6
Sorghum	398,089	622	14.1	1,326,963	2073	25.7
Oats	430,950	673	14.6	1,436,500	2245	26.7
Sweet Potatoes	587,593	918	17.1	1,958,643	3060	31.2
Cotton	1,414,141	2,210	26.5	4,713,803	7365	48.4

* Radius indicates the minimum distance in all directions from a hypothetical 1000 ODTPD Ethanol plant that land would have to be solely cultivated for the given crop to provide the residue necessary to sustain the plant.

wasted residue would be recovered. Half of the returned and wasted residue equal 30% of the total residue.

The next most productive agricultural residue producer is soybeans which requires a little more land than softwood at 237,547 acres or a 10.9 mile radius. At 30% recovery this equals 791,823 acres and a 19.8 mile radius. Next assuming full recovery is corn at 243,646 acres (11.0 mile radius), then Irish potatoes at 254,545 acres (11.3 mile radius), wheat at 267,388 acres (11.5 mile radius), and peanuts at 270,062 acres (11.6 mile radius). After peanuts there is barley at 331,108 acres (12.8 mile radius), rye at 394,571 acres (14.0 mile radius), sorghum at 398,089 acres (14.1 mile radius), and oats at 430,000 acres (14.6 mile radius). Hardwood would then follow oats in land requirement. The two worst residue producing crops analyzed are sweet potatoes at 587,593 acres (17.1 mile radius) and cotton at 1,414,141 acres (26.5 mile radius). All crops examined assuming total usage of residue were between radii of 9.1 and 14.6 miles except for sweet potatoes and cotton which were 17.1 and 26.5 miles respectively. Assuming only a 30% recovery of residue the radii for all crops examined extend from 16.6 miles to 26.7 miles excluding sweet potatoes and cotton which are 31.2 and 48.4 miles respectively. All this data indicates that if a 1,000 ODTPD plant is located in an agricultural intensive area it could be easily sustained by residues produced within a 50 mile radius of the plant and probably by residues produced within a 25 mile radius if need be.

2.1.4. Georgia Biomass Available

Estimates were made of the agricultural residue and

woody biomass potentially recoverable in the state of Georgia and the number of fermentation plants that could be sustained from this biomass. These estimates are contained in Table 2.8. Total agricultural residue in the state equals 976,775 dry tons. If all of this could be used it would be enough for only 2 1,000 ODTPD plants. If a 10%-33% recovery of this biomass is assumed then there is not even enough for 1 1,000 ODTPD plant.

The woody biomass total equals 10,479,895 dry tons. Assuming 10%-33% recovery of this biomass for fermentation plants 2-9* 1,000 ODTPD plants could be annually sustained by woody biomass. The total of agricultural and woody biomass equals 11,456,670 tons. Assuming a 10%-33% recovery of this total 3-10 1,000 ODTPD plants could be annually sustained. Obviously large scale fermentation plants in Georgia would be heavily oriented toward woody biomass rather than agricultural residue. There is significant potential for at least 2 1,000 ODTPD woody biomass fed fermentation plants in Georgia.

*Note: This data supplants the old estimate in Technical Progress Report No. 1 of the number of 1,000 ODTPD plants that could be annually sustained in Georgia at the 10%-33% recovery level (5-16 in Report 1 replaced by 2-9 in this report).

Table 2.8.

Georgia Biomass Potentially Available Annually
and the Plant Capacity and Number of Plants
Sustainable By the Biomass

	Annual Recoverable Biomass Tonnage Based on Percentages of Maximum Recoverable			
	<u>100%</u>	<u>50%</u>	<u>33%</u>	<u>10%</u>
<u>Agricultural</u>				
. Biomass Tonnage (ODT)	976,775	488,387	325,591	97,677
. Plant Capacity (ODTPD)	2,791	1,395	930	279
. Number of 1,000 ODTPD Plants	2	1	0	0
. Number of 2,000 ODTPD Plants	1	0	0	0
. Number of 5,000 ODTPD Plants	0	0	0	0
<u>Woody</u>				
. Biomass Tonnage (ODT)	10,479,895	5,239,948	3,493,298	1,047,990
. Plant Capacity (ODTPD)	29,943	14,971	9,981	2,994
. Number of 1,000 ODTPD Plants	29	14	9	2
. Number of 2,000 ODTPD Plants	14	7	4	1
. Number of 5,000 ODTPD Plants	5	2	1	0
<u>Agricultural and Woody</u>				
. Biomass Tonnage	11,456,670	5,728,335	3,818,889	1,145,667
. Plant Capacity	32,733	16,367	10,911	3,273
. Number of 1,000 ODTPD Plants	32	16	10	3
. Number of 2,000 ODTPD Plants	16	8	5	1
. Number of 5,000 ODTPD Plants	6	3	2	0

Note: All numbers were truncated when calculating the number of plants.

2.2. Chemical Composition of Biomass Feedstock

The average chemical composition of hardwood and softwood is summarized in Table 2.9. It gives the cellulose, hemicellulose, lignin, uronic anhydride, acetyl and ash content. Also mentioned are the pentosan and hexosan fractions of the hemicellulose. These values are based on extractive free wood and are derived from values mentioned in Table 2.4 of the First Quarterly Report, page 20¹.

Table 2.9. Chemical Composition of Hardwood and Softwood

Components	% Composition	
	Hardwood	Softwood
Cellulose	45.1	43.8
Hemicellulose	26.4	21.6
Pentosans	19.35	6.8
Hexosans	7.05	14.8
Lignin	20.3	29.5
Uronic Anhydride	4.1	3.6
Acetyl	3.9	1.4
Ash	0.3	0.2

The hardwood pentosans content is higher than that of softwood while the reverse is the case in hexosans. The lignin content of softwood is higher than that of hardwood. Appendix A shows the calculation of pentosans and hexosans of soft and hardwoods. The composition of corn stover with the cob² and without the cob is listed in Table 2.10. The pentosans and hexosans content of the hemicellulose were estimated using the values in Tables 2.10 and 2.11 of the First Quarterly Report^{2,3} (pages 26-27).

Table 2.11 gives the analysis of cornstalk where the individual sugar contents are shown. The estimated sugar content in the other parts of the plant(leaf, husk and cob) is based on the idea that they have the same distribution ratios as in corn stalk. Appendix A shows these calculations.

Table 2.10. Chemical Composition of Corn Stover

Component	% Composition	
	With the Cob ²	Without the Cob
Cellulose	32.82	32.30
Hemicellulose	28.34	25.96
Pentosans	20.15	18.45
Hexosans	8.19	7.50
Lignin	8.71	9.07
Protein	3.77	4.04
Soluble Sucrose	19.98	21.12
Extractives	1.41	2.08
Ash	4.88	5.40

The analysis did not show any difference between corn stover with or without cob. The amount of pentosans is similar to that of hardwood and lignin content is much less than that of soft or hardwoods.

The Battelle laboratories data² shows an average of 20% soluble sucrose. The results reported by Berkeley, California⁴ did not show this soluble sucrose and by personal communication with them we discovered that their samples were molded and covered with black fungus which probably was due to bacterial attack before analysis. The Berkeley corn stover analysis

on dry basis and cob free is in the following table:

Table 2.11. Corn Stover Composition (Berkeley, California)

	<u>California (Sacramento)</u> <u>(Fall 1975 crop)</u>	<u>Indiana Purdue</u> <u>(1977 crop)</u>
Glucan	35.1	33.0
Mannan	.25	0.8
Galactan	.75	1.6
Xylan	13.0	19.3
Araban	2.8	3.7
Lignin	15.1	13.7
Ash	4.3	5.3
Extractives	5.5	4.7
Protein	4.0	4.2
Unidentified Organics	18.0	1.2

Wheat straw composition is listed in Table 2.12. In wheat straw cellulose is the only source of glucan. This was confirmed by Berkeley California laboratory⁴.

Table 2.12. Composition of Wheat Straw

<u>Component</u>	<u>Percent</u>
Cellulose	32.9
Hemicellulose	21.9
Pentosans	19.0
Hexosans	2.9
Lignin	14.5
Extractives	7.2
Protein	3.0
Unidentified Organics	8.0
Ash	9.6

The cellulose content of agricultural residues (corn stover and wheat straw) is the same but less than that of soft and hardwoods. The hemicellulose content of all the lignocellulosic materials mentioned here is about the same. The pentosan contents of hardwood, corn stover and wheat straw are the same while the hexosan of softwood is higher than that of these above mentioned materials. Wheat straw hemicellulose has the least amount of hexosans.

Lignin content of softwood is higher than that of hardwood while both are higher than that of agricultural residues. The lignin content of wheat straw is in the midway between that of wood and corn stover. Table 2.13 presents the pentosans (xylose and arabinose) and hexosans (glucan and mannan and galactan) maximum theoretical yield as percent of the total carbohydrate content of the biomass feedstock.

Table 2.13. Pentosans and Hexosans Maximum Theoretical Yield

Material	% Total Carbohydrate	% Pentosans	% Hexosans
Hardwood	71.5	27.06	72.94
Softwood	65.4	10.39	89.61
Wheat Straw	54.8	34.67	65.33
<u>Corn Stover:</u>			
a) With cob	81.14	24.81	75.17
b) Without cob	79.38	23.26	76.74

The different types of sugars that constitute the hemicellulose of the feedstock are presented in Table 2.14:

Table 2.14. Hemicellulose Composition

Material	Pentosans			Hexosans			
	Xylan	Araban	Total	Glucan	Galactan	Mannan	Total
Hardwood	18.85	.5	19.35	3.9	0.8	2.35	7.05
Softwood	5.75	1.07	6.82	2.09	1.43	11.23	14.75
Wheat Straw	16.9	2.1	19.0	-	2.16	.72	2.88
<u>Corn Stover:</u>							
a) With Cob	17.96	2.19	20.15	6.19	1.30	.70	8.19
b) Without Cob	16.44	2.02	18.46	5.65	1.2	.65	7.50

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3.0. TENTATIVE PDU PROCESS

3.1. Main Process

The tentative PDU process includes steam explosion pretreatment to give the system the capability of removing the lignin. Prehydrolysis, hydrolysis (both acid and enzymatic are included). Provision is made for acid neutralization, sugar solution, clarification, concentration, detoxification and sterilization. Fermentation can be operated as batch, semicontinuous and continuous (atmospheric). Finally, alcohol recovery consists of a first stage 95% alcohol system followed by azeotropic distillation to produce anhydrous alcohol.

The tentative PDU Process is shown as a block diagram in Figure

3.1. The main stream system consists of the following processes:

- 1) Pretreatment - Steam Explosion (Iotech), Filtration and Washing, Delignification
- 2) Prehydrolysis - Dilute Sulfuric Acid
- 3) Hydrolysis -
 - a) Dilute Sulfuric Acid, Neutralization,
 - or
 - b) Enzymatic (CSTR) Detoxification
- 4) Fermentation - Clarification, Concentration, Sterilization, Continuous Fermentation (atmospheric), Yeast Separation, Yeast Recycle.
- 5) Alcohol Recovery - Alcohol Purification (95% alcohol), Azeotropic Distillation.

3.2. Alternate Processes

The following processes have been recommended either as alternates if problems arise with the main stream process or as additional processes

FIGURE 3.1

**Biomass Fermentation Facility
Process Block Diagram**

which are considered to have enough potential to warrant inclusion in the process.

1) Pretreatment -	(a) Acidic autoclaving
	(b) Dilute acid hydrolysis
	(c) Purdue Process
2) Prehydrolysis -	No alternate process.
3) Hydrolysis -	(a) Dilute acid plug flow
	(b) Concentrated acid (Hokkaido Process)
	(c) Autohydrolysis (Snyder)
4) Fermentation -	(a) Tower fermenter
	(b) Continuous vacuum
5) Alcohol Recovery -	No alternate process (membrane separation may be a future choice).

3.3. Material Balances

Twelve conceptual flow diagrams with material balances at the PDU scale are included. These calculations are for three process, i.e., the Enzymatic Hydrolysis route, the Modified Madison process, and the High Risk Snyder process. Each of these processes are considered for four lignocellulosic substrates, i.e., softwood, hardwood, wheat straw and corn stover. The expected yield of ethanol from the various processes using different substrates are shown in Table 3.1. These yields are calculated for one pass or without recycling of the unhydrolyzed cellulose. This aspect would be evaluated more realistically in the proposed PDU.

Table 3.1. Expected Yield of Absolute Ethanol at the PDU Scale
using Different Substrates (250 LB/HR, Oven Dried)

Processes	Yield of Ethanol LB/HR			
	Softwood	Hardwood	Wheat Straw	Corn Stover
Modified Madison Process	44.5	45.6	33.3	33.2
High Risk Snyder Process	79.1	70.4	48.2	79.6
Enzymatic Hydrolysis Route	26.7	27.4	20	19.9

FIGURE 3.2. MODIFIED MADISON PROCESS
SOFTWOOD

FIGURE 3.3 MODIFIED MADISON PROCESS - HARDWOOD

FIGURE 1.- MODIFIED MADISON PROCESS
CORN STOVER - COB

FIGURE 3.5 MODIFIED MADISON
WHEAT STRAW

FIGURE 3.6 ENZYMATIC HYDROLYSIS
SOFTWOOD

FIGURE 3.7 ENZYMATIC HYDROLYSIS - HARDWOOD

FIGURE 3.3 ENZYMATIC HYDROLYSIS - CORN STOWER

FIGURE 3.9 ENZYMATIC HYDROLYSIS - WHEAT STRAW

FIGURE 3.10 "H-CRISK" PROCESS - SOFT WOOD

FIGURE 3.11 "HIGH RISK" PROCESS - HARD WOOD
BASIS 250 LB./HR.

FIGURE 3.12 HIGH RISK - CORN STOWER (WITH COB)

4.0. RATIONALE FOR CONCEPTUAL DESIGN OF THE PDU

4.1. Introduction

In the preceeding section we have introduced a conceptual design for a three oven-dry ton per day process development unit (PDU) which proposes a "mainstream" process line upon which it is built, in an integral manner, optional unit operations and sub-systems which are felt to merit engineering investigation.

The total system, as presented, represents unit operations which in our estimation have high potential (and, in some instances, a corresponding risk) in fulfilling the ultimate objectives of this program: demonstration on a pilot scale of the economic and technical feasibility of producing alcohol from lignocellulosic biomass.

In subsequent subsections, the selection-elimination process which has been applied for the individual unit operations and the critical analysis of process economics will be examined, i.e., the factors which have led to the proposal conceptual design presented in Section 3.0.

Our approach in all instances was to estimate process potentialities and the needs for engineering R and D in Phases II and III of this program, the "Design, Fabrication and Operation of a Biomass Fermentation Facility".

4.2. Process Economics

Process Economics and Optimization for Hexose Production by Acid Hydrolysis

Previous published reports have estimated the cost of hexose produced by the dilute acid hydrolysis of cellulose (1,2). In these reports, the design was based on operating conditions which maximized hexose concentration exiting the reactor. Operating conditions which maximize hexose concentration would also represent the minimum cost for hexose produced if the cost of the cellulose raw materials were negligible. As was shown in a previous report, the cost of cellulose raw materials in the production of hexose is substantial (3). Cellulose raw materials costs must be considered in order to obtain a minimized hexose cost.

4.2.1.1. Cost Function

A generalized process to produce a hexose solution of given concentration by continuous dilute acid hydrolysis is shown in Figure 4.1. The assumptions made in constructing the model process are presented in Table 4-1. The model parameters to be investigated for the process are given in Table 4-2. The major cost elements of producing hexose by this process can be given as:

$$\begin{aligned} \frac{\text{cost}}{\text{kg hexose}} = & \frac{\text{cost of cellulose consumed}}{\text{kg hexose}} + \frac{\text{cost of acid-lime}}{\text{kg hexose}} + \frac{\text{cost of reactor}}{\text{kg hexose}} \\ & + \frac{\text{concentrator cost}}{\text{kg hexose}} + \frac{\text{cellulose recycle cost}}{\text{kg hexose}} \end{aligned} \quad (4.1)$$

The cost function (eq. 4.1) can be expressed symbolically as follows:

$$\begin{aligned} \frac{\text{cost}}{\text{kg hexose}} = & \frac{v_o (C'_{co} - \theta C'_c) \$c}{v_o C_g} + \frac{v_o C_A \$A}{C_g v_o} + \frac{V \$R}{C_g v_o} + (1/C_g - 1/C_g^*) \$_{\text{conc}} + \\ & \frac{\theta C'_c v_o \$_{\text{recycle}}}{C_g v_o} \end{aligned} \quad (4.2)$$

Figure 4.1. Process to Produce a Hexose Solution by the Dilute Acid Hydrolysis of Cellulose

Table 4-1 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. 90% recovery of unreacted cellulose from reactor product stream.
6. Lime neutralization of hydrolysis acid solution.
7. Multiple-effect evaporation.
8. 13% final hexose concentration.

Table 4-2 Model Parameters

1. Reactor types (CSTR, PFR, and Fixed Bed).
2. Cost of cellulose (wood).
3. Concentration of cellulose feed.
4. Concentration of sulfuric acid.
5. Temperature.
6. Cost of Reactor.
7. Cost of sulfuric acid and the equivalent lime for neutralization.
8. Cost of recycling unreacted cellulose.
9. Cost of concentrating hexose solution.
10. Concentration of final hexose solution.

where $\$C$ = cost of cellulose,
\$/kg equivalent hexose

$\$A$ = cost of acid-lime,
\$/kg acid

$\$R$ = cost of reactor
(fixed + operating
charges), \$/m³ reactor-hour

$\$_{conc}$ = concentrator charges,
\$/m³ evaporated

$\$_{recycle}$ = recycle charges,
\$/kg cellulose recycled

where v_o = volumetric flowrate,
m³/hr

θ = fraction of cellulose
exiting the reactor
which can be recovered
and recycled

C_A = concentration of acid,
kg/m³

V = volume of reactor, m³

C_g^* = desired concentration
of hexose, exit
concentrator, kg/m³

In order to minimize the cost of the hexose, a model of the process shown in Figure 4.1. was developed. The kinetics for the saccharification of cellulose and the degradation glucose reported by Saeman were used to model the reactions (4).

For cellulose disappearance

$$-\frac{dC'_c}{dt} = k_1 C'_c \quad (4.3.)$$

where C'_c = concentration of cellulose expressed as kg equivalent of hexose/m³

t = time in hours

k_1 = cellulose saccharification rate constant, hr⁻¹

For glucose appearance

$$\frac{dC_g}{dt} = k_1 C'_c - k_2 C_g \quad (4.4.)$$

where C_g = concentration of hexose, kg/m³

k_2 = glucose degradation rate constant, hr⁻¹

4.2.1.2. Optimization: Continuously Stirred Tank Reactor

A separate optimization had to be developed for each reactor, for the Continuous Stirred Tank Reactor (CSTR), a cellulose balance gives:

$$\frac{C'_{co} - C'_c}{k_1 C'_c} = \tau \quad (4.5.)$$

where C'_{co} = concentration of cellulose in the feed expressed as kg equivalent hexose/ m^3

τ = residence time, hours

$$\text{or } C'_c = \frac{C'_{co}}{1 + k_1 \tau} \quad (4.6)$$

Similarly, a hexose balance gives:

$$\frac{C_g - C_{go}}{k_1 C'_c - k_2 C_g} = \tau \quad (4.7)$$

where C_{go} = concentration of hexose in the feed, kg/m^3

For $C_{go} = 0$

$$C_g = \frac{k_1 C'_c \tau}{k_2 \tau + 1} \quad (4.8)$$

$$\text{or } C_g = \frac{C'_{co} k_1 \tau}{(1 + k_1 \tau)(1 + k_2 \tau)} \quad (4.9)$$

The C_g and C'_c for a CSTR can be substituted into the cost function (Eq 4.2.). The cost function thus can be differentiated with respect to τ and a minimum cost can be determined. Differentiating (4.2) and setting the expression equal to zero, the following form is obtained:

$$\frac{d(\frac{\text{cost}}{\text{kg hexose}})_{\text{CSTR}}}{d\tau} = \tau_{\text{opt}}^3 + P\tau_{\text{opt}}^2 + R = 0 \quad (4.10)$$

where $a = (C'_{co} \$c + C_A \$A + \$_{\text{conc}})/C'_{co}$

$b = \theta(\$_{\text{recycle}} - \$c)$

$c = \$R/C'_{co}$

$d = \$_{\text{conc}}/C_g^*$

$e = 1/k_1 (a+b)$

$f = 1/k_1 [a(k_1+k_2) + bk_2 + c]$

$g = 1/k_1 [ak_1k_2 + c(k_1+k_2)]$

$h = ck_2$

$P = g/2h > 0$ always $R = -e/2h < 0$ always

k_1 and k_2 are a function of acid concentration and temperature.

τ_{opt} for a CSTR thus can be numerically obtained as a function of temperature, acid concentration, and the constants associated with eq. 4.10. τ_{opt} can be substituted into eq. 4.2 to obtain the minimum cost of producing the hexose solution in a CSTR.

4.2.1.3. Optimization: Plug Flow Reactor

A similar minimum cost function can be obtained for a plug flow reactor (PFR). In a PFR the concentration of cellulose as a function of τ is:

$$C'_c \int_{C'_{co}}^{\frac{dC'_c}{C'_c}} = - \int_0^{\tau} k_1 d\tau \quad (4.11)$$

$$\text{or } C'_c = C'_{co} e^{-k_1 \tau} \quad (4.12)$$

The hexose concentration as a function of τ in a PFR is:

$$\frac{dC_g}{d\tau} = k_1 C'_c - k_2 C_g \quad (4.13)$$

Integrating gives:

$$C_g = \frac{k_1 C'_{co}}{k_2 - k_1} [e^{-k_1 \tau} - e^{-k_2 \tau}] \quad (4.14)$$

Now the expressions for C'_c and C_g in a PFR can be substituted into eq. 4.2. Differentiating the resultant equation and setting it equal to zero gives an equation of the following form:

$$\frac{d(\frac{\text{cost}}{\text{kg hexose}})_{PFR}}{d\tau} = (e + f\tau_{opt}) - (g + h\tau_{opt})e^{-(k_1+k_2)\tau_{opt}+pe^{-k_2\tau_{opt}}} = 0 \quad (4.15)$$

$$\text{where } a = \frac{C'_{co} \$c + C_A \$A + \$_{conc}}{C'_{co}}$$

$$b = \theta(\$_{recycle} - \$c)$$

$$c = \$R/C'_{co}$$

$$d = \$_{conc}/C_g *$$

$$e = c + ak_1$$

$$f = ck_1$$

$$g = c + ak_2$$

$$h = ck_2$$

$$p = b(k_1 - k_2)$$

τ_{opt} for a PFR thus can be numerically obtained as a function of temperature, acid concentration, and the constants associated with eq. 4.15. τ_{opt} can be substituted into eq. 4.10 to obtain the minimum cost of producing the hexose in a PFR.

4.2.1.4. Sensitivity Analyses for CSTR and PFR

A computer program was written to evaluate τ_{opt} for a CSTR and PFR as a function of temperature, acid concentration, feed cellulose concentration and the constants in equations 4.10 and 4.15. The program also evaluated the cost function (eq. 4.2) for a CSTR and PFR, to estimate the minimum hexose cost for each type of reactor. A listing of the program is shown in Appendix B. The program uses the rate constants for dilute acid hydrolysis of cellulose and the degradation of hexose reported by Saeman (4). The constants in equations 4.10 and 4.15 were estimated as shown in Appendix C and are summarized in Table 4-3 below. Also shown in Table 4-3 are base line operating parameters. The base line operating parameters represent reasonable operating conditions for both the CSTR and PFR systems.

Tables 4-4 and 4-5 show τ_{opt} for a CSTR and a PFR respectively as a function of temperature and feed cellulose concentrations (the other parameters are given in Table(4-3)). Figures 4.2 and 4.3 graphically present τ_{opt} given in Tables 4-4 and 4-5. The information for the above tables and figures were obtained from the sample computer printout in Appendix D. When these τ_{opt} 's were substituted into the cost equations, the minimum hexose costs as a function

Table 4-3 Base Line Costs and Base Line Operating Parameters

<u>Parameter</u>	<u>Value</u>	<u>Remarks</u>
C'_{co}	115 kg equivalent hexose per m^3	cellulose feed concentration equivalent to 10 wt% cellulose
C_A	1 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	483°K	temperature equivalent to 210°C
θ	0.9 kg cellulose recycled/ kg cellulose unreacted	fraction of unreacted cellulose recovered

Table 4-4 Optimization of Residence Time at Various Temperature and Feed Concentrations for CSTR

CSTR Temperature, °C	Optimum Residence Time, minutes		
	10% Cellulose	20% Cellulose	30% Cellulose
170	43	38	36
180	17	15	14
190	7.1	6.2	5.8
200	3.0	2.6	2.4
210	1.3	1.1	1.1
220	0.58	0.51	0.47

Figure 4.2. Effect of Temperature on the Optimum Residence Time in a CSTR System to Produce a 13% Hexose Solution (see Table 4-3 for other operating conditions).

Table 4-5 Optimization of Residence Times at Various Temperatures
and Feed Concentrations for PFR

PFR Temperature, °C	Optimum Residence Time, minutes		
	<u>10% Cellulose</u>	<u>20% Cellulose</u>	<u>30% Cellulose</u>
170	49	45	43
180	20	18	17
190	7.9	7.1	6.7
200	3.3	3.0	2.8
210	1.4	1.3	1.2
220	0.64	0.57	0.54

Figure 4.3. Effect of Temperature on the Optimum Residence Time in a PFR System to Produce a 13% Hexose Solution (see Table 4-3 for other operating conditions).

of temperature and feed cellulose concentration were obtained. These minimum costs are given in Table 4-6 and a plot of these minimum costs is shown in Figure 4.4. For series reactions where the desired product is an intermediate, PFR's have higher potential desired product produced per raw material consumed than do CSTR's. Figure 4.4 shows the benefits of using a PFR versus using a CSTR under the above conditions.

Under standard operating conditions, the minimized costs are listed in Table 4-7.

The effect of acid concentration on the minimized cost of hexose is given in Table 4-8 and shown graphically in Figure 4.5. The minimum cost for the hexose is typically between 1.0 and 1.5 wt percent sulfuric acid. As is apparent from the data, the feed concentration of the cellulose has a dramatic effect on the minimized hexose cost. A comparison of a PFR operating with 10%, 20% and 30% cellulose feed solutions is given in Table 4-9.

The operating conditions for the 20 percent case shown in Table 4-9 appear very reasonable. The operating conditions for the 30 percent case, on the other hand, are questionable. Whether a plug flow reactor can actually operate under these conditions must be determined experimentally. For all of these cases, however, the cost of the cellulose raw material is the major cost item in producing hexose from wood. The production cost of the hexose thus is very sensitive to the cost of the cellulose. Table 4-10 shows the sensitivity of hexose costs to wood costs. The current quote for wood chips in Georgia is \$28 per oven dry ton. Figure 6 graphically represents Table 4-10.

Ethanol at \$1.20/gal of 95% (\$15/MM BTU) is the equivalent of \$0.169/kg of hexose. The cost of converting hexose to 95% ethanol is approximately \$0.044 per kg of hexose. Thus, the cost of ethanol (95%) can be held to below

\$1.20/gal if hexose can be produced from cellulose for \$0.125 per kg hexose or less. Figure 4.6 indicates that using an optimized PFR recycle system will meet this cost criteria.

A similar optimization study for a fixed bed reactor system is currently underway and the results of this study will be reported in the future.

Table 4-6 Minimized Hexose Cost at Various Temperatures and Feed Concentrations for CSTR and PFR

<u>PFR Temperature, °C</u>	<u>Minimized Cost of Hexose, ¢/kg</u>		
	<u>10% Cellulose</u>	<u>20% Cellulose</u>	<u>30% Cellulose</u>
170	17.9	14.0	12.7
180	15.7	12.6	11.5
190	14.3	11.6	10.7
200	13.3	10.9	10.1
210	12.5	10.3	9.7
220	11.8	9.8	9.4

<u>CSTR Temperature, °C</u>	<u>Minimized Cost of Hexose, ¢/kg</u>		
	<u>10% Cellulose</u>	<u>20% Cellulose</u>	<u>30% Cellulose</u>
170	23.8	18.2	16.3
180	20.8	16.3	14.7
190	18.8	14.9	13.5
200	17.3	13.8	12.6
210	16.0	12.9	11.8
220	15.0	12.1	11.1

Figure 4.4. Effect of Temperature on the Minimized Cost of Producing a 13% Hexose Solution in a CSTR and a PFR System (see Table 4-3 for other operating conditions).

Table 4-7 Minimized Hexose Costs Under Base Line Operating Conditions

<u>Unit Costs</u>	<u>CSTR</u>		<u>PFR</u>	
	<u>\$/kg Hexose</u>	<u>Percent of Total Cost</u>	<u>\$/kg Hexose</u>	<u>Percent of Total Cost</u>
Cellulose Raw Material Cost	.1040	64.8	.0906	72.7
Acid and Equivalent Lime Cost	.0217	13.6	.0150	12.0
Reactor Cost	.0002	.1	.0002	.1
Hexose Concentration Cost	.0264	16.5	.0150	12.0
Cellulose Recycle Cost	.0080	5.0	.0040	3.2
TOTAL	.160	100.0	.125	100.0

Table 4-8 Minimized Hexose Cost at Various Acid Concentrations and Feed Concentrations for CSTR and PFR

PFR Sulfuric Acid Concentration Wt. Percent	Minimized Cost of Hexose, ¢/kg		
	10% Cellulose	20% Cellulose	30% Cellulose
0.5	12.5	10.5	9.9
1.0	12.5	10.3	9.7
1.5	12.8	10.3	9.7
2.0	13.1	10.4	9.7
2.5	13.6	10.5	9.8
3.0	14.0	10.7	9.9

CSTR Sulfuric Acid Concentration Wt. Percent	Minimized Cost of Hexose, ¢/kg		
	10% Cellulose	20% Cellulose	30% Cellulose
0.5	16.1	13.2	12.2
1.0	16.0	12.9	11.8
1.5	16.5	12.9	11.7
2.0	17.0	13.0	11.7
2.5	17.6	13.2	11.7
3.0	18.2	13.5	11.8

Figure 4.5. Effect of Sulfuric Acid Concentration on the Minimized Cost of Producing a 13% Hexose Solution in a CSTR and a PFR System (see Table 4-3 for other operating conditions).

Table 4-9 Effect of Feed Concentration on Hexose Production Cost for PFR Operation

Costs	Feed Cellulose Concentration					
	10%		20%		30%	
	\$/kg Hexose	Percent	\$/kg Hexose	Percent	\$/kg Hexose	Percent
Cellulose Cost	.0906	72.7	.0889	86.5	.0882	90.6
Cost of Acid and Equivalent Lime	.0150	12.0	.0069	6.7	.0041	4.2
Reactor Cost	.0002	0.1	.0001	0.1	.0000	0.1
Hexose Concentration Cost	.0150	12.0	.0024	2.3	.0000	0.0
Cellulose Recycle Cost	.0040	3.2	.0045	4.4	.0049	5.1
TOTAL	0.125	100.0	0.103	100.0	0.097	100.0
Hexose Concentration Exiting Reactor	5.5%		11.0%		16.6%	
Cellulose Conversion per Pass	61.8%		57.8%		55.8%	
kg of Hexose Produced/kg Cellulose Equivalent Hexose Consumed	0.77		0.80		0.81	
Residence Time	1.4 min		1.3 min		1.2 min	

Table 4-10 Minimized Hexose Cost at Various Feedstock Costs and Concentrations for CSTR and PFR

PFR Cost of Cellulose \$/ODT Wood	Minimized Cost of Hexose, ¢/kg		
	10% Cellulose	20% Cellulose	30% Cellulose
15	7.9	5.8	5.3
20	9.4	7.3	6.8
25	11.0	8.8	8.3
30	12.5	10.3	9.7
35	14.0	11.8	11.2

CSTR Cost of Cellulose \$/ODT Wood	Minimized Cost of Hexose, ¢/kg		
	10% Cellulose	20% Cellulose	30% Cellulose
15	10.8	7.7	6.7
20	12.5	9.5	8.4
25	14.3	11.2	10.1
30	16.0	12.9	11.8
35	17.8	14.6	13.5

Figure 4.6. Effect of Wood-Cost on the Minimized Cost of Producing a 13% Hexose Solution in a CSTR and a PFR System (see Table 4-3 for other operating conditions).

4.2.2. Process Economics: Enzymatic Hydrolysis

In the preceeding section 4.2.1., a detailed sensitivity analysis was undertaken on the cost of hexose production by acid hydrolysis. Among the benefits of such an analysis is the ability to predict the benefits and relative merits of production with different reactor designs. It has been shown that a plug flow reactor possesses substantially more potential for the economic production of alcohol via acid hydrolysis than does the employment of a well-stirred reactor system. Recent results, not reported, indicate that a fixed bed reactor is equally, if not more, promising as a reactor design for minimized cost of hexose production.

Central to the successful sensitivity analysis was the reliability of an accurate chemical model and reaction kinetics. In the case of enzymatic hydrolysis there is a real lack of data to effect such a study.

It is well known that cellulose degradation can be accomplished by various species of bacteria, protozoa and fungi. However, the various fermentation which have been reported have generally been performed only at bench-scale. Little emphasis has been given to the types of kinetic and strain selection studies which would be useful as a basis for the design of large-scale or pilot-scale process equipment.

In the First Quarterly Report (section 4.2., pp. 49-67) a review of current research on the enzymatic hydrolysis of cellulose was presented. It became obvious that a number of organisms have a significant level of cellulose activity and that major improvements in cellulolytic activity might be expected in the next few years by strain selection.

While kinetic studies are being undertaken as part of different research programs, e.g., M.I.T. is characterizing the kinetics of fermentation

of cellulose with Cl. thermocellum there is a dearth of information regarding reactor design and costs for enzymatic hydrolysis. Purdue⁵ recently initiated a series of experiments in hopes of developing an economic model based on actual experimental data to predict enzyme and reactor costs. They have based their analysis on the basis of complete conversion and used an empirical relationship developed by Migamoto and Nisizawa⁶:

$$x = k t^m L^n$$

where:

x = fraction of cellulose saccharified

k = empirical constant

t = time (hours)

L = enzyme concentration/lb. residue

m,n = empirical constants which are determined by the microbial source of the cellulases.

The equation has been claimed to be applicable to Aspergillus niger and Irpex lacteus cellulase-catalyzed reactions and was used by Purdue to fit the action of Trichoderma reesei. While a critical analysis of their derivation has not been completed there are certain assumptions, which have been made, which seem questionable as to practical application, e.g., 100% conversion of cellulose to glucose in periods of 5 hours has been assumed.

The baseline parameters used in Purdue's cost estimates follow:

Reactor, glass-lined (installed cost)	\$5/gal. (est.)
Enzyme Cost (Rutgers and Natick)	\$2/10 ⁶ IU
Sugar Production (as glucose)	0.4 lb/lb residue
Fraction Enzyme recovered (Berkeley)	0.3-0.7

The reactor cost is based on the 1968 data of Peters and Timmerhaus⁷,

~~\$2~~/gallon, and corrected for inflation.

Their economic analysis of enzyme-catalyzed saccharification of pretreated cellulose concluded that at $\$2/10^6$ IU enzyme, total reaction costs will be less than 0.2¢/lb. sugar produced and that at $\$20/10^6$ IU enzyme, total reaction costs will be less than 1¢/lb. sugar produced. The analysis is premised on the projections that net enzyme costs in terms of sugar yield decrease exponentially, markedly offsetting reactor cost increases, with increased reaction time and assumes the elimination of enzyme recovery at reaction times greater than 25 hours.

In section 4.4.4. of this report, a discussion of hardware or, more accurately, reactor configurations for enzymatic hydrolysis is discussed with the objective of defining a system which is applicable to incorporation in the proposed process development unit (PDU). As has been indicated in this discussion and in our First Quarterly Report, significant advances in the research on enzymatic hydrolysis at Rutgers, at MIT, at the University of Pennsylvania, and at Berkeley, among others may be expected with strain selection and improvements in terms of stability, processability, cellulolytic activity, and production economics. The case for incorporation of enzymatic hydrolysis processes within the PDU system seems very well justified, all the more so, by the lack of engineering data and kinetic data which has been generated heretofore. The improvements being made in the glucose conversion efficiencies and in production rates of various enzymes has led us to the conclusion that an ancillary enzyme production and sub-system should not be included in the PDU and that an approach which emphasizes flexibility and versatility of design of the enzymatic reactor should be applied. Further details are presented in Section 4.4.4.

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4.3. Pretreatment

It has been proposed by many researchers that the chemical reactions of cellulose are primarily controlled by its highly crystalline structure. The chemical accessibility is limited by this crystallinity to the crystallite surfaces; therefore the overall conversion rates are much lower than the conversion rates of more open amorphous materials such as starch.

In the acid hydrolysis of cellulose the sugar is produced and decomposed at the same reaction conditions. Thus, the overall sugar yield is governed by the relative rates of sugar production and sugar degradation. In contrast, in the hydrolysis of starch, the sugar yields are almost quantitative since the rate of destruction of sugar is far exceeded by the rate of sugar formation. It is no surprise that the reaction rate for hydrolyzing cellulose to sugar and rates of sugar decomposition is the same order of magnitude. Because of this maximum yields of sugar from wood hydrolysis have been limited.

A further deterrent to reacting cellulose in ligno-cellulosics is the lignin constituent. There is a great deal of evidence, that the cellulose is "protected" by the lignin particularly from enzymatic attack. Many feeding trials of wood which contains 70-80% total carbohydrates have shown that these carbohydrates are essentially unavailable to the animal. The wood cellulose has also been shown to be unavailable to high-potency cellulolytic enzymes in laboratory experiments. The exact mechanism of this inhibition is not yet understood.

However, the reactivity of cellulose in lignocellulosic material has been enhanced by a wide variety of physical and chemical treatments.

Many of these processes were reviewed in the First Quarterly Report¹ and are shown in Table 4.1.. The selection of processes to be considered for inclusion in the PDU is based on the following:

- 1) The process must be effective.
- 2) The process must be applicable to a wide variety of materials.
- 3) The process must be low-cost,

The majority of pretreatment processes can be classified as chemical or physical. Many of these can be immediately rejected for not meeting one or more of the previously stated requirements. The chemical treatments of pulping is much too costly to be a viable system for inclusion in the PDU. Alkali treatments are either too costly or treated materials differ widely in their degree of susceptibility to hydrolysis.

The physical treatments of irradiation while showing interesting improvements in digestibility of cellulose are much too expensive to be considered. The final selection was narrowed to the following processes:

- 1) Steam explosion with and without delignification
- 2) Autoclaving; proprietary process developed at U. of Calif.
- 3) Prehydrolysis with dilute sulfuric acid
- 4) Cellulose "dissolution" with concentrated sulfuric acid (Purdue process).

The main difficulty encountered has been the lack of good cost data for these processes. But, based on the estimates available the steam explosion process has been selected as the primary process for inclusion in the PDU. The question of whether to remove the lignin at this stage of the process is being postponed to the actual operation of the PDU. The flexibility

of the system will permit operation with lignin removal and without lignin. A comparison of both the technical aspects of the process as well as the economics of aspects under both operations can be made. At this time there are several steam explosion processes available. Iotech Corporation has developed a batch process which operates at 600-1250 psi. Stake Technology has developed a continuous process which operates in the range of 350 psi. Also General Electric has worked with a low pressure system.

It is believed that for the PDU the Iotech process offers more versatility since it can operate in a much wider pressure range. The Iotech, since it is a batch system and because it can operate at very high pressures, will also permit the investigation of the Snyder process for autohydrolysis, thereby extending the flexibility of the PDU.

Three other processes which also meet the process requirement have been selected for possible inclusion as alternate pretreatments. One is a proprietary process developed at the Univ. of California² which was high shear mixing under pressure with dilute acid to prehydrolyze and reduce the biomass to a high concentration pumpable slurry.

The second alternative is the prehydrolysis process with dilute sulfuric acid. Researchers at Auburn University have estimated operating costs of approximately at 0.6¢/lb. of wood.

The last process is the Purdue process for "dissolution" of cellulose with concentrated sulfuric acid as developed by Tsao.

Because of the uncertainties of the economics as well as large scale technical operation the only way to determine the best pretreatment system may be to operate all of them to get a direct comparison.

Table 4.11. Pretreatment CostsEstimated Cost
\$/Biomass ODT

I. Chemical

Swelling with Alkaline Agents

1)	Sodium Hydroxide	10-55
2)	Ammonia	

Delignification

1)	Pulping	200+
2)	ClO ₂	200
3)	Ammonium Bisulfate	
4)	SO ₂	40-100
5)	Sodium Chlorite	
6)	Organic Solvents	

Cellulose Dissolution

1)	Tsao/Purdue Process
2)	Cellulose "Solvents"

II. Physical

1)	Steam	
	a) Iotech	6-10
	b) State Technology	6-10
	c) G.E.	
	d) Autoclaving	
2)	Grinding	
	a) Ball Milling	100
	b) Roll Milling	18-50
3)	Irradiation	
	a) Gamma	100
	b) Electron	100
	c) UV	
	d) Heat	
4)	Freezing	
5)	Pressure	

III. Miscellaneous

1)	Dilute Sulfuric Acid (Prehydrolysis)	12
2)	Acidic Autoclaving	

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4.3.1. Laboratory Examination of Steam-Exploded Wood

Samples of steam-exploded poplar and the untreated poplar wood chips were received from IOTTECH, Corporation. A laboratory analytical process was initiated to characterize the composition of the steam-exploded wood. The analytical scheme and results are given in Figure 4.7.

4.3.1.1. Experimental

A sample of steam-exploded poplar wood, prepared by its proprietary process and submitted by Iotech, Ltd. (Canada), and the corresponding untreated poplar wood chips were analyzed as follows:

Steam-exploded Wood

(1) Approximately 100 grams of steam exploded poplar wood was weighed (± 0.1 mg) and transferred to a fitted glass crucible fitted for suction filtration.

(2) The steam-exploded wood was extracted and washed repeatedly with room temperature distilled water.

(3) A portion of the extracted wood (Residue "A") remaining in the crucible was weighed into a weighed dry beaker, dried to constant weight at 105°C in an air-circulating oven to determine its moisture content (The dried weight of Residue "A" plus the weight of extractables in the filtrate was taken as the dry weight of the initial sample).

$$\% \text{ Residue "A"} = \frac{\text{Wt. Residue "A" (dried @ } 105^{\circ}\text{C)} \times 100}{\text{Wt. Residue "A" (dry) + wt. "Extractables (No. 1)"}}$$

(4) From the remaining ("wet") Residue "A", three samples weighing approximately four grams (± 0.1 mg) were placed in stainless steel wire gauze capsules. A fourth sample weighing approximately eight grams (± 0.1 mg) was similarly prepared.

Figure 4.7.

Analytical Scheme and Results of Characterization of Steam-Exploded Poplar from the Iotech Process

(5) The three four-gram samples were placed in individual Erlenmeyer flasks to which were added 300 cm³ of one of three solvents and which were fitted with water-cooled reflux condensers. The solvents were ethanol (95%), a mixture of acetone (76% w/w) and water (24% w/w), and a mixture of n-butanol (76% w/w) and water (24% w/w), respectively.

(6) The one eight-gram sample was prepared as in step (5), but water was used as the solvent.

(7) Each of the four samples were immersed and extracted in the boiling solvent. Aliquots of 10 cm³ were taken at intervals of 15 minutes (min.), 30 min., 60 min., and every 60 mins. as warranted. See step (8)

(8) The aliquots are pipetted and transferred to weighed, dry aluminum dishes and dried. Air-drying was used for ethanol until visual "dryness" was evidenced. In the case of the the other solvents, a hot plate adjusted to 95°C was employed. This initial drying was followed by oven-drying at 105°C for short periods until constant weight was achieved. Sampling was terminated when near repeatable weights of extractables were achieved.

(9) To calculate % "Extractables (No. 2)":

$$\begin{array}{l} \% \text{ "Extractables (No. 2)" } \\ \text{in Residue "A"} \end{array} = \frac{\text{Wt. of Extractables (No. 2)} \times 100}{\text{Wt. Residue "A" sample} \times \frac{(100 - \% \text{H}_2\text{O in Residue A})}{100}}$$

$$\begin{array}{l} \% \text{ "Extractables (No.2)" } \\ \text{in Steam Exploded Wood} \end{array} = \frac{\% \text{ "Extractables (No.2)" } \\ \text{Residue "A"} \quad \times \quad \% \text{ Residue "A" in } \\ \text{Steam-Exploded Wood}}{100}$$

(10) The filtrate and washings, from the room-temperature distilled water operation, were evaporated to dryness

under vacuum. The resultant extract ("Extractables No. 1") was weighed.

$$\begin{array}{l} \% \text{ "Extractables No. 1"} \\ \text{in Steam-Exploded Wood} \end{array} = \frac{\text{Weight "Extractables No. 1"} \times 100}{\text{Weight of Residue "A"(dry) + wt. of Extractables No. 1"}}$$

(11) This extract (Extractables No. 1) was heated to 65°C in order to render the non-sugar components insoluble in cold water.

(12) The heat-treated extract was again treated with room temperature distilled water to dissolve the sugar components.

(13) The undissolved (non-sugar) components are removed by filtration.

(14) The filtrate from step (13), which contains the sugar fraction of "Extractables No. 1", is evaporated to constant weight under vacuum.

$$\begin{array}{l} \% \text{ Sugars in} \\ \text{"Extractable No. 1"} \end{array} = \frac{\text{Wt. Sugar Fraction Residue} \times 100}{\text{Wt. "Extractables No. 1"}}$$

(15) The composition of individual sugars in the sugar fraction is determined gas chromatographically (see Appendix for the procedure).

Poplar Wood Chips

The poplar wood chips were analyzed according to steps (3) through (10) for the steam-exploded wood. The procedure is a standardized analytical procedure for the determination of lignin in wood.

4.3.1.2. Results and Discussion

The primary function of steam explosion is to break the lignin-cellulose/hemicellulose "complex" or "bond" in order, in the first instance, to increase the accessibility of cellulose for

subsequent hydrolysis by acids or enzymes. If this is indeed the case then application of known lignin solvents might be expected to show higher rates and yields of lignin from steam-exploded wood (in which lignin and cellulose or hemicellulose may be conceived as existing in discrete phases rather than as a strong "complex").

Secondly, steam explosion might also provide an effective pre-treatment if, as we indicated in our First Quarterly Report, enzymatic hydrolysis is facilitated by lignin removal (Section 3.0. and Figures 3.1. and 3.2., Technical Progress Report No. 1) and that substantial economics accruing from increased effective reactor volume in later unit operations is achievable. That is, a facile delignification unit operation may be applicable. Thirdly, steam-explosion as a multiple-effect pre-treatment could have added value if, during the process, a substantial portion of the hemicellulose and/or cellulose is converted to sugars, hexoses and pentoses, without resultant degradation of these key products. That is, steam explosion might have some of the attributes claimed in the Snyder patent, namely hydrolysis being combined with pretreatment for lignin-cellulose/hemicellulose complex bond breaking.

Delignification

The results shown in Table 4.12 and Figures 4.8 and 4.9 indicate that substantial and significant increases in the yields of the "Extractable No. 2" fraction is achieved with steam exploded wood when compared to untreated poplar chips. The major component of the "Extractables No. 2" fraction is lignin according to the reported procedure. Ultraviolet spectroscopic analysis of the extract in this study provided supporting evidence.

Table 4.12. Results of Extraction of Water-washed Steam Exploded Wood and of Poplar Wood Chips

Solvents	% Extractables							
	Hot Water		Ethanol		Acetone/H ₂ O		Butanol/H ₂ O	
	Wood Chips	Exploded Wood	Wood Chips	Exploded Wood	Wood Chips	Exploded Wood	Wood Chips	Exploded Wood
15 min.	3.8	1.8	2.9	10.6	2.9	7.7	1.5	1.5
30 min.	-	4.2	-	18.8	-	12.7	-	8.8
45 min.	4.9	-	4.3	-	4.3	-	2.3	-
1 hr.	5.0	6.1	4.1	24.3	4.3	15.5	2.2	6.2
2 hr.	4.3	7.2	4.2	24.0	4.6	16.5	2.2	12.7
3 hr.	6.1	7.9	4.8	25.3	5.4	17.0	3.3	16.1
4 hr.	6.4	7.8	5.3	24.5	6.7	16.7	4.4	16.8
5 hr.	6.1	7.5	5.2	24.1	7.1	17.1	4.4	17.3

Figure 4.8. BATCH EXTRACTION OF EXPLODED POPLAR

Figure 4.9. BATCH EXTRACTION OF POPLAR WOOD CHIPS

If one were to assume that the "Extractable No. 2" fraction corresponded entirely to lignin, the results would indicate that ethanol shows a five-fold increase, acetone/water a 2 1/2-fold increase, and butanol/water a four-fold increase in delignification efficiency. The fact that hot water shows only about a 1.2-1.25 fold increase, and a yield of 6.9% of the steam-exploded wood, indicates that hot water may be acting, in one extreme, to dissolve non-lignin components and, on the other extreme, that it is extracting a low-molecular weight fraction of the lignin only. If it acts in the former mode, and assuming that 21% of the raw material (poplar) is in the form of lignin, then taking ethanol as the example, 15.3% (22.2% - 6.9%) of the lignin may be considered to have been removeable. That is a delignification efficiency of 73%. If we are to take the other (ideal) extreme, and assume that all of the 22.2% yield from ethanol extraction corresponds to lignin, then delignification efficiency of 100% may be claimed as a result of steam explosion.

Sugar Production and Degradation

The analysis on the filtrate gave the following results (all results on a dry wood basis):

Room-temperature Water Solubles = 12.3%

Free Sugar Fraction in Steam Exploded Wood = 11.7%

Non-Sugar Water-Soluble Fraction = 0.5% (by difference)

about 1/8th of the dry steam exploded wood appears to consist of sugars.

A gas chromatographic analysis of this fraction was undertaken based on an available method in the literature (Appendix E). The results and identification of each peak's chemical composition is highly tentative

at present.

Table 4.13. Gas Chromatographic Analysis of the Composition of the Sugar Fraction from Steam-Exploded Poplar

<u>Sugar</u>	<u>%</u>
Arabinose	4.17
Unknown (?)	3.29
Unknown (?)	4.39
Xylose	27.85
Fructose	26.31
Galactose	9.87
Glucose*, (α - D?)	10.31
D-Glucose (Dextrose)*, (B-D ?)	2.85
Lactose (?)	5.26
Unknowns	5.70

* Dextrose (anhydrous D-glucose) gave two peaks. The first peak eluted at the same retention time as a single peak for a lab sample of "glucose". Confirmation of purity required.

If the gas chromatographic analysis is correct, it appears that substantial saccharification of cellulose, in addition to the hemicellulose fraction, has occurred. A pentose (xylose and arabinose) yield of 4.7% of the exploded wood is realized. From Table 2.4, however, we might expect yields of 19 or 20% if hemicellulose were completely converted. Of the total sugar fraction, moreover, the pentoses have a combined content of 32.0% only. If the sugar fraction derived exclusively from the hemicellulose component a combined

content of 73.3% (From Table 2.4) would be expected. Three alternative explanations could be advanced for the discrepancy: (1) cellulose has partially degraded and "diluted" the pentose content, (2) the sugar fraction has contributions from naturally occurring free sugars with poplar, or (3) the gas chromatographic peaks do not correspond only to the sugars as identified chemically (for example, degradation products of the various sugars might display the same retention time as some of the individual sugars). The first explanation might help in interpreting the results of the two chromatographic peaks attributed to glucose, the principal sugar derivative of cellulose, if correct (13% total D-glucose). The second explanation is plausible but, since the untreated poplar chips were not subjected to the room temperature water extraction, evidence is presently absent. Finally, the third explanation warrants scrutiny since both research teams at Berkeley and at MIT have reported difficulties with enzymatic hydrolysis of steam exploded wood which they felt might be attributable to degradation products.

4.4 HYDROLYSIS

4.4.1. Dilute Acid Hydrolysis

Dilute acid hydrolysis was developed because the economic recovery of acid which is necessary for the concentrated acid process to be feasible could not be solved. Because of the small amount of acid required for the dilute acid process recovery is unnecessary; therefore the acid is simply neutralized.

The dilute acid process was first industrialized as the Scholler process which was later modified as the Madison and the TVA processes. In these processes vertical reactor is filled with wood chips. Dilute sulfuric acid is percolated through the wood chips and the acid/sugar solution is discharged for subsequent neutralization and concentration prior to fermentation. For the dilute acid to hydrolyze wood cellulose the process must be conducted at elevated temperature. Unfortunately at the temperatures necessary for the hydrolysis to occur the sugars formed are decomposed. Therefore the yields of sugar from this process is the total sugar produced less the sugar decomposed. Published data indicate that sugar yields are approximately 75% in a 5-6% solution. The fixed bed dilute acid hydrolysis was selected for inclusion in "main stream" process in PDU for several reasons. As stated previously the fixed bed dilute acid process was developed and industrial size plants actually built. Data is available on sugar yields and operating conditions for the Madison and TVA process. This makes this process ideal as the standard for comparison. Since the process has not been operated for a number of years, improvements in materials and process technology make significant improvements in the process both technical and economic highly probable. For example, different pretreatment of the wood prior to hydrolysis may improve the yields or reduce the processing time.

Another dilute acid process is suggested for inclusion in the PDU is continuous hydrolysis in a plug flow reactor which was developed by Grethlein. This process from the kinetic and optimization studies reported earlier in this report show that the lowest cost of sugar of any of the processes modeled to date. Its inclusion would permit the verification of this analysis and direct comparison with the fixed bed reactor system.

4.4.2. Concentrated Acid Hydrolysis

Wood is almost quantitatively hydrolyzed by sufficient amount of concentrated acid with essentially no degradation of the resultant sugar. Therefore, the concentrated acid process should be the ideal process to produce sugars from woody biomass. However, this is not the case since there are three main problems which will have to be solved before a concentrated acid process can be commercialized. The problems are: (1) how to economically recover the concentrated acid for reuse, (2) how to mix a small quantity of acid with wood and (3) how to shorten permeation and mixing time. A number of different types of equipment were devised to solve the problem of mixing and permeation time. Among the equipment developed were internal roll type, expeller type, extruder type and flash mixer type. The problem with the mechanical equipment used for mixing is the large amount of power which is required. Power amounts as high as 2000 kwh per ton of reducing sugar have been reported for mixing ratio of 0.3 acid to wood. In addition to large power requirements, some difficulty is encountered in trying to filter the sugar solution from the lignin which remains after the main hydrolysis. To overcome the difficulty of mixing and filtering a process was devised which soaked the prehydrolyzed wood in dilute sulfuric acid. The acid was removed and the wood air dried at 40-60°C. The sulfuric

is concentrated in the wood by the removal of water by the drying process and the hydrolysis process at the same time.

Hydrochloric acid more easily permeates wood than concentrated sulfuric acid. However, with hydrochloric acid the surface is more likely to hydrolyze first thereby making the surface sticky from the sugar which is formed. This sticky mess causes the particles to clump making material handling difficult and restricting the diffusion of acid into the interior of the wood particles which results in non-uniform hydrolysis. Various methods have been devised to eliminate or minimize the stickiness of the wood particles and the associated problems. The material has been impregnated with hydrochloric acid below 38% concentration so no hydrolysis will take place. This material is then treated with HCl gas to increase the hydrochloric acid concentration in the wood. Finally the wood is hydrolyzed by raising the temperature of the material with hot HCl gas. By this process it is possible to suppress the hydrolysis during acid impregnation and the absorption of HCl gas so the stickiness problem is minimized which eliminated the non-uniformity of the reaction. Stickiness is controlled by controlling moisture content of the wood particles. Pulverized lignin has been used to coat the surface of wood particles which almost completely prevented stickiness.

However, the primary problem is the recovery of the concentrated acid. Since sulfuric acid and sugar are both soluble in water and both are not volatile they cannot be separated by distillation. Several processes were proposed which made use of the sulfuric acid to produce by-products such as gypsum, ammonium phosphate, ammonium sulfate and others, but these processes create serious additional problems which must be solved. Diffusion dialysis was industrialized with the Hokkaido process. Sulfuric acid recovery reached 85% and sugar losses amounted to 1.82% of the total sugar.

The acid losses are too high for the process to be economic. The Purdue process developed by Dr. Tsao proposes an interesting acid recovery scheme. The wood is "dissolved" in concentrated sulfuric acid. The acid is removed by working with methanol and then the alcohol and acid are separated by evaporation.

Since hydrochloric acid is volatile theoretically it can be recovered. However, hydrogen chloride and water form an azeotrope at 23.5% HCl gas, which makes recovery much more complicated. In addition the material of construction for the recovery system are expensive because of the extreme corrosiveness of hot hydrochloric acid and hydrogen chloride gas.

Clearly significant and difficult problems exist which must be solved before an economically viable concentrated acid process can be developed. It is believed that several areas of promise are being investigated which could alter the present outlook. First, the process developed at Purdue offers a different approach for the recovery of concentrated sulfuric acid. It is believed that the PDU should have the capabilities of investigating this process to determine on a pilot plant scale necessary data to evaluate its potential. Secondly, Dr. Gregor at Columbia has proposed to develop membrane separation of concentrated hydrochloric acid from sugar solution. If his work proves successful a concentrated hydrochloric acid hydrolysis process might be the most practical economically. With the proposed flexibility built into the PDU design pilot plant data on such a process can be made.

4.4.3. Auto Hydrolysis

Another novel approach to the hydrolysis of wood to produce sugars has been proposed by Snyder in his patent. Basically the

processes consist of impregnating the woody material with an alkaline or buffer reagent and then subjecting the material to elevated pressure and temperature for a relatively short time. The pressures used are in the range of 600-1250 psi saturated steam with corresponding temperatures. The amount of catalyst used is the amount required so that the pH of the reaction mass at the end of the process will be between 3.1 and 3.4. If the pH is lower the yield of sugars will be reduced by the production. If the pH is too high the sugar yield will be reduced by incomplete conversion of cellulose. According to the patent any of alkali or alkali metal including ammonium or mixtures can be used as the catalyst.

The reaction time varies from about 60 seconds to five minutes depending upon the amount of alkali and the pressure employed. Snyder estimates that approximately 30 percent of the pentoses are converted to furfural which can be recovered by distillation. Further, about 150 pounds of acetic acid per ton wood is produced depending upon specie. The liquid reaction product contains approximately 30 percent glucose and xylose and relatively low polysaccharides. Heating with acid will convert these polysaccharides into monosaccharides. Snyder claims that 80 to 90% of the theoretical xylose and glucose can be realized.

The inclusion of the Iotech "steam explosion" process to pretreat the biomass prior to process will, with minor modification, permit the examination of the Snyder process to determine if indeed biomass can be converted directly into sugars. If this process does produce sugar with the projected yields then a significant improvement in the economic production of alcohol from biomass will have been demonstrated.

4.4.4. Enzymatic Hydrolysis

In the First Quarterly Report¹ various enzymatic hydrolysis methods were discussed. It was also pointed out that the simultaneous saccharification and fermentation route has a relatively better future at this stage as compared with the multistage enzymatic hydrolysis and fermentation processes where enzyme production, saccharification to produce glucose, and fermentation of glucose to yield ethanol are conducted in three separate stages.

The SSF type process is relatively less capital intensive as compared with the Natick type multistage enzymatic hydrolysis and fermentation process. According to W.S. Fong² the enzyme production and hydrolysis plant sections represent the most costly plant sections accounting for 31% and 24% of the fixed capital investment respectively.

The above mentioned major capital investment is relatively reduced in SSF type operation. According to G.H. Emert³, in an SSF type process the ethanol yield is enhanced as much as 40% because of the immediate conversion of glucose as it forms. This obviously eliminates the usual inhibition of the cellulose hydrolysis by glucose that otherwise would occur. The conversion can be increased to 90% with suitable additions to the enzyme inoculum. In this section an attempt is made to review the various designs of bioreactors. Due to long residence times required the operating volume of bioreactors tend to be very large.

4.4.4.1. Stirred Tank Reactor (Batch/Continuous)

A CSTR is a conventional design and is very easy to adapt for many of the enzymatic hydrolysis processes. Some of the

examples of the processes where WSTR type design has been used include the Natick Process, the Indiana Institute of Technology Process, the Berkeley (Wilke) Process, and the G.E. - University of Pennsylvania Process. This type of reactor allows a plant to be operated in batches or continuous modes. There are inherent weaknesses in CSTR-based process designs for enzymatic hydrolysis. Depending on the rheological properties of the feed slurry and reactor product stream this can be an energy intensive operation. Hence, a feed slurry with a high solid concentration cannot be fed on a continuous basis. This problem has been solved in the Natick process by operating it under a semi-batch condition. This is done by gradually building up the solid concentration in the reactor so that a relatively high sugar solution can be observed in the product stream. CSTR type reactors can be operated continuously in series². This design has also been investigated by the G.E. - Penn team⁴ by using an eight stage counter-current CSTR type cellulose hydrolysis reactor system.

4.4.4.2. Fixed Bed Reactor

This concept is being evaluated and developed by MIT⁵, Dynatech R & D Company⁶ and the Tokyo Institute of Technology⁷. The University of Pennsylvania⁸ is developing a similar design called EXFERM where the fixed bed is kept away from the main column and can easily be replaced. This can be adapted as a cellulose enzyme reactor. At present this design is being studied in a batch type reactor. This can be converted into a semicontinuous type operation by introducing a number of reactors in the series and by replacing the depleted bed by a fresh one. There are some serious problems with fixed bed type

bioreactors which need to be solved at pilot scale before these can be scaled up and considered for commercial type operation. Fixed beds can get plugged by biomass accumulation. Smaller particles in the bed can lead to the reduction of bed porosity thus causing a high pressure drop in the bed. The removal of the inactivated part of the bed without discarding the whole bed can be a problem. A uniform distribution of flow throughout the bed is also difficult to achieve.

Finally, a packed bed or fixed bed type reactor may be used for immobilizing enzymes but this concept is suitable only for soluble substrates. In the case of feed slurry containing insoluble substrate such as cellulose the cellulase immobilized on the fixed bed can be relatively ineffective and therefore this design appears to lack the potential for productivity and economy at this stage of development.

4.4.4.3. Fluidized Bed Reactor

The use of a fluidized bed reactor for enzymatic hydrolysis is an interesting concept. It is being developed at Tokyo Institute of Technology⁸ in Japan. In this approach the cellulase enzyme was immobilized in a collagen fibril matrix. The use of this immobilized enzyme in a packed bed indicated that a longer reaction time (120 hours) would be required for this mode of operation in order to compare favorably with the native enzyme. Other difficulties associated with the fixed bed system such as the plugging of beds, high pressure drops, and non-uniform distribution of flow were also observed. This led to the investigation of a fluidized bed reactor. This design appears to be superior to the fixed bed type reactor for the following reasons:

(1) Since the bed consisting of immobilized enzyme is in an expanded state the possibility for plugging of the bed, when it is fluidized, is eliminated.

(2) Unlike the fixed bed system no compaction can take place; therefore, the smaller particles with large surface area can be used without causing any increase in the pressure drop and can also result into faster rate of reaction.

(3) In the fixed bed reactor it is essential to decide at what stage the bed has diminishing return and then it has to be replaced. In the fluidized type design it is very easy to replace the inactivated bed and to recover and recycle active bed particles continuously.

According to Isao Karube⁷ cellulase immobilized in a collagen fibril matrix was more stable than the native cellulase. The immobilized cellulase was used in a fluidized bed reactor where no excessive pressure drop was observed. Cellulose was quantitatively hydrolyzed to glucose in this mode of operation. The minimum flow velocity was 0.5 cm/sec and the optimum flow velocity of the cellulose hydrolysis was 1 cm/sec.

Oak Ridge National Laboratory has developed a modified design called a "tapered fluidized-bed Bioreactor". This design can be used for the production of glucose from cellulose by fluidizing the immobilized cellulase enzyme. According to W.W. Pitt⁹, the tapered fluidized bed differs from the more conventional fluidized bed by a configuration that resembles an inverted, truncated cone (with a small vortex angle) rather than a constant cross-sectional column. Thus,

the cross-sectional area of the column gradually increases over the column height from a relatively small entry area to a much larger area at the top. This design allows a wide range of flow rates without loss of bed materials. The shape of the reactor allows for a stable feed introduction without gross eddies and significant back mixing (Figures 4.10 and 4.11). The practicality of this design needs to be investigated more thoroughly for economic feasibility and application as a cellulase enzyme reactor since the residence required for high yield of glucose is very long.

4.4.4.4. Summary

On the basis of the evaluation of the various reactor designs it appears that the fixed bed type reactor has a long way to go before it can be considered for a commercial operation to produce glucose from undissolved cellulose.

The fluidized type design has potential, and the tapered fluidized bed design appears interesting. However, the long residence time needed for the hydrolysis makes it uneconomical at present, and, therefore, some improvement in this design and selection of a suitable enzyme system is needed.

After a careful evaluation of these designs a continuously stirred tank reactor is proposed for the process development unit. This is a reasonably well understood and well developed design which offers versatility in operation. It can be specified in a variety of sizes and configurations and bought conveniently. Its flexibility or versatility is apparent in its ability to be operated in batch and continuous modes. If the CSTR type is bought with a large height/diameter

$$R = (Z_0 + Z) \tan \theta,$$

$$= R_0 + Z \tan \theta,$$

$$= R_0 (1 + \xi).$$

where

$$\xi = \frac{Z}{R_0} \tan \theta,$$

and $R_0 = Z \tan \theta$.

$$\xi = \frac{Z}{R_0} \tan \theta = \frac{Z}{Z_0}.$$

Fig. 410 Coordinate system for the tapered fluidized bed.

Fig. 411 Fluidization of a tapered bed.

ratio, within limits it can also be adapted for operation as a fluidized type reactor. In addition, it can be operated as a fixed bed type reactor with appropriate ancillary piping.

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4.5. Fermentation

In the first quarterly report all the available designs of fermenters and the relevant fermentation processes were reviewed very thoroughly. In this report it is desirable to describe briefly the advantages or the flexibility of the PDU fermentation unit.

It is decided to select the deep vat fermenter which can be used as open vat fermenter, to evaluate if a strict asepsis is needed. It can also be used as a deep vat fermenter with or without asepsis, and to study the extent of power requirement depending on the degree of agitation. The fermenter can also be used in SSF type operation. Therefore, this universal design is quite flexible and can be operated in three different modes. The same fermenter would also be used for continuous vacuum fermentation as well as simultaneous saccharification and fermentation type operations. The flow diagram (Fig. 4.12.) of a conventional continuous fermentation type operation indicates that carbon dioxide produced during the course of fermentation caused extra load on the vacuum system. This is undesirable. The proposed PDU unit will include the provision for SSF and continuous fermentation with indirect vacuum (Fig. 4.13.). This is superior to the classical vacuum fermentation; first, carbon dioxide is recovered separately without causing any extra load on the vacuum system; second, since the flashed liquor is recycled it does reduce the requirement of cooling water for the fermenter. Finally, since the fermentation itself is carried out under normal conditions, its control is much simpler as compared with the conventional vacuum fermentation.

The tower fermenter is another desirable option. Its inclusion to handle full scale throughput rate would be controlled by its cost but a

Figure 4.12. CONTINUOUS VACUUM FERMENTATION (CONVENTIONAL)

FIGURE 4.13. CONTINUOUS FERMENTATION WITH INDIRECT VACUUM (PDU)

small scale unit to process a side stream is definitely recommended for the following reasons:

1. Considerable increase¹ in the efficiency is reported by the European brewing industry. The fermentation time as low as 2 hours as compared with the batch fermentation times of 3-5 days are reported.

2. The unit is very simple to maintain and operate.

3. Because of its shape the tower fermenter occupies a much smaller floor space as compared with conventional CSTR type system.

4. Recycling of yeast becomes a much lesser problem

A.P.V. Company² has been contacted to get some definite information regarding the hardware and capital cost involved. Contact has also been made with the University of Aston, Birmingham, England for more basic design data required to scale up the tower fermenter. A. Weisenberger³ of the Eckes International, West Germany conducted the development of a continuous wine making process using a tower fermenter (Fig. 4.14.). Some of the benefits described include:

1. The equipment is compact and needs little floor space.

Plant buildings are therefore smaller. The equipment can be installed readily. In the case of a production facility already in operation, existing capacity can be extended.

2. Compared with the conventional batch process, capital cost is less for land, buildings and plants.

3. Since fermentation time is very short (3-4 hours for apples and 6 hours for grapes) the fermented product is ready for bottling within days.

4. Labor costs are lower since less man power is needed.

Figure 4.14.

CONTINUOUS WINE MAKING USING A TOWER FERMENTER

5. Since this is a continuous process with relatively shorter residence time, uniform steam, power and liquid consumption eliminates peak load problems. Power generating equipment can thus be smaller.

Thus the tests in West Germany demonstrated that continuous processing of wine using the tower fermenter can reduce the production costs by 25-40%, plant building costs by as much as 75%. The effluent waste stream from the fermenter would be monitored and is discussed in the section on waste treatment monitoring.

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4.6. Ethanol Recovery

A number of methods that can be used to recover absolute ethanol have been mentioned in the First Quarterly Report. In this report some of the systems have been described in more detail. Although the azeotropic distillation method is very energy intensive, it still remains to be the best available system to produce absolute ethanol. Anhydrous ethanol can also be produced by the use of molecular sieves, vacuum distillation, solvent extraction and membranes. At present these are very uneconomic and can be eliminated in comparison with the azeotropic distillation. It is recommended that PDU should have the capability of evaluating any new development to produce anhydrous ethanol by any of the systems mentioned above. For economic reasons these options can be included in the PDU flow scheme at a scale smaller than the full throughput rate.

4.6.1. Azeotropic and Extractive Distillation

It is significant that contemporary commercial schemes for the dehydration of ethyl alcohol are based upon azeotropic distillation utilizing an entrainer such as benzene or cyclohexane wherein the water is removed by vaporization as a portion of the overhead vapor and the bulk of the ethyl alcohol is removed as bottoms without undergoing vaporization. Extractive distillation, an alternate dehydration procedure, on the other hand, requires the vaporization of all of the ethyl alcohol as an overhead vapor while the water is removed from the first column in solution with the extracting solvent, without vaporization. All of the water is then vaporized in the second stage

column for extractive distillation.

Neglecting reflux, the following are preliminary theoretical estimates for the vaporization loads to produce the distillate portion of the distillation column overhead vapors for an azeotropic distillation versus an extractive type distillation. The benzene, water, ethanol system is assumed for the azeotropic distillation and the extractive distillation system only assumes a non-volatile solvent is used. The feed in both cases is assumed to be 4.4 percent water and 95.6 percent ethanol, by weight. The basis is one pound absolute ethyl alcohol produced.

AZEOTROPIC

EXTRACTIVE

DISTILLATION

DISTILLATION

Distillates formed
(Combined weights)

Distillates formed
(Combined weights)

Water	0.06 lbs.
Ethyl alcohol	0.22 lbs.
Benzene	<u>0.59 lbs.</u>
TOTAL	0.87 lbs.

Water	0.046 lbs.
Ethyl alcohol	<u>1.000 lbs.</u>
TOTAL	1.046 lbs.

The heat required for vaporizing the liquids which are the sources of these distillates is much greater, proportionally for the extractive distillation than for the azeotropic distillation, because of the relative heats of vaporization of benzene, ethanol and water. The pure component latent heat of vaporization

of benzene is only 170 Btu/lb., of ethanol is 367 Btu/lb and of water is 970 Btu/lb, all taken at their normal boiling points.

It is estimated that the ratio of latent heat input required to vaporize the extractive distillation distillates is about 1.7 times that required for the azeotropic distillation distillates, based on one pound absolute ethanol product in both cases. If the reflux ratios for the azeotropic distillations were fixed at the same values for the azeotropic and extractive distillates, the total latent heat input to the two systems overhead vapors would still be about 1.7:1.

The foregoing tends to confirm the statement "Azeotropic distillation is particularly useful when the feed component selected to come overhead as an azeotrope with the agent is present in the feed in small amounts. In such an instance, the amount of agent needed to be circulated is small, resulting in only small additional steam costs because of the presence of the agent, and in low agent recovery cost".¹

Black and Ditsler² compare extractive distillation using ethylene glycol as a solvent to azeotropic distillation using n-pentane as the azeotrope former with respect to heat requirements for the dehydration of ethanol. Starting with 85.64 mole percent ethanol (93.84 weight percent). They found that the heat loads and capital costs for the extractive distillation were higher than for the azeotropic distillation, for this separation. The ratio of total heat loads to the reboilers was over 2.32:1 and to the condensers was over 1.5:1 for the extractive distillation compared to the azeotropic distillation.

The following is a partial listing of azeotrope formers that could be considered for dehydration of ethyl alcohol by azeotropic distillation:³

AZEOTROPE FORMER	AZEOTROPE COMPOSITION, WEIGHT %			AZEOTROPE BP, °C @ 760 mm
	Azeotrope Former	Water	Ethanol	
Benzene	74.1	7.4	18.5	64.6
Cyclohexane	76.0	7.0	17.0	62.1
Heptane	60.9	6.1	33.0	68.8
Hexane	85.0	3.0	12.0	56.0
Isopropyl Ether	89.5	4.0	6.5	61.0
Ethyl Acetate	82.6	9.0	8.4	70.2
Isopropyl Acetate	70.8	9.8	19.4	74.8
Methyl Ethyl Ketone	75	11	14	73.2
Toluene	51	12	37	74.4
Triethylamine	75	10	15	74.7
Ethyl Ether	98.7	1.3	0	34.15

The following are latent heats of vaporization taken at the normal boiling points:

SUBSTANCE	LATENT HEAT OF VAPORIZATION Btu/lb
Ethanol	367
Water	970
Benzene	170
Cyclohexane	154
Heptane (n)	138
Hexane (n)	145
Ethyl Acetate	184
Methyl Ethyl Ketone	191
Toluene	156
Ethyl Ether	151
Pentane (n)	154

The equipment requirements for dehydration of ethanol using cyclohexane as the azeotrope former are expected to be similar to those when using benzene. Note the azeotrope compositions, boiling points, and latent heats of vaporization in the foregoing tabulations. The liquid phase relationships after ternary azeotrope condensation are also similar.⁴ Cyclohexane's principal advantage is that it is considerably less toxic than benzene. In 1975 for daily continuous 8 hour industrial exposures, permissible concentrations in air were 10 p.p.m. benzene vapor or 300 p.p.m. cyclohexane vapor. More recent developments are expected to reduce the allowable concentration of benzene in air but are not expected to affect the cyclohexane limit. It has been reported that Vogelbusch (Bohler Brothers of America, Inc.) uses cyclohexane as an entrainer (azeotrope former) for the dehydration of ethanol. See GIT/EES Project No. A-2256-000 Technical Progress Report No. 1, January 1979, page 89.

Gasoline has been suggested as a possible azeotrope former for the dehydration of ethanol. One reason for considering gasoline is that when absolute ethanol is produced for use in gasohol, the gasoline present in the ethanol would not be a contaminant or a loss and would only slightly increase the amount of ethanol product to be used in gasohol. Gasoline has been defined as "a complex mixture of hydrocarbons which distills within the range 100° to 400°F" (Marks Handbook, p. 7-23). It may consist of blends of straight-run, cracked, reformed, and natural gasoline. Hydrocarbon molecules containing five to eleven carbon atoms would

typically be present in gasoline. This would include but is not limited to isomers of pentane, hexane, heptane, octane, nonane, decane, and hendecane. Included are the n isomers of pentane, hexane, and heptane, which are shown in the above lists for reference, even though gasoline usually includes only small portions of these n isomers. Many other aliphatic hydrocarbons in gasoline, however, are expected to behave similarly to these three with respect to azeotrope formation, and that is the reason for their inclusion in the lists. The allowable concentration of hexane in air is 500 p.p.m. and of pentane is 1000 p.p.m., for industrial exposure. However, gasoline normally contains aromatic hydrocarbons which would probably reduce the allowable concentration of gasoline in air to somewhat lower values. In any case, gasoline would present a considerably lower health hazard than benzene. It has been reported that A.C.R. Process Corporation uses gasoline as an entrainer (azeotrope former) for the dehydration of ethanol. (GIT/EES Project No. A-2256-000 Technical Progress Report No. 1, January 1979, page 90).

The examples of dehydration by azeotropic distillation cited above involve a minimum boiling ternary azeotrope consisting of three components: water, ethanol, and azeotrope former. In certain cases, for example the system comprised of water, ethanol, and ethyl ether, the minimum boiling azeotrope is a binary one, comprised only of water and ethyl ether. The low boiling point of the azeotrope, 34.15°C (93.5°F) presents a problem for condensers at atmospheric pressure. Pressure operation, for example, at 100 psig

is normal⁵. Although the allowable concentration of ethyl ether in air is 400 p.p.m. for industrial exposure and it therefore is much less toxic than benzene, it is, of course, an anaesthetic by inhalation and it has other limitations. Because of its low boiling point at atmospheric pressure, its vapor pressure is relatively high at ambient conditions. Its vapor pressure is 400 mm mercury at 64°F. Spillage results in rapid vaporization and rapid buildup to the 400 p.p.m. maximum allowable concentration for industrial exposure of personnel, and rapid buildup to its lower flammable limit in air which is 1.9 percent by volume.

One of the principal hazards associated with ethyl ether, however, is its unusually low ignition temperature, which is only 320°F. This means a flammable mixture of ethyl ether in air could be ignited by contact with bare steam piping or even a steam valve stem or pressure gage "pigtail" at saturated steam pressures in excess of 75 psig. The low ignition temperature also means that static electricity and mechanical sparks will more readily ignite ethyl ether than most other flammable vapors and liquids. A 320°F "spark" is not even visible. Ethyl ether has even been ignited by static electricity associated with normal use of clothing made of synthetic fibers.

Because of the low ignition temperature, ordinary flame arrestors, such as are commonly used on storage tank vents and other vents in petroleum refineries are ineffective for ethyl ether. Flame arrestors in refineries are used on vents to prevent propagation of flames from external sources back into storage

vessels and other equipment utilized for handling flammable liquids and vapors. Such propagation could otherwise result in an explosion. Because of the ineffectiveness of flame arrestors for ethyl ether, good engineering practice mandates the extensive use of inert gas blanketing for all process and storage vessels, to exclude air. Nitrogen is commonly used. Nitrogen purge and blanketing costs add to the capital and operating costs associated with the use of ethyl ether.

Prolonged storage of ethyl ether can also result in the buildup of organic peroxides. These can explosively decompose during certain ether process operations, serving as an internal source of ignition in vessels and other equipment. Suppliers commonly add inhibitors to reduce or eliminate peroxide formation, but the inhibitors have limited life and may be absent in recycled ether due to removal during distillation. This factor must be provided for in designs where ethyl ether is used or stored.

As for any flammable liquid, all possible sources of ignition must be positively excluded from all areas where flammable vapors may accumulate or where flammable liquids might spill or leak. Pumps and valves, for example, are expected to develop minor leaks periodically. Engineering design for outdoor equipment on a college campus must positively exclude unauthorized personnel and burning debris (for example cigarettes) from the vicinity of equipment that might leak flammable liquids or vapors.

Also, because of its high vapor pressure, vent losses of

ethyl ether are expected to be greater than for the other azeotrope formers listed (except for n-pentane), unless special provisions are made. Refrigerated vent condensers are recommended to avoid excessive losses.

The advantage associated with the use of ethyl ether as an azeotrope former is a reduction of net dehydration energy requirements as compared to the use of benzene. Vulcan Cincinnati is reported to have proprietary technology that will enable them to cut energy needs to only 20,000 Btu/gal. of anhydrous ethanol from fermented mash. This is approximately half the amount of energy needed with a benzene azeotrope. It is also reported that only two distillation columns are required for alcohol purification and dehydration by the Vulcan ether-vapor reuse process as compared to perhaps seven or eight for a traditional combination beverage and anhydrous alcohol purification and dehydration facility. Vulcan Cincinnati has designed⁶ ethanol dehydration systems using ethyl ether for at least five clients.

4.6.2 Molecular Sieves (7,8)

Molecular sieves are crystalline metal aluminosilicates with a three-dimensional interconnecting network structure of silica and alumina tetrahedra. The tetrahedra are formed by four oxygen atoms surrounding a silicon or aluminum atom. Each oxygen has two negative charges and each silicon has four positive charges. This structure permits a neat sharing arrangement, building tetrahedra uniformly in four directions. The trivalency of aluminum causes the alumina tetrahedra to be negatively charged requiring an additional cation to balance the system. Thus, the final structure has sodium, potassium or calcium cations in the network. These "charge balancing" cations are the exchangeable ions of the zeolite structure.

In the crystalline structure, up to half of the quadrivalent silicon atoms can be replaced by trivalent aluminum atoms. By regulating the ratios of the starting materials, it is possible to produce zeolites containing different ratios of silicon to aluminum ions and different crystal structures containing various cations. Molecular sieves generally behave as physical adsorbents. Thus, when molecules enter the internal sieve structure, they are held (adsorbed) by physical forces of the Vander Waals type, following Langmuir's Theory. In some cases these forces are augmented by an ion dipole interaction and the "adsorbing" force is appreciably strengthened. Langmuir assumes that points of valency on the adsorbent surface can only hold one molecule of adsorbate, therefore, the adsorbed layer can only be one molecule

thick.

In molecular sieve the amount of material adsorbed increases rapidly to the equilibrium value as its concentration increases in the fluid phase (Fig. 4.15). At equilibrium any further increase in concentration causes no change in the quantity of material adsorbed by the molecular sieve. Because of this adsorption mechanism, molecular sieves differ from all other types of commercially available adsorbents in that they have an extremely high equilibrium adsorption capacity for water and polar compounds at very low concentrations of these compounds in the fluid phase.

At certain temperatures, another unusual effect is sometimes observed. The adsorption of molecules with critical diameters larger than the effective pore openings of the sieves. This seemingly impossible behavior is attributed to a combination of elasticity of the adsorbed molecule and to the crystalline vibration of the basic molecular sieve structure combined with the mobility of the blocking cation. This unique phenomenon stresses the fact that pore dimensions, as generally used, and critical dimensions of molecules are not finite. Molecular dimensions must be used as a guide, when choosing a type of molecular sieve for a specific use.

Molecular sieves must also desorb with the equal efficiency before they can be acceptable commercially. In desorbing, molecular sieves show virtually no hysteresis. This means adsorption is almost totally reversible. The ease with which a molecular sieve

Figure 4.15.
Comparison of Relative Humidity
Effect on Various Desiccants
(Equilibrium Capacity)

can be desorbed or regenerated can be one of the most important factors for its selection or rejection.

Union Carbide has developed a hydrophobic crystalline silica molecular sieve called Silicalite⁷. After contacting the company it was discovered that this product has not gone beyond pilot plant batch. We have yet to receive a sample and more technical information from Union Carbide regarding Silicalite before any concluding remark can be made.

Davison Chemical Division of W.R. Grace Co.⁸ has a product 3A molecular sieve which they claim can selectively remove moisture from aqueous ethanol solution. This type of molecular sieve is mainly used for drying unsaturated hydrocarbons i.e., ethylene, propylene, butadiene, N₂-H₂ mixtures made by cracking NH₃, and such polar fluids as methanol and ethanol. The type 3A molecular sieves will adsorb molecules with effective diameters less than 3A^o and will exclude those which are larger (ethanol = 4.4A^o) 8-12 mesh size is used for dehydration of liquids.

The 3A molecular sieves appear to be less economical and quite energy intensive. Its equilibrium water capacity is 21% weight. Therefore, a large quantity of 3A molecular sieves in the form of fixed type column would be required to dehydrate ethanol in a commercial plant. This will add to the capital investment. Its regeneration is very energy intensive. The beads have to be heated to 350-500^oF range. This temperature must be reached slowly while purging with a carrier gas. After this step the molecular sieve is ready to be reused. Depending on the

product life periodically this material has to be replaced which further adds to the overall cost of producing anhydrous ethanol. Thus it is recommended that this system should not be considered for PDU mainstream but a provision should be made only for a small scale evaluation of this product so that some reliable figures for its technical and economic feasibility can be generated.

4.6.3. Membrane Separation

The complexity and product value of aqueous solutions vary greatly. Membrane separations are of interest at both ends of cost spectrum bounded by desalination and water purification at low cost end and food and beverage processing at the high-cost extreme. In both cases the energy requirements are lower as compared with distillation because of the high heat required to vaporize water. But the (trouble free) operation of a membrane system, the life of a membrane and the capital cost involved in using these in commercial scale plants make it expensive. The membrane system still has an uphill battle ahead in displacing multieffect evaporators with or without mechanical vapor recompression or an efficient distillation system in terms of its overall process economics. H.P. Gregor⁹ has been doing work in developing membrane technology. According to him membrane permeation technologies for ethanol separation do not require any new breakthrough. The basic principles involved are well understood and also the techniques for making selectively permeable membranes. He has proposed various applications of membranes in ethanol fermentation process.

A conceptual flow diagram of a membrane controlled fermentation of sugars to ethanol is proposed (Fig.4.16). By the use of a reverse osmosis type membranes selectively permeable to water, one can dehydrate the ethanol to 99.5%. Membranes selectively permeable to water over alcohol at selectivity ratios of approximately 50 to 1 are known but their capability at elevated temperatures and in the presence of high concentrations of alcohol as opposed to water need to be explored. This can lead to a substantial cost savings in the conventional fermentation process. Standard Oil Company¹⁰ has developed a membrane permeation process for dehydrating aqueous-organic chemical mixture. A hydrolyzed polyvinyl acetate membrane is used from which up to 98% of its acetyl groups are removed by hydrolysis. The stability towards water is improved by curing the under anaerobic condition at a temperature greater than 100°C.

Standard Oil Company's scientists have conducted experiments using the membrane unit. An azeotropic ethanol-water composition containing 6 weight percent water was charged to the laboratory permeation apparatus. 99+% hydrolyzed polyvinyl acetate membrane was employed in this run. The observations made are indicated by the following results:

<u>Percentage Water in Feed</u>	<u>Percentage Water in Permeate</u>
5.9	58.0
5.3	55.0
4.9	51.0

The above results look encouraging except that the duration for each separation or the figures for water flux are not reported.

Figure 4.16.

MEMBRANE-CONTROLLED FERMENTATION OF SUGARS TO ETHANOL

Therefore, at this stage, enough is not known about the membrane application to recover ethanol. But it may be recommended that a provision for a relatively small RO-type system be made to be run on side stream of PDU operation for its proper evaluation.

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4.7. By-Product Utilization

During the operation of the proposed Process Development Unit (PDU) all the streams producing any product other than ethanol would be monitored and evaluated for its commercial value. It is not intended to propose a separate pilot plant at this stage to process each of these streams to produce various products. Here it would be emphasized to evaluate these by-products in terms of their fuel values.

The various streams are described as follows:

After the delignification stage the attempt would be made to produce lignin in the dry form. This would be the purest form of lignin available for other contractors to evaluate this by-product for a variety of novel uses in addition to its fuel value.

During the prehydrolysis stage where hemicellulose is converted into C_5 and C_6 sugars, the quantities of C_5 and C_6 would depend on the type or the source of hemicellulose. It has been known to be very profitable to produce a single cell protein (SCP), Furfural or Xylitol from C_5 sugars. Our emphasis would be in utilizing the hydrolyzate of hemicellulose to produce liquid fuel (MIT, Penn.- G.E.). Acetone and Butanol can be produced from C_5 sugars and the extensive research program is in progress at various research laboratories. Some work has also been reported by MIT and Berkeley groups to convert C_5 into ethanol. C_5 can also be converted into 2,3,Butane Diols (Purdue, Auburn). Therefore, any future breakthrough can easily be utilized in the proposed PDU for the total conversion of hemicellulose and cellulose into liquid fuel.

The fermentation stage produces two by-products; first, carbon dioxide which can only be monitored in terms of its value as dry ice, or as

a gas for food industry. Liquified CO_2 is also a very valuable solvent to extract various organic components from beans (decaffeination of coffee beans). It has been proven to be relatively cheaper to regenerate the carbon by liquified CO_2 as compared with the high temperature conventional furnace system. Second, the excess amount of yeast produced can be sold as SCP or a source of vitamin B complex. Therefore, at this time we intend to evaluate these by-product streams by monitoring only.

4.8. Waste Treatment Monitoring

The PDU system would produce three kinds of wastes:

1. Solid waste or sludge produced by the neutralization of acid stream. This will be separated and disposed of in a conventional manner.
2. Very diluted liquid waste stream generated by wash water during the various stages of operation.
3. Organic liquid waste streams, generated during enzymatic hydrolysis and fermentation operations.

The second and third items described above would be of main concern to us.

In PDU operation, it is planned to collect samples of every effluent stream on a 24 hour basis, homogenize these samples and then analyze the samples for BOD, COD, N, P, K, SO_4 , NO_3 , carbohydrates, etc. The above analysis will help us in generating the data for scaled up operations (e.g., 2000 ODT/day plant). We will also be able to evaluate the possibility of recycling these streams and their effects on the overall operation of the PDU system. It is also desirable to have two small tanks where one can be used as an effluent holding tank to homogenize the waste streams and the other tank can be used as an aeration tank to reduce the BOD values of the

effluent before discharging it into the Atlanta sewer system. The above information regarding agitation, aeration and the power requirement to treat the organic waste would be very valuable for a commercial scale design.

4.9. Materials of Construction

A general review of the materials of construction used in the hydrolysis and fermentation processes to date is carried out in the following discussion.

4.9.1. Hydrolysis

4.9.1.1. Dilute Sulfuric Acid

Dilute (1/2 to 1%) sulfuric acid may be present at temperatures up to 374°F. Using wood pretreated per the GIT process, however, the required temperature may be only 257°F. A Monel hydrolyzer was used by TVA¹ at temperatures up to 380°F. Carpenter 20 stainless steel was also used for accessories. Monel, Incoloy and Carpenter 20 type stainless steels are under investigation as possible materials of construction. Lead lined equipment is also to be considered, as are the Hastelloys.

The following materials² are reported to have corrosion rates of less than 20 mils per year at temperatures up to 280°F at concentrations up to 55% sulfuric acid:

Glass	Impervious graphite
Silicon iron	Tantalum
Hastelloy B and D	Gold
Lead	Platinum
Monel (air free)	Zirconium
	Molybdenum

At temperatures up to 375°F at concentrations up to 75% sulfuric acid, this same reference lists only the following:

Glass,	Silicon iron
Hastelloy B & D (20-50 mpy)	Tantalum
Gold	Platinum

A plant test for Monel alloy 400 indicated a corrosion rate of only 0.0031 ipy (3.1 mils per year) in approximately 10% sulfuric acid plus pyroligneous liquor in pressure digestion of wood. Temperature was 170°C (338°F) at 100 psig pressure.

Monel³ and Incoloy are trademarks of Huntington Alloys, Inc. (subsidiary of International Nickel Company). Carpenter 20 and Carpenter 20-Cb are trademarks of Carpenter Technology Corporation. Hastelloy is a trademark of Stellite Division of Cabot Corporation. Literature has been requested from these firms and from National Lead Industries, Inc. Stellite Division maintains a laboratory in which corrosion testing may be performed. Generally, 304 and 316 stainless steels are not used for sulfuric acid because of their higher corrosion rates. (Fontana & Greene, op.cit., p. 233).

4.9.1.2. Concentrated Sulfuric Acid

After pretreatment or prehydrolysis, the Hokaido and Purdue (Tsao) processes utilize concentrated sulfuric acid at room temperature for dissolution of cellulose. Concentrations of 40% to 80% sulfuric acid may occur.

The following materials are reported to have corrosion rates of less than 20 mils per year at concentrations of about 62 to 78 percent sulfuric acid at temperatures up to 100°F:

Steel	Ni-Resist
Glass	Impervious graphite
Silicon iron	(up to 96% H_2SO_4)
Hastelloy B & D	Tantalum
Lead (up to 96% H_2SO_4)	Gold
Durimet 20	Platinum
Worthite	Zirconium

(Fontana and Greene, op,cit, pp. 236-237)

Actually, the corrosion rate of steel is reported as 20-50 mpy elsewhere. Furthermore, Monel has been reported to corrode at less than 20 mpy at temperatures up to 100°F at up to 80% sulfuric acid concentration. The 304⁴ and 316 stainless steels are not suitable for 40-80% sulfuric acid.

The following non-metallic materials are also usable for 40 to 80 percent sulfuric acid at ambient temperatures:

Polyvinyl chloride
Polyethylene
Polypropylene
Polyether (Penton)
Teflon
Kynar
Polyesters
Phenolics
Hypalon
Glass
Acidproof brick

Impervious graphite

(Fontana and Greene, op.cit., p. 240).

4.9.1.3. Concentrated Hydrochloric Acid

The Bergius-Rheinau and the Udic-Rheinau processes for dissolution and hydrolysis of cellulose are based upon the use of concentrated hydrochloric acid (40%+). A variation first impregnates the wood with dilute hydrochloric acid and then adds further hydrogen chloride gas to produce a concentrated hydrochloric acid condition.

The following materials are reported to exhibit corrosion of less than 20 mpy with about 40% hydrochloric acid concentration up to 120°F:

Chlorimet 2	Haveg
Glass	Saran
Silver	Rubber
Platinum	Molybdenum
Tantalum	Zirconium
Hastelloy B (chlorine free)	Impervious graphite
Durichlor (FeCl ₃ free)	

(Fontana and Greene, op.cit., pages 252 and 253).

Steel and ordinary stainless steel are not considered resistant to aqueous hydrochloric acid at any concentration, even at room temperature.

The following non-metallic materials are considered generally suitable for handling concentrated hydrochloric acid at temperatures up to 120°F:

Polyvinyl chloride	Fiberglass reinforced polyesters
--------------------	----------------------------------

Vinyl esters

Phenolics

Soft natural rubber
linings

Special hard rubber linings

Pyrex glass

Chemical glass linings

Polyethylene

Penton

Saran

Kynar

FEP and TFE fluorinated
polymers

Polypropylene

Impervious graphite

Chemical stoneware

Acidproof brick

4.9.2. Fermentation

Equipment used in this stage of operation would be of stainless steel. This includes fermenter, pipes, equipment used for the separation of solids, and also for the recovery of ethanol.

REFERENCES

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I & E Chem., Vol. 44, No. 7, July 1952
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1967, pp.236-237, Fig. 7-12
3. The International Nickel Company, Inc.
Resistance of Nickel and High Nickel Alloys to Corrosion by Sulfuric Acid
Bulletin CEB-1 Inco, New York, 1963 & 1975, p.8.
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"Corrosion Charts: Guide to Materials Selection"
Chemical Engr., pages 194-195, Nov. 12, 1962.

5.0. FUTURE WORK

At a scheduled meeting at the Solar Energy Research Institute, Golden, Colorado on May 9, 1979, estimated costs of construction of the three oven-dry ton per day process development unit will be presented to the SERI program management. One formal (DOE Contractor's Meeting) and one public presentation of the conceptual design of the PDU will be given in June at the annual Fuels-From-Biomass Conference to be held in Colorado.

Costings will be projected so as to provide both a technical and economic basis for selection of the finalized conceptual design. In effect, part II of this Phase I contract, i.e., the detailed engineering design, is being performed and the initial results will be presented.

During the coming quarter, the sensitivity analysis for the acid hydrolysis of cellulose using a fixed bed reactor will be completed and compared to the continuously stirred tank reactor (CSTR) and plug flow reactor (PFR) systems. The primary thrust of the next quarter's work will be to develop accurate costs on major equipment, piping, and instrumentation. Plant lay-out will also be undertaken.

An attempt to accelerate the "detailed engineering design" part of Phase I is being undertaken and it is anticipated that a proposal for Phase II funding may be achievable by the end of the quarter and hopefully, prior to that time. Phase II deals with the construction, start-up, and acceptance testing of the PDU and has been scheduled for a period of 17 months. In order to minimize time lags between phases and to facilitate placement of equipment orders, the acceleration of the detailed engineering design has been proposed and accepted with the provision that the researchers will apply their best efforts given the stringent time constraints.

APPENDIX A

CALCULATIONS FOR CHEMICAL COMPOSITION OF CELLULOSIC BIOMASS

Appendix A

The glucan content of soft or hardwood shown in Table 2.4, page 20, of the First Quarterly Report¹ is that of α -cellulose and of hemicellulose added together. Therefore, if we subtract the cellulose - glucan from the total glucan content we get the glucan of the hemicellulose.

Therefore, in the case of hardwood: $49.0 - 45.1 = 3.9\%$
By adding these values of glucan (3.9) to galactan, mannan, araban and xylan content, we get the hemicellulose content because it is the only source of these sugars.

$$\begin{aligned}\text{The hemicellulose of hardwood} &= 3.9 + 0.8 + 2.35 + 0.5 + 18.85 \\ &= 26.40 \%\end{aligned}$$

Softwood hemicellulose is calculated by the same way
 45.9 (Total Glucan) - 43.8 (cellulose) = 2.1 (Hemicellulose glucan).

$$\begin{aligned}\text{The hemicellulose of softwood} &= 2.1 + 1.43 + 11.23 + 1.7 + 5.75 \\ &= 21.58\end{aligned}$$

Estimation of the chemical composition of corn stover without the cob and the pentosans and hexosans contents of hemicellulose:

The following table² shows the composition of corn stover with cob included and the analysis of the individual parts of the plant.

Composition of Corn Stover with Cob

	Cob	Husk	Leaf	Stalk	Total
FOR 100 KG (DRY BASIS) CORN RESIDUE ^(a)					
Total	21.3	13.0	11.7	53.9	99.9
Lignin	1.58	0.87	0.60	5.66	8.71
Cellulose	7.43	4.28	2.57	18.54	32.82
Hemicellulose	7.94	4.73	2.90	12.77	28.34
Sucrose (solubles)	3.37	2.20	2.93	11.48	19.98
Extractives	0.09	0.12	0.28	0.92	1.41
Protein	0.60	0.36	0.82	1.99	3.77
Ash	0.30	0.44	1.60	2.54	4.88
(a) 52.7% moisture as gathered when kernel moisture is 23%.					

By excluding the cob contribution to the Total and normalizing on the basis of 100 kg. of cob-free corn stover we get the following values for the % residue:

Parts of the Plant:	<u>Stalk</u>	<u>Husk</u>	<u>Leaf</u>	<u>Total</u>
% Residue	53.9	13.0	11.7	78.5
Normalized % Resistance	68.58	16.54	14.88	100.0

As example for this calculation:

The % residue of the corn stover without cob is obtained by adding the % residues of the stalk, husk and leaf, which equals to 78.6%, but if we start with 100 kg of corn stover without cob these values will change to, for example:

$$\text{Stalk residue} = \frac{53.9 \times 100}{78.6} = 68.58\%$$

The results of analysis of the individual parts of the plant that constitute the corn stover without the cob will also change according to the new value of % residue. The following table shows the new values:

Composition of Corn Stover without Cob

	Stalk	Husk	Leaf	Total
Total	68.58	16.54	14.88	100.0
Cellulose	23.59	5.44	3.27	32.30
Hemicellulose	16.25	6.02	3.69	25.96
Lignin	7.2	1.12	.76	9.08
Sucrose (Solubles)	14.61	2.80	3.72	21.12
Extractives	1.17	.56	.37	2.10
Protein	2.54	.46	1.04	4.04
Ash	3.22	.14	2.04	5.40

As an example of the above estimation, we take the cellulose content of the stalk which is 18.54% when the residue is 53.9%. When the residue changes to 68.58% the cellulose will accordingly change to

$$18.54 \times \frac{68.58}{53.9} = 23.59\%$$

The same can be followed to calculate the percentage of the other components.

Estimation of the pentosans and hexosans content of the hemicellulose.

The analysis of corn stalk mentioned in Table 2.11, page 27, of the First Quarterly Report³ is used as the basis of these calculations. The total glucose content in that table is 37.7% and is the sum of glucose from the cellulose and the glucose from hemicellulose. The cellulose content is 29.3% and it gives only glucose on hydrolysis amount to

$$29.3 \times \frac{180}{162} = 32.5\%$$

The difference between the total glucose and this value (32.5%) is the glucose content of the hemicellulose (i.e., $37.7 - 32.5 = 5.2\%$). The other sugars mentioned in Table 2.11 of the First Quarterly Report came from hemicellulose hydrolysis. Therefore, the corn stalk hemicellulose sugars are:

glucose	5.2	Hexoses $C_6 = 6.9$, Hexosans = $6.9 \times \frac{162}{180} = 6.21$
galactose	1.1	
mannose	.6	
arabinose	1.9	Pentoses $C_5 = 17.4$, Pentosans = $17.4 \times \frac{130}{148} = 15.28$
xylose	15.5	
		Total 21.48

This shows that the corn stalk hemicellulose is 21.49% according to values of Table 2.11 of the First Quarterly Report and consists of 6.21% hexosans and 15.28% pentosans.

Assuming that this distribution holds for the other parts of the plant and for the whole plant, then we can calculate the pentosans and hexosans of corn stover. The following table shows these results:

<u>Component</u>	<u>Corn Stalk</u>	<u>Corn Stover</u>	
		<u>With Cob</u>	<u>Without Cob</u>
Hemicellulose	21.49	25.96	28.34
Hexosans	6.21	7.5	8.19
Pentosans	15.28	18.46	20.15

REFERENCES

1. Timell, T., Tappi, 40 (17) 568 (1957)
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3. Enzymatic Conversion of Cellulosic Materials, Technology Application, by Elmer C. Graden, Jr. 1976. An Interscience publication, John Wiley & Sons, New York, London, Sydney, Toronto, p.249.
4. C.R. Wilke, R.D. Yang, A.S. Sciamanna and R.P. Freitas, "Raw Materials Evaluation and Process Development Studies for Conversion of Biomass to Sugars and Ethanol", the Second Annual Symposium on Fuels from Biomass, Rensselaer Polytechnic Institute, Troy, New York, June 20-22, p. 421 (1978).

APPENDIX B

COMPUTER PROGRAM: SENSITIVITY ANALYSIS

CSTR AND PFR

C	FOR THE TWO CASES.	GTECH 52
C		GTECH 53
C	READ THE REACTOR OPTION, AND THE INPUT DATA	GTECH 54
C		GTECH 55
	READ (1, 1000) IOPT	GTECH 56
	READ (1, 1010) CCO, DC, CA, DA, DRECY, DREAC, DCONC, TEMP,	GTECH 57
1	THETA, CGSTR	GTECH 58
		GTECH 59
C		GTECH 60
C	READ THE NUMBER OF THE PARAMETER WHICH WILL VARY IN THE	GTECH 61
C	SENSITIVITY ANALYSIS	GTECH 62
C		GTECH 63
	READ (1, 1000) J	GTECH 64
	KASE = 0	GTECH 65
C		GTECH 66
C	CALCULATE THE CONSTANTS	GTECH 67
C		GTECH 68
	CAS = F0 (CA, CCO)	GTECH 69
	A = F1 (CCO, DC, CAS, DA, DCONC)	GTECH 70
	B = F2 (THETA, DRECY, DC)	GTECH 71
	C = F3 (DREAC, CCO)	GTECH 72
	D = F4 (DCONC, CGSTR)	GTECH 73
	RK1 = F5 (TEMP, CA)	GTECH 74
	RK2 = F6 (TEMP, CA)	GTECH 75
C		GTECH 76
C	CALCULATE THE OPTIMUM RESIDENCE TIME, COST OF HEXOSE, AND	GTECH 77
C	THE INDIVIDUAL COST COMPONENTS	GTECH 78
C		GTECH 79
	100 CALL FUNC	GTECH 80
	KASE = KASE + 1	GTECH 81
	RK1T = RK1 * TOPT	GTECH 82
	RK2T = RK2 * TOPT	GTECH 83
	IF (IOPT .EQ. 2) GO TO 104	GTECH 84
	CC = CCO / (1.0 + RK1T)	GTECH 85
	CG = RK1T * CC / (1.0 + RK2T)	GTECH 86
	GO TO 108	GTECH 87
104	CC = CCO * EXP (- RK1T)	GTECH 88
	CG = (CC - CCO * EXP (- RK2T)) / R	GTECH 89
108	D1 = (CCO - THETA * CC) * DC / CG	GTECH 90
	D2 = CAS * DA / CG	GTECH 91
	D3 = TOPT * DREAC / CG	GTECH 92
	D4 = (1.0 / CG - 1.0 / CGSTR) * DCONC	GTECH 93
	D5 = CC * DRECY * THETA / CG	GTECH 94
	PT = 100.0 / COST	GTECH 95
	P1 = D1 * PT	GTECH 96
	P2 = D2 * PT	GTECH 97
	P3 = D3 * PT	GTECH 98
	P4 = D4 * PT	GTECH 99
	P5 = D5 * PT	GTECH100
	CONV = (CCO - CC) * 100.0 / CCO	GTECH101
	RATIO = (CCO - CG - CC) / CG	GTECH102
	FRAC = 1.0 / (1.0 + RATIO)	

PROGRAM MAIN (INPUT, OUTPUT, TAPE1=INPUT, TAPE2=OUTPUT)	GTECH	1
	GTECH	2
THIS PROGRAM OPTIMIZES THE COST OF PRODUCING A HEXOSE SOLUTION	GTECH	3
OF A DESIRED CONCENTRATION IN A CSTR/PFR SYSTEM IN WHICH THE	GTECH	4
CELLULOSE IN THE PRODUCT STREAM FROM THE REACTOR IS RECYCLED.	GTECH	5
A SENSITIVITY ANALYSIS CAN BE PERFORMED BASED ON FLUCTUATIONS	GTECH	6
IN ANY PARAMETER WHICH COMPRISES THE MATHEMATICAL MODEL OF	GTECH	7
THIS REACTOR SYSTEM.	GTECH	8
	GTECH	9
COMMON /BOX1/ A, B, C, D, RK1, RK2, IOPT	GTECH	10
COMMON /BOX2/ TOPT, COST, P, R, E, F, G, H	GTECH	11
	GTECH	12
DEFINITION OF INPUT VARIABLES :	GTECH	13
-----	GTECH	14
1. CCO = CONC. OF HYDROLYZABLE CELLULOSE. KG PER CU M	GTECH	15
2. DC = COST OF CELLULOSE, \$ PER KG	GTECH	16
3. CA = CONCENTRATION OF THE PURE ACID, WT. PERCENT	GTECH	17
4. DA = COST OF THE ACID & EQUIV. LIME, \$ PER KG	GTECH	18
5. DRECY = COST OF RECYCLING THE CELLULOSE, \$ PER KG	GTECH	19
6. DREAC = COST OF THE REACTOR, \$ PER CU M PER HOUR	GTECH	20
7. DCONC = COST OF CONCNG. THE HEXOSE SOLN., \$ PER CU M	GTECH	21
8. TEMP = TEMPERATURE IN KELVINS	GTECH	22
9. THETA = FRACTION OF THE CELLULOSE RECOVERED FROM THE	GTECH	23
PRODUCT STREAM	GTECH	24
10. CGSTR = DESIRED CONC. OF THE HEXOSE SOLN., KG PER CU M	GTECH	25
	GTECH	26
OTHER PROGRAM VARIABLES :	GTECH	27
-----	GTECH	28
RK1 = RATE CONSTANT FOR THE DECOMPOSITION OF CELLULOSE	GTECH	29
RK2 = RATE CONSTANT FOR THE DECOMPOSITION OF HEXOSE	GTECH	30
CAS = CONCENTRATION OF ACID IN THE REACTOR	GTECH	31
TOPT = OPTIMUM RESIDENCE TIME, HOURS	GTECH	32
COST = MINIMUM COST OF HEXOSE PRODUCED, \$ PER KG	GTECH	33
D1 = CELLULOSE COST, \$/KG HEXOSE	GTECH	34
D2 = ACID & LIME COST, \$/KG HEXOSE	GTECH	35
D3 = REACTOR COST, \$/KG HEXOSE	GTECH	36
D4 = EVAPORATION COST, \$/KG HEXOSE	GTECH	37
D5 = CELLULOSE-RECYCLE COST, \$/KG HEXOSE	GTECH	38
P1-P5 = PERCENTAGES OF TOTAL COST OF HEXOSE	GTECH	39
CORRESPONDING TO D1,...,D5, RESPECTIVELY	GTECH	40
CC = CELLULOSE CONC. IN REACTOR PRODUCT STREAM	GTECH	41
CG = HEXOSE CONC. IN REACTOR PRODUCT STREAM	GTECH	42
RATIO = KG DEGRAD. PRODUCTS/KG HEXOSE PRODUCED	GTECH	43
CONV = CELLULOSE CONVERSION PER PASS, PERCENTAGE	GTECH	44
FRAC = FRACTION OF CELLULOSE REACTED TO HEXOSE	GTECH	45
IOPT = 1 FOR CSTR	GTECH	46
= 2 FOR PFR	GTECH	47
A, B, C, D, E, F, G, H, P, & R ARE DEFINED IN THE	GTECH	48
DERIVATION OF THE MATHEMATICAL MODEL. A, B, C, & D	GTECH	49
ARE DEFINED IDENTICALLY FOR BOTH THE CSTR AND THE	GTECH	50
PFR. DEFINITIONS FOR E, F, G, H, P, & R DIFFER	GTECH	51

C	TMIN	= TOPT * 60.0	GTECH103
C			GTECH104
C	PRINT THE RESULTS		GTECH105
C			GTECH106
	WRITE (2, 2000)		GTECH107
	IF (IOPT .EQ. 1) WRITE (2, 2004)		GTECH108
	IF (IOPT .EQ. 2) WRITE (2, 2008)		GTECH109
	WRITE (2, 2010) KASE		GTECH110
	WRITE (2, 2020) CCO, CA, CGSTR, DC, DA, DRECY, DREAC, DCONC,		GTECH111
	1 TEMP, THETA		GTECH112
	WRITE (2, 2030)		GTECH113
	WRITE (2, 2040) A, F, B, G, C, H, D, P, E, R		GTECH114
	WRITE (2, 2045) RK1, RK2		GTECH115
	WRITE (2, 2050)		GTECH116
	WRITE (2, 2060) TOPT, TMIN, CC, CG, D1, P1, D2, P2, D3, P3,		GTECH117
	1 D4, P4, D5, P5, COST		GTECH118
	WRITE (2, 2070) CONV, RATIO, FRAC		GTECH119
C			GTECH120
C	READ CHANGED PARAMETER VALUE FOR THE SENSITIVITY ANALYSIS		GTECH121
C			GTECH122
	READ (1, 1010) DUMMY		GTECH123
	IF (DUMMY .EQ. 0.0) GO TO 210		GTECH124
C			GTECH125
C	RECALCULATE THE AFFECTED CONSTANTS		GTECH126
C			GTECH127
	GO TO (110, 120, 130, 140, 150, 160, 170, 180, 190, 200), J		GTECH128
C			GTECH129
C	INITIAL CONCENTRATION OF CELLULOSE IS VARIED		GTECH130
C			GTECH131
	110 CCO = DUMMY		GTECH132
	CAS = F0 (CA, CCO)		GTECH133
	A = F1 (CCO, DC, CAS, DA, DCONC)		GTECH134
	C = F3 (DREAC, CCO)		GTECH135
	GO TO 100		GTECH136
C			GTECH137
C	COST OF CELLULOSE IS VARIED		GTECH138
C			GTECH139
	120 DC = DUMMY		GTECH140
	A = F1 (CCO, DC, CAS, DA, DCONC)		GTECH141
	B = F2 (THETA, DRECY, DC)		GTECH142
	GO TO 100		GTECH143
C			GTECH144
C	CONCENTRATION OF THE ACID IS VARIED		GTECH145
C			GTECH146
	130 CA = DUMMY		GTECH147
	CAS = F0 (CA, CCO)		GTECH148
	A = F1 (CCO, DC, CAS, DA, DCONC)		GTECH149
	RK1 = F5 (TEMP, CA)		GTECH150
	RK2 = F6 (TEMP, CA)		GTECH151
	GO TO 100		GTECH152
C			GTECH153

C	COST OF THE ACID IS VARIED	GTECH154
C		GTECH155
	140 DA = DUMMY	GTECH156
	A = F1 (CCO, DC, CAS, DA, DCONC)	GTECH157
	GO TO 100	GTECH158
C		GTECH159
C	CELLULOSE-RECYCLE COST IS VARIED	GTECH160
C		GTECH161
	150 DRECY = DUMMY	GTECH162
	B = F2 (THETA, DRECY, DC)	GTECH163
	GO TO 100	GTECH164
C		GTECH165
C	REACTOR-COST IS VARIED	GTECH166
C		GTECH167
	160 DREAC = DUMMY	GTECH168
	C = F3 (DREAC, CCO)	GTECH169
	GO TO 100	GTECH170
C		GTECH171
C	COST OF CONCENTRATING THE HEXOSE SOLUTION IS VARIED	GTECH172
C		GTECH173
	170 DCONC = DUMMY	GTECH174
	A = F1 (CCO, DC, CAS, DA, DCONC)	GTECH175
	D = F4 (DCONC, CGSTR)	GTECH176
	GO TO 100	GTECH177
C		GTECH178
C	TEMPERATURE IS VARIED	GTECH179
C		GTECH180
	180 TEMP = DUMMY	GTECH181
	RK1 = F5 (TEMP, CA)	GTECH182
	RK2 = F6 (TEMP, CA)	GTECH183
	GO TO 100	GTECH184
C		GTECH185
C	FRACTION OF CELLULOSE RECYCLED IS VARIED	GTECH186
C		GTECH187
	190 THETA = DUMMY	GTECH188
	B = F2 (THETA, DRECY, DC)	GTECH189
	GO TO 100	GTECH190
C		GTECH191
C	DESIRED HEXOSE CONCENTRATION IS VARIED	GTECH192
C		GTECH193
	200 CGSTR = DUMMY	GTECH194
	D = F4 (DCONC, CGSTR)	GTECH195
	GO TO 100	GTECH196
C		GTECH197
	210 CONTINUE	GTECH198
C		GTECH199
C	INPUT FORMATS	GTECH200
C		GTECH201
	1000 FORMAT (I2)	GTECH202
	1010 FORMAT (F15.5)	GTECH203
		GTECH204

C		GTECH205
C	OUTPUT FORMATS	GTECH206
C		GTECH207
	2000 FORMAT (1H1)	GTECH208
	2004 FORMAT (//, 15X, 38HCONTINUOUS STIRRED TANK REACTOR SYSTEM, //)	GTECH209
	2008 FORMAT (//, 22X, 24HPLUG FLOW REACTOR SYSTEM, //)	GTECH210
	2010 FORMAT (//, 2X, 12, 1X, 10HINPUT DATA, /, 5X, 10(1H-))	GTECH211
	2020 FORMAT (/, 7X, 39HCONCENTRATION OF HYDROLYZABLE CELLULOSE, 2X,	GTECH212
1	2H= , F7.3, 20H KG EQ. HEXOSE/CU. M,	GTECH213
2	/, 7X, 35HCONCENTRATION OF PURE ACID SOLUTION, 6X,	GTECH214
3	2H= , F7.3, 12H WT. PERCENT,	GTECH215
4	/, 7X, 40HDESIRED CONCENTRATION OF HEXOSE SOLUTION, 1X,	GTECH216
5	2H= , F7.3, 13H KG/CU. METER,	GTECH217
6	/, 7X, 17HCOST OF CELLULOSE, 24X, 2H= , F7.3,	GTECH218
7	16H \$/KG EQ. HEXOSE,	GTECH219
8	/, 7X, 23HCOST OF ACID & EQ. LIME, 18X, 2H= , F7.3, 5H \$/KG,	GTECH220
9	/, 7X, 27HCOST OF RECYCLING CELLULOSE, 14X, 2H= , F7.4,	GTECH221
A	16H \$/KG EQ. HEXOSE,	GTECH222
B	/, 7X, 15HCOST OF REACTOR, 26X, 2H= , F7.3,	GTECH223
C	15H \$/CU. METER/HR,	GTECH224
D	/, 7X, 37HCOST OF CONCENTRATING HEXOSE SOLUTION, 4X,	GTECH225
E	2H= , F7.3, 12H \$/CU. METER,	GTECH226
F	/, 7X, 11HTEMPERATURE, 30X, 2H= , F7.3, 8H KELVINS,	GTECH227
G	/, 7X, 30HFRACTION OF CELLULOSE RECYCLED, 11X, 2H= , F7.3)	GTECH228
	2030 FORMAT (//, 5X, 7HRESULTS, /, 5X, 7(1H-))	GTECH229
	2040 FORMAT (/, 7X, 3HA =, E11.5, 4X, 3HF =, E11.5,	GTECH230
1	/, 7X, 3HB =, E11.5, 4X, 3HG =, E11.5,	GTECH231
2	/, 7X, 3HC =, E11.5, 4X, 3HH =, E11.5,	GTECH232
3	/, 7X, 3HD =, E11.5, 4X, 3HP =, E11.5,	GTECH233
4	/, 7X, 3HE =, E11.5, 4X, 3HR =, E11.5)	GTECH234
	2045 FORMAT (/, 7X, 5HRK1 =, E11.5, 1X, 4H1/HR,	GTECH235
1	/, 7X, 5HRK2 =, E11.5, 1X, 4H1/HR)	GTECH236
	2050 FORMAT (/, 7X, 18HOPTIMAL SOLUTION :, /, 7X, 18(1H-))	GTECH237
	2060 FORMAT (/, 9X, 14HRESIDENCE TIME, 13X, 1H=, E11.5, 1X, 3HHRS,	GTECH238
+	2H =, E11.5, 4H MIN, /,	GTECH239
1	/, 9X, 23HCELLULOSE CONCENTRATION, 4X, 1H=, F7.3,	GTECH240
2	1X, 28HKG EQUIV. HEXOSE/CUBIC METER,	GTECH241
3	/, 9X, 20HHEXOSE CONCENTRATION, 7X, 1H=, F7.3, 1X,	GTECH242
4	14HKG/CUBIC METER, /,	GTECH243
5	/, 9X, 28HCOST OF CELLULOSE CONSUMED =, F6.4, 1X,	GTECH244
6	11H\$/KG HEXOSE, F6.2, 2H %,	GTECH245
7	/, 9X, 23HCOST OF ACID & EQ. LIME, 4X, 1H=, F6.4, 1X,	GTECH246
8	11H\$/KG HEXOSE, F6.2, 2H %,	GTECH247
9	/, 9X, 12HREACTOR COST, 15X, 1H=, F6.4, 1X,	GTECH248
A	11H\$/KG HEXOSE, F6.2, 2H %,	GTECH249
B	/, 9X, 25HHEXOSE-CONCENTRATION COST, 2X, 1H=, F6.4, 1X,	GTECH250
C	11H\$/KG HEXOSE, F6.2, 2H %,	GTECH251
D	/, 9X, 22HCELLULOSE-RECYCLE COST, 5X, 1H=, F6.4, 1X,	GTECH252
E	11H\$/KG HEXOSE, F6.2, 2H %, /,	GTECH253
F	/, 9X, 10HTOTAL COST, 17X, 1H=, F6.4, 1X,	GTECH254
G	11H\$/KG HEXOSE, /)	GTECH255

2070 FORMAT (/ , 9X, 25HCELLULOSE CONVERSION/PASS, 3X,	GTECH256
1 1H=, F6.2, 2H %,	GTECH257
2 /, 9X, 23HDEGRAD. PRODUCTS/HEXOSE, 5X, 1H=,	GTECH258
3 F6.3, 6H KG/KG,	GTECH259
4 /, 9X, 29HCELLULOSE REACTED TO HEXOSE =, F6.3,	GTECH260
5 6H KG/KG, ///)	GTECH261
C	GTECH262
STOP	GTECH263
END	GTECH264
C-----	GTECH265
FUNCTION F0 (CA, CCO)	GTECH266
C	GTECH267
C FG = KC EQUIVALENT HEXOSE/KG CELLULOSE	GTECH268
C SGCEL = SP. GRAVITY OF CELLULOSE	GTECH269
C SGACID = SP. GRAVITY OF PURE ACID	GTECH270
C SGSOLN = SP. GRAVITY OF DILUTE ACID SOLUTION	GTECH271
C X = VOL. RATIO OF INITIAL ACID TO INITIAL CELLULOSE	GTECH272
C	GTECH273
DATA FG, SGCEL, SGACID / 1.11, 1.50, 1.83 /	GTECH274
C	GTECH275
X = FG * SGCEL * 1000.0 / CCO - 1.0	GTECH276
SGSOLN = 1.0 - 0.01 * CA * (1.0 - 1.0 / SGACID)	GTECH277
SGSOLN = 1.0 / SGSOLN	GTECH278
F0 = CA * 0.01 * 1000.0 * SGSOLN / (1.0 + 1.0 / X)	GTECH279
RETURN	GTECH280
END	GTECH281
C-----	GTECH282
FUNCTION F1 (CCO, DC, CAS, DA, DCONC)	GTECH283
F1 = (CCO * DC + CAE * DA + DCONC) / CCO	GTECH284
RETURN	GTECH285
END	GTECH286
C-----	GTECH287
FUNCTION F2 (THETA, DRECY, DC)	GTECH288
F2 = THETA * (DRECY - DC)	GTECH289
RETURN	GTECH290
END	GTECH291
C-----	GTECH292
FUNCTION F3 (DREAC, CCO)	GTECH293
F3 = DREAC / CCO	GTECH294
RETURN	GTECH295
END	GTECH296
C-----	GTECH297
FUNCTION F4 (DCONC, CGSTR)	GTECH298
F4 = DCONC / CGSTR	GTECH299
RETURN	GTECH300
END	GTECH301
C-----	GTECH302
FUNCTION F5 (TEMP, CA)	GTECH303
DATA RK10, RM, E1, RG /1.73E+19, 1.34, 42900.0, 1.9872 /	GTECH304
ERT = E1 / (RG * TEMP)	GTECH305
F5 = RK10 * CA ** RM * EXP(- ERT) * 60.0	GTECH306

RETURN	GTECH307
END	GTECH308
C-----	GTECH309
FUNCTION F6 (TEMP, CA)	GTECH310
DATA RK20, RN, E2, RG /2.38E+14, 1.02, 32870.0, 1.9872 /	GTECH311
ERT = E2 / (RG * TEMP)	GTECH312
F6 = RK20 * CA ** RN * EXP(- ERT) * 60.0	GTECH313
RETURN	GTECH314
END	GTECH315
C-----	GTECH316
SUBROUTINE FUNC	GTECH317
C	GTECH318
C THIS SUBROUTINE CALCULATES THE OPTIMUM RESIDENCE TIME AND THE	GTECH319
C MINIMUM COST OF PRODUCING 1 KG OF HEXOSE IN A CSTR OR A PFR	GTECH320
C SYSTEM	GTECH321
C	GTECH322
COMMON /BOX1/ A, B, C, D, RK1, RK2, IOPT	GTECH323
COMMON /BOX2/ TOPT, COST, P, R, E, F, G, H	GTECH324
C	GTECH325
IF (IOPT .EQ. 2) GO TO 50	GTECH326
C	GTECH327
C EVALUATE THE CONSTANTS FOR THE CSTR CASE	GTECH328
C	GTECH329
RK12 = RK1 + RK2	GTECH330
E = (A + B) / RK1	GTECH331
F = (A * RK12 + B * RK2 + C) / RK1	GTECH332
G = (A * RK1 * RK2 + C * RK12) / RK1	GTECH333
H = C * RK2	GTECH334
P1 = 0.5 / H	GTECH335
P = P1 * G	GTECH336
R = P1 * E	GTECH337
GO TO 70	GTECH338
C	GTECH339
C EVALUATE THE CONSTANTS FOR THE PFR CASE	GTECH340
C	GTECH341
50 RK12 = RK1 - RK2	GTECH342
E = A * RK1 + C	GTECH343
F = C * RK1	GTECH344
G = A * RK2 + C	GTECH345
H = C * RK2	GTECH346
P = B * RK12	GTECH347
R = - RK12 / RK1	GTECH348
C	GTECH349
C START SOLVING FOR THE OPTIMUM RES. TIME (NEWTON-RAPHSON)	GTECH350
C	GTECH351
C	GTECH352
70 T1 = 0.25	GTECH353
C	GTECH354
DO 100 I = 1, 50	GTECH355
TOLD = T1	GTECH356
IF (IOPT .EQ. 2) GO TO 80	GTECH357
FT = T1 ** 3 + P * T1 ** 2 - R	

DFT	= 3.0 * T1 ** 2 + 2.0 * P * T1	GTECH358
GO TO 90		GTECH359
80 A1	= E + F * T1	GTECH360
A2	= G + H * T1	GTECH361
A3	= EXP (RK12 * T1)	GTECH362
A4	= P * EXP (- RK2 * T1)	GTECH363
FT	= A1 - A2 * A3 + A4	GTECH364
DFT	= F - (H + A2 * RK12) * A3 - A4 * RK2	GTECH365
90 TDEL	= FT / DFT	GTECH366
T1	= T1 - TDEL	GTECH367
DELTI	= ABS((T1 - TOLD) / T1)	GTECH368
IF ((DELTI .LE. 1.E-5) .AND. (ABS(TDEL) .LE. 1.E-5)) GO TO 200		GTECH369
100 CONTINUE		GTECH370
C		GTECH371
WRITE (2, 1000)		GTECH372
200 COST	= 0.0	GTECH373
C		GTECH374
IF (T1 .LE. 1.E-20) GO TO 500		GTECH375
IF (IOPT .EQ. 2) GO TO 400		GTECH376
COST	= E / T1 + F + G * T1 + H * T1 * T1 - D	GTECH377
GO TO 500		GTECH378
400 E1	= EXP (- RK1 * T1)	GTECH379
E2	= EXP (- RK2 * T1)	GTECH380
COST	= R * (A + B * E1 + C * T1) / (E1 - E2) - D	GTECH381
500 CONTINUE		GTECH382
TOPT	= T1	GTECH383
1000 FORMAT(/, 34HWARNING... NEWTON DID NOT CONVERGE,/)		GTECH384
C		GTECH385
RETURN		GTECH386
END		GTECH387

APPENDIX C
BASELINE COSTS

Basis for Estimated Costs

A. $\$C$ - Cost of Cellulose

The current quoted price for wood chips in Georgia is approximately \$30 per oven dry ton. Assuming the wood is 45 percent cellulose, the cost is \$0.066/kg cellulose expressed as equivalent kg of hexose. No credits are taken for the value of the liquid or hemicellulose, nor is the cost of extracting these materials considered.

B. $\$A$ - Cost of Sulfuric Acid and Equivalent Lime

The current quoted price for sulfuric acid is \$60 per ton (100 percent). The acid must be eventually neutralized before fermentation. Lime costs \$35 per ton. To neutralize one ton of sulfuric acid, 0.57 ton of lime is required. The cost of the sulfuric acid and the equivalent lime for neutralization would be \$0.088 per kg of sulfuric acid.

C. $\$_{\text{recycle}}$ - Cost of Recycling Unreacted Cellulose

Assume that a loading of $20 \text{ kg/m}^2 \text{ hr}$ is possible. The purchased cost of 100 ft^2 drum filter was \$26,000 in 1967.* Auxiliary equipment was estimated at fifty percent of the installed drum filter price. Depreciation was based on 10 years straight line. Operating charges plus fixed charges were estimated to equal twice the fixed charges. The 1979 cost of recycling the unreacted cellulose which results is \$0.0055/kg cellulose expressed as equivalent hexose.

D. $\$R$ - Cost of the Reactor

This cost was based on a 1000 gal CSTR reactor costing \$20,000 in 1967.* Installation charges were estimated to be 50 percent of the purchased cost of the purchased cost of the reactor. Ten years straight line depreciation was

*Peters, Max S. and Klaus D. Timmerhaus, Plant Design and Economics for Chemical Engineers, 2nd Edition, McGraw-Hill Book Company, New York, 1968.

used. Operating charges plus fixed charges were estimated to equal twice the fixed charges. The above assumptions give the 1979 cost of the CSTR reactor as $\$0.40/\text{m}^3 \text{ hr.}$

E. $\$_{\text{conc}}$ - Cost of Concentrating the Hexose Solution

An overall heat transfer coefficient of $400 \text{ BTU/hr-ft}^2\text{-}^\circ\text{F}^{**}$ and driving force of 15°F were assumed to calculate the energy flux. The cost of an evaporator with 2000 sq. ft. of surface area was $\$30,000$ in 1967.* Ten year straight line depreciation was used. Assuming five effects per train, and energy costs of $\$2/\text{MM BTU}$, the 1979 cost of concentrating hexose was estimated to be $\$1.39/\text{m}^3$ of water evaporated.

*Peters, Max S. and Klaus D. Timmerhaus, Plant Design and Economics for Chemical Engineers, 2nd Edition, McGraw-Hill Book Company, New York, 1968.

**Perry's Chemical Engineers' Handbook, 4th Edition, Robert H. Perry, et al., eds., McGraw-Hill Book Company, p. 11-34, 1963.

APPENDIX D
SAMPLE COMPUTER PRINT-OUTS
CSTR AND PFR

(References: Tables 4-4 and 4-5)

CONTINUOUS STIRRED TANK REACTOR SYSTEM

1 INPUT DATA

```

CONCENTRATION OF HYDROLYZABLE CELLULOSE = 115.000 KG. EQ. HEXOSE/CU. M
CONCENTRATION OF PURE ACID SOLUTION      = 1.000 WT. PERCENT
DESIRED CONCENTRATION OF HEXOSE SOLUTION  = 135.000 KG/CU. METER
COST OF CELLULOSE                         = .066 $/KG EQ. HEXOSE
COST OF ACID & EQ. LIME                   = .088 $/KG
COST OF RECYCLING CELLULOSE               = .0055 $/KG EQ. HEXOSE
COST OF REACTOR                           = .400 $/CU. METER/HR
COST OF CONCENTRATING HEXOSE SOLUTION     = 1.390 $/CU. METER
* TEMPERATURE                             = 443.000 KELVINS
FRACTION OF CELLULOSE RECYCLED            = .900
  
```

RESULTS

```

A = .85243E-01    F = .12772E+00
B = -.54450E-01   G = .81793E-01
C = .34783E-02    H = .30219E-02
D = .10296E-01    I = .13532E+02
E = .43270E-01    J = .71594E+01
  
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RK1 = .71165E+00 1/HR
RK2 = .86979E+00 1/HR
  
```

OPTIMAL SOLUTION :

```

RESIDENCE TIME          = .70904E+00 HRS = .42542E+02 MIN
CELLULOSE CONCENTRATION  = 76.433 KG EQUIV. HEXOSE/CUBIC METER
HEXOSE CONCENTRATION     = 23.866 KG/CUBIC METER

COST OF CELLULOSE CONSUMED = .1278 $/KG HEXOSE 53.70 %
COST OF ACID & EQ. LIME   = .0345 $/KG HEXOSE 14.49 %
REACTOR COST              = .0119 $/KG HEXOSE 4.99 %
HEXOSE-CONCENTRATION COST = .0479 $/KG HEXOSE 20.15 %
CELLULOSE-RECYCLE COST    = .0159 $/KG HEXOSE 6.66 %

TOTAL COST               = .2390 $/KG HEXOSE

CELLULOSE CONVERSION/PASS = 33.54 %
DEGRAD. PRODUCTS/HEXOSE   = .616 KG/KG
CELLULOSE REACTED TO HEXOSE = .619 KG/KG
  
```

CONTINUOUS STIRRED TANK REACTOR SYSTEM

2 INPUT DATA

CONCENTRATION OF HYDROLYZABLE CELLULOSE = 115.000 KG EQ. HEXOSE/CU. M
 CONCENTRATION OF PURE ACID SOLUTION = 1.000 WT. PERCENT
 DESIRED CONCENTRATION OF HEXOSE SOLUTION = 135.000 KG/CU. METER
 COST OF CELLULOSE = .066 \$/KG EQ. HEXOSE
 COST OF ACID & EQ. LIME = .088 \$/KG
 COST OF RECYCLING CELLULOSE = .0055 \$/KG EQ. HEXOSE
 COST OF REACTOR = .400 \$/CU. METER/HR
 COST OF CONCENTRATING HEXOSE SOLUTION = 1.390 \$/CU. METER
 * TEMPERATURE = 453.000 KELVINS
 FRACTION OF CELLULOSE RECYCLED = .900

RESULTS

A = .85243E-01 F = .11414E+00
 B = .54450E-01 G = .17545E+00
 C = .34783E-02 H = .68904E-02
 D = .10296E-01 P = .12746E+02
 E = .14757E-01 R = .10708E+01

RK1 = .20867E+01 1/HR
 RK2 = .19810E+01 1/HR

OPTIMAL SOLUTION :

RESIDENCE TIME = .28465E+00 HRS = .17199E+02 MIN
 CELLULOSE CONCENTRATION = 71.958 KG EQUIV. HEXOSE/CUBIC METER
 HEXOSE CONCENTRATION = 27.453 KG/CUBIC METER
 COST OF CELLULOSE CONSUMED = .1208 \$/KG HEXOSE 58.00 %
 COST OF ACID & EQ. LIME = .0300 \$/KG HEXOSE 14.40 %
 REACTOR COST = .0042 \$/KG HEXOSE 2.01 %
 HEXOSE-CONCENTRATION COST = .0403 \$/KG HEXOSE 19.37 %
 CELLULOSE-RECYCLE COST = .0130 \$/KG HEXOSE 6.23 %
 TOTAL COST = .1282 \$/KG HEXOSE
 CELLULOSE CONVERSION/PASS = 37.43 %
 DEGRAD. PRODUCTS/HEXOSE = .549 KG/KG
 CELLULOSE REACTED TO HEXOSE = .339 KG/KG

CONTINUOUS STIRRED TANK REACTOR SYSTEM

3 INPUT DATA

CONCENTRATION OF HYDROLYZABLE CELLULOSE = 115.000 KG EQ. HEXOSE/CU. M
 CONCENTRATION OF PURE ACID SOLUTION = 1.000 WT. PERCENT
 DESIRED CONCENTRATION OF HEXOSE SOLUTION = 125.000 KG/CU. METER
 COST OF CELLULOSE = .066 \$/KG EQ. HEXOSE
 COST OF ACID & EQ. LIME = .088 \$/KG
 COST OF RECYCLING CELLULOSE = .0055 \$/KG EQ. HEXOSE
 COST OF REACTOR = .400 \$/CU. METER/HR
 COST OF CONCENTRATING HEXOSE SOLUTION = 1.390 \$/CU. METER
 * TEMPERATURE = 463.000 KELVINS
 FRACTION OF CELLULOSE RECYCLED = .900

RESULTS

A = .85243E-01 F = .10892E+00
 B = -.54450E-01 G = .37765E+00
 C = .34783E-02 H = .15162E-01
 D = .10296E-01 P = .12454E+02
 E = .52720E-02 R = .17386E+00

RK1 = .58409E+01 1/HR
 RK2 = .43590E+01 1/HR

OPTIMAL SOLUTION :

RESIDENCE TIME = .11760E+00 HRS = .70560E+01 MIN
 CELLULOSE CONCENTRATION = 68.173 KG EQUIV. HEXOSE/CUBIC METER
 HEXOSE CONCENTRATION = 30.958 KG/CUBIC METER
 COST OF CELLULOSE CONSUMED = .1144 \$/KG HEXOSE 60.84 %
 COST OF ACID & EQ. LIME = .0266 \$/KG HEXOSE 14.14 %
 REACTOR COST = .0015 \$/KG HEXOSE .81 %
 HEXOSE-CONCENTRATION COST = .0346 \$/KG HEXOSE 18.41 %
 CELLULOSE-RECYCLE COST = .0109 \$/KG HEXOSE 5.80 %
 TOTAL COST = .1880 \$/KG HEXOSE
 CELLULOSE CONVERSION/PASS = 40.72 %
 DEGRAD. PRODUCTS/HEXOSE = .513 KG/KG
 CELLULOSE REACTED TO HEXOSE = .661 KG/KG

CONTINUOUS STIRRED TANK REACTOR SYSTEM

4 INPUT DATA

```

CONCENTRATION OF HYDROLYZABLE CELLULOSE = 115.000 KG EQ. HEXOSE/CU. M
CONCENTRATION OF PURE ACID SOLUTION      = 1.000 WT. PERCENT
DESIRED CONCENTRATION OF HEXOSE SOLUTION = 135.000 KG/CU. METER
COST OF CELLULOSE                        = .066 $/KG EQ. HEXOSE
COST OF ACID & EQ. LIME                  = .088 $/KG
COST OF RECYCLING CELLULOSE              = .0055 $/KG EQ. HEXOSE
COST OF REACTOR                          = .400 $/CU. METER/HR
COST OF CONCENTRATING HEXOSE SOLUTION    = 1.390 $/CU. METER
* TEMPERATURE                            = 473.000 KELVINS
FRACTION OF CELLULOSE RECYCLED           = .900
  
```

RESULTS

```

A = .85243E-01    F = .10372E+00
B = -.54450E-01   G = .79633E+00
C = .34783E-02    H = .32267E-01
D = .10294E-01    P = .12340E+02
E = .19673E-02    R = .30484E-01
  
```

```

RK1 = .15653E+02 1/HR
RK2 = .92769E+01 1/HR
  
```

OPTIMAL SOLUTION :

```

RESIDENCE TIME                = .49604E-01 HRS = .29762E+01 MIN
CELLULOSE CONCENTRATION        = 64.737 KG EQUIV. HEXOSE/CUBIC METER
HEXOSE CONCENTRATION           = 34.423 KG/CUBIC METER

COST OF CELLULOSE CONSUMED     = .1088 $/KG HEXOSE 63.00 %
COST OF ACID & EQ. LIME       = .0239 $/KG HEXOSE 13.85 %
REACTOR COST                   = .0006 $/KG HEXOSE .33 %
HEXOSE-CONCENTRATION COST     = .0301 $/KG HEXOSE 17.42 %
CELLULOSE RECYCLE COST        = .0093 $/KG HEXOSE 5.39 %

TOTAL COST                     = .1727 $/KG HEXOSE

CELLULOSE CONVERSION/PASS     = 43.71 %
DEGRAD. PRODUCTS/HEXOSE      = .460 KG/KG
CELLULOSE REACTED TO HEXOSE   = .685 KG/KG
  
```

CONTINUOUS STIRRED TANK REACTOR SYSTEM

5 INPUT DATA

CONCENTRATION OF HYDROLYZABLE CELLULOSE = 115.000 KG EQ. HEXOSE/CU. M
 CONCENTRATION OF PURE ACID SOLUTION = 1.000 WT. PERCENT
 DESIRED CONCENTRATION OF HEXOSE SOLUTION = 135.000 KG/CU. METER
 COST OF CELLULOSE = .066 \$/KG EQ. HEXOSE
 COST OF ACID & EQ. LIME = .088 \$/KG
 COST OF RECYCLING CELLULOSE = .0055 \$/KG EQ. HEXOSE
 COST OF REACTOR = .400 \$/CU. METER/HR
 COST OF CONCENTRATING HEXOSE SOLUTION = 1.390 \$/CU. METER
 * TEMPERATURE = 483.000 KELVINS
 FRACTION OF CELLULOSE RECYCLED = .900

RESULTS

A = .85243E-01 F = .99962E-01
 B = .54450E-01 G = .16363E+01
 C = .34783E-02 H = .66558E-01
 D = .10296E-01 P = .12292E+02
 E = .76468E-03 R = .57444E-02

RK1 = .40269E+02 1/HR
 RK2 = .19136E+02 1/HR

OPTIMAL SOLUTION :

RESIDENCE TIME = .21599E-01 HRS = .12959E+01 MIN

CELLULOSE CONCENTRATION = 61.505 KG EQUIV. HEXOSE/CUBIC METER
 HEXOSE CONCENTRATION = 37.951 KG/CUBIC METER

COST OF CELLULOSE CONSUMED = .1040 \$/KG HEXOSE 64.82 %
 COST OF ACID & EQ. LIME = .0217 \$/KG HEXOSE 13.55 %
 REACTOR COST = .0002 \$/KG HEXOSE .14 %
 HEXOSE-CONCENTRATION COST = .0264 \$/KG HEXOSE 16.47 %
 CELLULOSE-RECYCLE COST = .0090 \$/KG HEXOSE 5.01 %

TOTAL COST = .1604 \$/KG HEXOSE

CELLULOSE CONVERSION/PASS = 46.52 %
 DEGRAD. PRODUCTS/HEXOSE = .413 KG/KG
 CELLULOSE REACTED TO HEXOSE = .708 KG/KG

CONTINUOUS STIRRED TANK REACTOR SYSTEM

6 INPUT DATA

CONCENTRATION OF HYDROLYZABLE CELLULOSE = 115.000 KG EQ. HEXOSE/CU. M
 CONCENTRATION OF PURE ACID SOLUTION = 1.000 WT. PERCENT
 DESIRED CONCENTRATION OF HEXOSE SOLUTION = 135.000 KG/CU. METER
 COST OF CELLULOSE = .066 \$/KG EQ. HEXOSE
 COST OF ACID & EQ. LIME = .088 \$/KG
 COST OF RECYCLING CELLULOSE = .0055 \$/KG EQ. HEXOSE
 COST OF REACTION = .400 \$/CU. METER/HR
 COST OF CONCENTRATING HEXOSE SOLUTION = 1.390 \$/CU. METER
 * TEMPERATURE = 493.000 KELVINS
 FRACTION OF CELLULOSE RECYCLED = .900

RESULTS

A = .85243E-01 F = .97114E-01
 B = .54450E-01 G = .32721E+01
 C = .34783E-02 H = .13332E+00
 D = .10296E-01 P = .12272E+02
 E = .30885E-03 R = .11583E-02

RK1 = .99704E+02 1/HR
 RK2 = .38379E+02 1/HR

OPTIMAL SOLUTION :

RESIDENCE TIME = .97114E-02 HRS = .58269E+00 MIN
 CELLULOSE CONCENTRATION = 58.427 KG EQUIV. HEXOSE/CUBIC METER
 HEXOSE CONCENTRATION = 41.227 KG/CUBIC METER
 COST OF CELLULOSE CONSUMED = .0999 \$/KG HEXOSE 44.43 %
 COST OF ACID & EQ. LIME = .0200 \$/KG HEXOSE 13.27 %
 REACTOR COST = .0001 \$/KG HEXOSE .06 %
 HEXOSE-CONCENTRATION COST = .0234 \$/KG HEXOSE 15.57 %
 CELLULOSE-RECYCLE COST = .0070 \$/KG HEXOSE 4.66 %
 TOTAL COST = .1504 \$/KG HEXOSE

CELLULOSE CONVERSION/PASS = 49.19 %
 DEGRAD. PRODUCTS/HEXOSE = .372 KG/KG
 CELLULOSE REACTED TO HEXOSE = .729 KG/KG

PLUG FLOW REACTOR SYSTEM

1 INPUT DATA

CONCENTRATION OF HYDROLYZABLE CELLULOSE = 115.000 KG EQ. HEXOSE/CU. M
 CONCENTRATION OF PURE ACID SOLUTION = 1.000 WT. PERCENT
 DESIRED CONCENTRATION OF HEXOSE SOLUTION = 135.000 KG/CU. METER
 COST OF CELLULOSE = .066 \$/KG EQ. HEXOSE
 COST OF ACID & EQ. LIME = .038 \$/KG
 COST OF RECYCLING CELLULOSE = .0055 \$/KG EQ. HEXOSE
 COST OF REACTOR = .400 \$/CU. METER/HR.
 COST OF CONCENTRATING HEXOSE SOLUTION = 1.390 \$/CU. METER
 * TEMPERATURE = 443.000 KELVINS
 FRACTION OF CELLULOSE RECYCLED = .900

RESULTS

A = .85243E-01 F = .24753E-02
 B = .54450E-01 G = .77537E-01
 C = .34783E-02 H = .30219E-02
 D = .10296E-01 P = .85562E-02
 E = .64142E-01 R = .22001E+00

RK1 = .71165E+00 1/HR
 RK2 = .86879E+00 1/HR

OPTIMAL SOLUTION :

RESIDENCE TIME = .01628E+00 HRS = .48977E+02 MIN
 CELLULOSE CONCENTRATION = 64.330 KG EQUIV. HEXOSE/CUBIC METER
 HEXOSE CONCENTRATION = 35.072 KG/CUBIC METER
 COST OF CELLULOSE CONSUMED = .1075 \$/KG HEXOSE 60.15 %
 COST OF ACID & EQ. LIME = .0235 \$/KG HEXOSE 13.13 %
 REACTOR COST = .0093 \$/KG HEXOSE 5.21 %
 HEXOSE-CONCENTRATION COST = .0293 \$/KG HEXOSE 16.42 %
 CELLULOSE-RECYCLE COST = .0091 \$/KG HEXOSE 5.08 %
 TOTAL COST = .1786 \$/KG HEXOSE
 CELLULOSE CONVERSION/PASS = .44.06 %
 DEGRAD. PRODUCTS/HEXOSE = .445 KG/KG
 CELLULOSE REACTED TO HEXOSE = .692 KG/KG

PLUG FLOW REACTOR SYSTEM

2 INPUT DATA

CONCENTRATION OF HYDROLYZABLE CELLULOSE	=	115.000 KG EQ. HEXOSE/CU. M
CONCENTRATION OF PURE ACID SOLUTION	=	1.000 WT. PERCENT
DESIRED CONCENTRATION OF HEXOSE SOLUTION	=	135.000 KG/CU. METER
COST OF CELLULOSE	=	.066 \$/KG EQ. HEXOSE
COST OF ACID & EQ. LIME	=	.088 \$/KG
COST OF RECYCLING CELLULOSE	=	.0055 \$/KG EQ. HEXOSE
COST OF REACTOR	=	.400 \$/CU. METER/HR
COST OF CONCENTRATING HEXOSE SOLUTION	=	1.390 \$/CU. METER
* TEMPERATURE	=	453.000 KELVINS
FRACTION OF CELLULOSE RECYCLED	=	.900

RESULTS

A = .85243E-01	F = .72581E-02
B = -.54450E-01	G = .17234E+00
C = .34783E-02	H = .68904E-02
D = .10296E-01	P = -.57571E-02
E = .18136E+00	R = -.50669E-01

RK1 = .20867E+01 1/HR
 RK2 = .19810E+01 1/HR

OPTIMAL SOLUTION :

RESIDENCE TIME	=	.32538E+00 HRS = .19523E+02 MIN
CELLULOSE CONCENTRATION	=	50.321 KG EQUIV. HEXOSE/CUBIC METER
HEXOSE CONCENTRATION	=	40.287 KG/CUBIC METER
COST OF CELLULOSE CONSUMED	=	.1024 \$/KG HEXOSE 65.05 %
COST OF ACID & EQ. LIME	=	.0204 \$/KG HEXOSE 12.97 %
REACTOR COST	=	.0032 \$/KG HEXOSE 2.05 %
HEXOSE-CONCENTRATION COST	=	.0242 \$/KG HEXOSE 15.37 %
CELLULOSE-RECYCLE COST	=	.0072 \$/KG HEXOSE 4.55 %
TOTAL COST	=	.1574 \$/KG HEXOSE
CELLULOSE CONVERSION/PASS	=	49.29 %
DEGRAD. PRODUCTS/HEXOSE	=	.407 KG/KG
CELLULOSE REACTED TO HEXOSE	=	.711 KG/KG

PLUG FLOW REACTOR SYSTEM

3 INPUT DATA

CONCENTRATION OF HYDROLYZABLE CELLULOSE = 115,000 KG EQ. HEXOSE/CU. M
 CONCENTRATION OF PURE ACID SOLUTION = 1,000 WT. PERCENT
 DESIRED CONCENTRATION OF HEXOSE SOLUTION = 135,000 KG/CU. METER
 COST OF CELLULOSE = .066 \$/KG EQ. HEXOSE
 COST OF ACID & EQ. LIME = .088 \$/KG
 COST OF RECYCLING CELLULOSE = .0055 \$/KG EQ. HEXOSE
 COST OF REACTOR = .400 \$/CU. METER/HR
 COST OF CONCENTRATING HEXOSE SOLUTION = 1.390 \$/CU. METER
 * TEMPERATURE = 463,000 KELVINS
 FRACTION OF CELLULOSE RECYCLED = .900

RESULTS

A = .85243E-01 F = .20316E-01
 B = -.54450E-01 G = .37505E+00
 C = .34783E-02 H = .15162E-01
 D = .10296E-01 P = -.80689E-01
 E = .50137E+00 R = -.25371E+00

RK1 = .58409E+01 1/HR
 RK2 = .43590E+01 1/HR

OPTIMAL SOLUTION :

RESIDENCE TIME = .13232E+00 HRS = .79390E+01 MIN
 CELLULOSE CONCENTRATION = 53,095 KG EQUIV. HEXOSE/CUBIC METER
 HEXOSE CONCENTRATION = 45,334 KG/CUBIC METER
 COST OF CELLULOSE CONSUMED = .0979 \$/KG HEXOSE 68.27 %
 COST OF ACID & EQ. LIME = .0182 \$/KG HEXOSE 12.66 %
 REACTOR COST = .0012 \$/KG HEXOSE .91 %
 HEXOSE-CONCENTRATION COST = .0204 \$/KG HEXOSE 14.21 %
 CELLULOSE-RECYCLE COST = .0058 \$/KG HEXOSE 4.04 %
 TOTAL COST = .1433 \$/KG HEXOSE
 CELLULOSE CONVERSION/PASS = 53.83 %
 DEGRAD. PRODUCTS/HEXOSE = .344 KG/KG
 CELLULOSE REACTED TO HEXOSE = .732 KG/KG

PLUG FLOW REACTOR SYSTEM

4 INPUT DATA

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CONCENTRATION OF HYDROLYZABLE CELLULOSE = 115.000 KG EQ. HEXOSE/CU. M
CONCENTRATION OF PURE ACID SOLUTION      = 1.000 WT. PERCENT
DESIRED CONCENTRATION OF HEXOSE SOLUTION = 135.000 KG/CU. METER
COST OF CELLULOSE                        = .066 $/KG EQ. HEXOSE
COST OF ACID & EQ. LIME                  = .088 $/KG
COST OF RECYCLING CELLULOSE              = .0055 $/KG EQ. HEXOSE
COST OF REACTOR                          = .400 $/CU. METER/HR
COST OF CONCENTRATING HEXOSE SOLUTION    = 1.390 $/CU. METER
* TEMPERATURE                           = 473.000 KELVINS
FRACTION OF CELLULOSE RECYCLED           = .900
  
```

RESULTS

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A = .85243E-01    F = .54444E-01
B = -.54450E-01   G = .79427E+00
C = .34783E-02    H = .32267E-01
D = .10296E-01    P = -.34716E+00
E = .13378E+01    R = -.40733E+00
  
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RK1 = .15653E+02 1/HR
RK2 = .92769E+01 1/HR
  
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OPTIMAL SOLUTION :

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RESIDENCE TIME = .55367E-01 HRS = .33220E+01 MIN

CELLULOSE CONCENTRATION = 48.341 KG EQUIV. HEXOSE/CUBIC METER
HEXOSE CONCENTRATION    = 50.242 KG/CUBIC METER

COST OF CELLULOSE CONSUMED = .0939 $/KG HEXOSE 70.68 %
COST OF ACID & EQ. LIME   = .0164 $/KG HEXOSE 12.33 %
REACTOR COST              = .0004 $/KG HEXOSE .33 %
HEXOSE-CONCENTRATION COST = .0174 $/KG HEXOSE 13.07 %
CELLULOSE-RECYCLE COST    = .0048 $/KG HEXOSE 3.58 %

TOTAL COST = .1329 $/KG HEXOSE

CELLULOSE CONVERSION/PASS = 57.96 %
DEGRAD. PRODUCTS/HEXOSE   = .327 KG/KG
CELLULOSE REACTED TO HEXOSE = .754 KG/KG
  
```


PLUG FLOW REACTOR SYSTEM

5 INPUT DATA

CONCENTRATION OF HYDROLYZABLE CELLULOSE = 115.000 KG EQ. HEXOSE/CU. M
 CONCENTRATION OF PURE ACID SOLUTION = 1.000 WT. PERCENT
 DESIRED CONCENTRATION OF HEXOSE SOLUTION = 135.000 KG/CU. METER
 COST OF CELLULOSE = .036 \$/KG EQ. HEXOSE
 COST OF ACID & EQ. LIME = .088 \$/KG
 COST OF RECYCLING CELLULOSE = .0055 \$/KG EQ. HEXOSE
 COST OF REACTOR = .400 \$/CU. METER/HR
 COST OF CONCENTRATING HEXOSE SOLUTION = 1.390 \$/CU. METER
 * TEMPERATURE = 483.000 KELVINS
 FRACTION OF CELLULOSE RECYCLED = .900

RESULTS

A = .85243E-01 F = .14007E+00
 B = -.54450E-01 G = .16346E+01
 C = .34783E-02 H = .66558E-01
 D = .10296E-01 P = -.11507E+01
 E = .34362E+01 R = -.52481E+00

RK1 = .40269E+02 1/HR
 RK2 = .19136E+02 1/HR

OPTIMAL SOLUTION :

RESIDENCE TIME = .23892E-01 HRS = .14335E+01 MIN
 CELLULOSE CONCENTRATION = 43.940 KG EQUIV. HEXOSE/CUBIC METER
 HEXOSE CONCENTRATION = 54.996 KG/CUBIC METER
 COST OF CELLULOSE CONSUMED = .0906 \$/KG HEXOSE 72.66 %
 COST OF ACID & EQ. LIME = .0150 \$/KG HEXOSE 12.01 %
 REACTOR COST = .0002 \$/KG HEXOSE .14 %
 HEXOSE-CONCENTRATION COST = .0150 \$/KG HEXOSE 12.02 %
 CELLULOSE-RECYCLE COST = .0040 \$/KG HEXOSE 3.17 %
 TOTAL COST = .1246 \$/KG HEXOSE
 CELLULOSE CONVERSION/PASS = 61.79 %
 DEGRAD. PRODUCTS/HEXOSE = .292 KG/KG
 CELLULOSE REACTED TO HEXOSE = .774 KG/KG

PLUG FLOW REACTOR SYSTEM

6 INPUT DATA

CONCENTRATION OF HYDROLYZABLE CELLULOSE = 115.000 KG EQ. HEXOSE/CU. METER
 CONCENTRATION OF PURE ACID SOLUTION = 1.000 WT. PERCENT
 DESIRED CONCENTRATION OF HEXOSE SOLUTION = 135.000 KG/CU. METER
 COST OF CELLULOSE = .066 \$/KG EQ. HEXOSE
 COST OF ACID & EQ. LIME = .088 \$/KG
 COST OF RECYCLING CELLULOSE = .0035 \$/KG EQ. HEXOSE
 COST OF REACTOR = .400 \$/CU. METER/HR
 COST OF CONCENTRATING HEXOSE SOLUTION = 1.390 \$/CU. METER
 * TEMPERATURE = 493.000 KELVINS
 FRACTION OF CELLULOSE RECYCLED = .900

RESULTS

A = .85243E-01 F = .34680E+00
 B = -.54450E-01 G = .32707E+01
 C = .34783E-02 H = .13332E+00
 D = .10296E-01 P = -.33419E+01
 E = .85025E+01 R = -.61558E+00

RK1 = .99704E+02 1/HR
 RK2 = .38328E+02 1/HR

OPTIMAL SOLUTION :

RESIDENCE TIME = .10629E-01 HRS = .63772E+00 MIN

CELLULOSE CONCENTRATION = 39.854 KG EQUIV. HEXOSE/CUBIC METER
 HEXOSE CONCENTRATION = 59.564 KG/CUBIC METER

COST OF CELLULOSE CONSUMED = .0877 \$/KG HEXOSE 74.36 %
 COST OF ACID & EQ. LIME = .0139 \$/KG HEXOSE 11.72 %
 REACTOR COST = .0001 \$/KG HEXOSE .06 %
 HEXOSE-CONCENTRATION COST = .0130 \$/KG HEXOSE 11.06 %
 CELLULOSE-RECYCLE COST = .0033 \$/KG HEXOSE 2.81 %

TOTAL COST = .1179 \$/KG HEXOSE

CELLULOSE CONVERSION/PASS = 65.34 %
 DEGRAD. PRODUCTS/HEXOSE = .262 KG/KG
 CELLULOSE REACTED TO HEXOSE = .793 KG/KG

APPENDIX E

GAS CHROMATOGRAPHIC ANALYSIS OF
SUGAR FRACTION FROM STEAM-EXPLODED POPLAR

APPENDIX E

Gas Chromatographic Procedure for Sugar Analysis:

Reagent TRI-SIL Z Trimethylsilylimidazole in dry pyridine (1.5 mg/ml)

References:

1. G.D. Brittain and L. Schewe, "Recent Advances in Gas Chromatography", edited by I.I. Domskey and J.A. Perry, Marcel Dekker, Inc., New York, N.Y., p. 223-629 (1971).
2. K.M. Brobst and C.E. Lott, Jr., "Cereal Chemistry", 43, 35-43 (1966).

Procedure:

- 1) Accurately weigh 10-15 mgs (dry basis) of sugar mixture into a 3-5 ml screw cap septum vial.
- 2) Add 1.0 ml of pyridine and heat for 30 min. at 70-75°C.
- 3) Cool to room temperature and add 1.0 ml trimethylsilylimidazole. Cap and shake for 30 seconds. Allow to stand at room temperature for 30 minutes.
- 4) Analyze aliquot using μ l syringe on a 6' x 8" O.D. column packed with 2% OV-17 and 1% OV-210 on Chromasorb W 80/100 mesh. Program immediately from 140-325°C at 10°C/min. after, sample injection using carrier gas at 40 ml/min. and FID detector.

Gas Chromatogram of Sugar Analysis

METHODS OF SILYLATION

REAGENTS REQUIRED:

"MSTFA" (N-Methyl-N-TMS-Trifluoroacetamide) (See page 161.)

Solvents, optional, use Silylation Grade.

Follow instructions for Method 6, substituting MSTFA for BSA.

METHOD 3:

TRI-SIL 'Z' is a prepared reagent with unique qualities. It will silylate in the presence of moderate amounts of water. It silylates sugars very rapidly and smoothly and with less anomerization than has been observed with any other method. It silylates hydroxy and carboxyl groups only and does not react with amines. It was developed primarily for use with syrups but has been found to be useful for all classes of hydroxyl compounds. It is formulated from "TSIM", N-TMS-imidazole in dry pyridine. For sugar solutions containing ~1% or less total sugars, use a 50/50 v/v TSIM/pyridine solution as the reagent. Evaporate 50 μ l sugar solution to a glassy syrup in a 0.3 ml Reacti-Vial. Add ~50 μ l of the reagent, heat at ~60°C to dissolve the sugars. Analyze directly on GC (3% OV-1 or OV-17). This will give full scale peaks at ~ mid-range sensitivity settings on FID's. See also Methca 21 for sugar syrup analysis.

REAGENTS REQUIRED:

TRI-SIL 'Z' (See page 165.)

Introduce 10-15 mg of sample and 1 ml TRI-SIL 'Z' into a screw cap septum vial. Shake occasionally until dissolved—may be heated to 60-70°C if necessary. Sugars are usually completely silylated when dissolved. Inject reacted mixture directly into the gas chromatograph.

METHOD 9:

This method is basically the same as Method 8 except the reagent and solvent are mixed before use and the solvent is one of choice. TSIM may be used straight with carbohydrates or as a 50% solution with pyridine for wet sugars to keep reaction volumes small. It is a preferred reagent for steroids. See Method 16. It is also excellent for C₁ through C₅ fatty acids in serum and urine.^{6,6}

METHOD 10:

The method of Brobst and Lott [*Cereal Chemistry* 43, 35-43 (1966)]. This method was developed primarily for silylating syrups and concentrated aqueous solutions of sugars such as starch hydrolysates. The method works well when the procedure is closely followed. Use caution since considerable heat and ammonia gas pressure are evolved. The reagents cannot be pre-mixed. (See next page.)

SAMPLE
CURVE
OF SOME
SILYLATED
SUGARS