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DESIGN, FABRICATION AND OPERATION OF A BIOMASS FERMENTATION FACILITY

FIRST QUARTERLY REPORT

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ABSTRACT

The objective of this project is to design, fabricate, and operate a fermentation facility which will demonstrate on a pilot-scale level (3 oven-dry tons per day of feedstock) the economic and technical feasibility of producing anhydrous ethyl alcohol from lignocellulosic biomass residues (wood, corn stover, and wheat straw principally).

The resultant process development unit (PDU) will be flexibly designed so as to evaluate current and projected unit operations, materials of construction, chemical and enzymatic systems which offer the potential of significant technological and economic breakthroughs in alcohol production from biomass. The principal focus of the project is to generate fuels from biomass. As such, in addition to alcohol which can be used as a transportation fuel, by-products are to be directed where possible to fuel applications.

The project consists of two parts: (1) Conceptual Design, and (2) Detailed Engineering Design.

The first quarter's activities have focused on a critical review of several aspects of the conceptual design of the 3ODT/day PDU, viz.,

(1) Biomass Cost, Availability, and Characterization
(2) Pretreatment Processes for Lignocellulosic Residues
(3) Hydrolytic Processes (Enzymatic and Acidic)
(4) Fermentation Processes
(5) Alcohol Recovery Systems
(6) By-Product Streams Utilization
(7) Process Economics

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1.0. INTRODUCTION

The object of this project is to design, fabricate, and operate fermentation facility which will demonstrate on a pilot scale the feasibility of producing alcohol from lignocellulosic biomass. The facility will also be used to provide processing and economic data which can be used to predict the costs of producing alcohol from various cellulosic raw materials and to provide data to base the design of large scale alcohol plants. This facility will also offer the opportunity to test and evaluate different processing concepts on a pilot plant scale. The facility as envisioned is divided into the following processes; pretreatment , hydrolysis, fermentation , alcohol recovery, monitoring and evaluation of by-products produced.

The first phase of this project is to develop the conceptual design of the PDU facility followed by a detailed engineering design. In order to develop the basis for the conceptual design a review of the proposed feedstocks to determine costs and availability has been made. A review of chemical constituents of the feedstock has also been made. The various pretreatment methods, hydrolysis (acid and enzymatic), fermentation, alcohol separation and by-product utilization processes which would be included in the PDU have been reviewed. In addition to the review of the technical aspects of the various processes,review of the economics of selected processes have been made.

2.0. BIOMASS FEEDSTOCK

2.1. Cost and Availability of Biomass

The primary feed stock projected for utilization by the PDU are: wood (hardwoods and softwoods), wheat straw and corn stover. Other potential materials such as, rice straw, oat straw, rye straw, sugar cane bagasse, sorghum residue, and other agricultural waste, are also being investigated to determine what potential they might have as a feedstock. The work done during this quarter has been primarily directed toward the wood, wheat straw and corn stover. The survey of wood resources has been completed for both the PDU and potential large scale facility. The survey of the cost and availability of wheat straw and corn stover for the PDU is also complete. Some additional information relevant to large scale use of these feed stocks remain to be done.

Large producers of chips, sawdust, shavings and bark were surveyed in three different areas. The first area was within a 10 mile radius of Georgia Tech, the second within a 30 mile radius, and the third marginally within 40 miles.

Green chips are the hardest resource to acquire because the Georgia Kraft pulp and paper mill in Rome seems to buy all chips available within at least 100 miles of the mill. Southwire Wood Products in Carrollton and Black Sawmill in Dallas seemed to be companies most open to supplying 6-7 tons of green chips per day to Georgia Tech. Almost all of the companies contacted sold chips to Georgia Kraft exclusively. However, if Georgia Tech made a firm offer for the relatively small supply of chips needed (6-7 tons/day) they may cooperate. Southwire sells only hardwood chips while Black sells hardwood and softwood. Georgia Tech has dealt with Black in the past and has had some delivery problems. The cost of chips delivered to Tech would likely run $33-$35/cord which is $13.20-$14.00/ton for most companies. The cost of the chipped wood without transportation cost is roughly $20.00/cord to $25/cord which is $7.50-$10.00/ton. However, Harry Van Lock of Buckeye Cellulose in Oglethorpe, Georgia says the cost is $15/ton which is $37.50 per cord. That seems very high in light of all the other information collected. Transportation costs seem to run 5-6¢/ton-mile though there were some deviations from this average higher than this (14-16¢/ton-mile).

The amount of chips supplies by the companies that would give this information ranged from a low of 20 tons/day to a high of 85 tons/day. Therefore the amount of chips that would have to be diverted from Georgia Kraft to Georgia Tech (6-7 tons/day) would be 8%-35% of total daily volume of any one of the individual plants surveyed.

Sawdust is available to Georgia Tech from 4 or 5 various companies. McClure Brothers of College Park, the closest source to Tech, could guarantee 6-7 tons per day delivery to Tech at a cost of $45 per delivered load ($6.00-$6.43/ton). Of that $45, $35 is for the sawdust ($4-$5/ton) and $10 is for delivery (10-14¢/ton-mile). The cost of the sawdust at $4.00/ton before delivery checks out with another source, Hardwoods of Georgia. Separated softwood and hardwood sawdust can be provided by Black sawmill as well as McClure Brothers for $45/load (weight of the load is unknown). Good cost data was difficult to compile because most companies could only quote a price per load, of which they knew neither the weight nor the volume.

Shavings could also be delivered by McClure Brothers at the same price as sawdust but hardwood and softwood could not be separated. Harrison Lumber Company could deliver a truckload of softwood shavings 25-30 miles for $80/load (18 ft. truck bed). Joe K. Smith Trucking Company in Gainesville could possibly deliver a load at $95/load (25 yd^3) which (assuming a density range of 14-24 lb/ft^3) is $20-$11.73/ton and seems expensive.

McClure Brothers is willing to sell bark at the same price as sawdust and they can separate softwood from hardwood. Hardwoods of Georgia in Coweta Co. will sell hardwood bark at $4/ton (they <u>don't</u> deliver) which is similar to McClure Brothers delivery price. They have 75 tons/day of bark produced which they at present don't sell but would like to dispose of. Joe K. Smith Trucking of Gainesville will sell bark at $11.25/yd^3 which (assuming a density range of 14-24 16/ft^3) comes out to $60-$35/ton, extremely high. Southwire Wood Products is willing to sell hardwood bark though they don't at present. However, Georgia Kraft is soon going to start buying sawdust and bark from them which may forbode a trend of Georgia Kraft consuming all reasonably available sawdust, shavings and bark just as they presently do with chips.

In summary McClure Brothers may be the best bet for bark, sawdust, and possibly shavings, Hardwood shavings may be hard to acquire from any source. Chips could probably be obtained from Black Sawmill and Southwire Wood Products (hardwood only) but if the right kind of approach is taken other companies such as McClure Brothers may also sell to

Georgia Tech some of what they normally sell to Georgia Kraft. Both hardwood and softwood chips are available from Griffin Lumber Company in Cordele, but a premium price must be paid to obtain them ($40-$45/ton delivered; $17.78-20/ton for the wood and 13.9 - 15.6¢/ton-mile for transportation). Georgia Tech has used a Griffin Lumber Company in the past as a supplier.

All the information compiled on the eleven companies researched is contained on the following tables.

A 1000 oven dry ton (ODT) per day plant operating 350 days per year would require 700,000 tons of green wood (50% moisture content) per year to operate. This plant would require 233,333 acres of softwood to provide a constant supply in perpetuity. This is based on the assumption that a three ton/year/acre sustained yield can be obtained. The same size would require double the acreage, 466,667 acres, if supplied with hardwood, because the sustained yield of hardwood is only 1.5 tons per acre. In an idealized situation, the 1000 ODT per day plant would require all the softwood within a 10.8 mile radius or all the hardwood within a 15.2 mile radius, assuming there is nothing but commercial forest surrounding the plant. In actuality, it would be very unlikely that a plant could be located in the center of that much forest land. There always will be competing uses for nearby wood and not all available timber would be for sale or dedicated to a single purpose.

Assuming green woodchips as feed to the plant and a price ceiling of $2.00 per million BTU for delivered chips, a plant could acquire chips from as far as 100 miles away at today's prices and still be economically feasible. This is assuming as average pre-transportation price of $10.00

Table 2.1.

RESOURCE COST AND AVAILABILITY FOR PDU

CHIPS

	10 Miles of Ga. Tech.	30 Miles of Ga. Tech.	Marginally Within 30 Mi. of Georgia Tech. (30-40 Mi. Roughly)								Other Sources	
	McClure Bros. Lumber Co. Fulton Co. College Park	Sims Bros. Lumber Co. Gwinnett Co. Swannee	Hardwoods of Ga. Coweta Co. Raymond	Harris Lumber Co. Cherokee Co. Ball Ground	J. P. Haynes Lumber Co. Cherokee Co. Canton	Southwire Wood Products Carroll Co. Carrollton	Black Sawmill Paulding Co. Dallas	Williams Bros. Lbr. Co. Newton Co. Covington	Joe K. Smith Trucking Co. Hall Co. Gainesville	Harrison Lbr. Co. Walton Co. Monroe	Griffin Lumber Co. Crisp Co. Cordelle	Information from Harry Vanlock Buckeye Cellulose
1) Do you sell?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
2) To whom?	Ga. Kraft Exclusively	Ga. Kraft Exclusively	Under contract. Would not identify	Ga. Kraft Exclusively	Ga. Kraft Exclusively	Ga. Kraft	Ga. Kraft	Jack Smith Trucking Co.	To pulp mill in Macon exclusively		Anyone	
3) How much do you have available?		48-50 tons/day green			About 20 cords/day					20-25 tons/day		
4) How much do you sell?		48-50 tons/day	1 train car/day (about 84 tons/day)		About 20 cords/day (2 trailers)	1 train car/day (about 85 tons/day)						
5) Would you sell 6-7 green tons/day to Ga.Tech.?	Doubtful	Doubtful	Doubtful	Doubtful	Doubtful	Yes	Yes	No	Doubtful	Perhaps	Perhaps if arrange for transportation**	
6) Is the wood softwood, hardwood, or both?	Probably Both		Most likely hardwood			Hardwood only	Both			Softwood	Both	
7) Can hardwood and softwood be separated?							Yes				Yes	
8) What would be a) delivered cost to Ga. Tech.?		$33.75/cord to Rome ($13.50/ton) $26.25/cord to G.T. ($10.50/ton)		$33.60/cord	$33/cord	50 mi.del. $28.60/cord $11.44/ton by truck and $22/cord ($8.80/ton) by train	40 mi.del. $7.50-$10.00/ton			$35/cord $14/ton for 80 miles	$900/load $40-45/ton	
b) Wood cost?		$21.25/cord ($8.50/ton)		Unknown	Unknown		Unknown			$25/cord $10/ton	$17.78-$20/ton	$15/ton
c) Transportation cost		5¢/ton mile		Unknown	Unknown		Estimated 2-8¢/ton mi.			5¢ ton-mile	13.9-15.6/ton-mile	5-6¢/ton-mile

Table 2.1. (cont'd.)

RESOURCE COST AND AVAILABILITY FOR PDU

SAWDUST

	10 Miles of Ga. Tech.	30 Miles of Ga. Tech.	Marginally Within 30 Mi. of Georgia Tech. (30-40 Mi. Roughly)								Other Sources	
	McClure Bros. Lumber Co. Fulton Co. College Park	Sims Bros. Lumber Co. Gwinnett Co. Swannee	Hardwoods of Ga. Coweta Co. Raymond	Harris Lumber Co. Cherokee Co. Ball Ground	J. P. Haynes Lumber Co. Cherokee Co. Canton	Southwire Wood Products Carroll Co. Carrollton	Black Sawmill Paulding Co. Dallas	Williams Bros.Lbr.Co. Newton Co. Covington	Joe K. Smith Trucking Co. Hall Co. Gainesville	Harrison Lbr. Co. Walton Co. Monroe	Griffin Lumber Co. Crisp Co. Cordelle	Information from Harry Vanlock Buckeye Cellulose
1) Do you sell?	Yes	No	Yes (but don't deliver	Yes	No (use for fuel	Will sell (but don't at present	Yes	Yes		Yes		
2) To whom?	Anyone		Anyone	Locally		Anyone, Ga. Kraft soon to start buying	Anyone	Joe K. Smith Trucking Co. Exclusively				
3) How much do you have available?							80,000/ lb./day					
4) How much do you sell?	5-6 loads/day (35-40 tons) of sawdust, shavings, bark											
5) Would you sell 6-7 green tons/ day to Ga.Tech.?	Yes			Not likely				No	Maybe			
6) Is the wood softwood, hardwood, or both?	Both						Both			Softwood		
7) Can hardwood and softwood be separated?	Yes						Yes					
8) What would be a) delivered cost to Ga. Tech.?	$45/load $6-6.43/ton			$8/load			$45/truck load		$85/load (25 cu.yd./ load	$75/load (25-30 mi. 18 ft. truck load		
b) Wood cost?	$35/load $4-5/ton		$4/ton									
c) Transportation cos	$10/load 10-14¢											

Table 2.1. (cont'd.)

RESOURCE COST AND AVAILABILITY FOR PCU

SHAVINGS

	10 Miles of Ga. Tech.	30 Miles of Ga. Tech.	Marginally Within 30 Mi. of Georgia Tech. (30-40 Mi. Roughly)								Other Sources	
	McClure Bros. Lumber Co. Fulton Co. College Park	Sims Bros. Lumber Co. Gwinnett Co. Swannee	Hardwoods of Ga. Coweta Co. Raymond	Harris Lumber Co. Cherokee Co. Ball Ground	J. P. Haynes Lumber Co. Cherokee Co. Canton	Southwire Wood Products Carroll Co. Carrollton	Black Sawmill Paulding Co. Dallas	Williams Bros.Lbr.Co. Newton Co. Covington	Joe K. Smith Trucking Co. Hall Co. Gainesville	Harrison Lbr. Co. Walton Co. Monroe	Griffin Lumber Co. Crisp Co. Cordelle	Information from Harry Vanlock Buckeye Cellulose
1) Do you sell?	Yes	Yes	No	Yes	No	No			Yes			
2) To whom?	Anyone	Ga. Kraft Exclusively		Locally					Anyone			
3) How much do you have available?												
4) How much do you sell?	5-6 loads/day (35-40 tons) of shavings, bark, sawdust											
5) Would you sell 6-7 green tons/day to Ga.Tech.?	Yes	Doubtful							Maybe			
6) Is the wood softwood, hardwood, or both?	Both									Softwood		
7) Can hardwood and softwood be separated?	No									Yes		
8) What would be a) delivered cost to Ga. Tech.?	$45/load $6-6.43/ton			$8 load				$95/load (25 yds./load)	$80/load (within 25-30 miles) 18' truck bed			
b) Wood cost?	$35/load $4-5/ton											
c) Transportation cost	$10/load 10-14¢/ton mile											

Table 2.1. (cont'd.)

RESOURCE COST AND AVAILABILITY FOR PDU

BARK

	10 Miles of Ga. Tech.	30 Miles of Ga. Tech.	Marginally Within 30 Mi. of Georgia Tech. (30-40 Mi. Roughly)								Other Sources	
	McClure Bros. Lumber Co. Fulton Co. College Park	Sims Bros. Lumber Co. Gwinnett Co. Swannee	Hardwoods of Ga. Coweta Co. Raymond	Harris Lumber Co. Cherokee Co. Ball Ground	J. P. Haynes Lumber Co. Cherokee Co. Canton	Southwire Wood Products Carroll Co. Carrollton	Black Sawmill Paulding Co. Dallas	Williams Bros.Lbr.Co. Newton Co. Covington	Joe K. Smith Trucking Co. Hall Co. Gainesville	Harrison Lbr. Co. Walton Co. Monroe	Griffin Lumber Co. Crisp Co. Cordelle	Information from Harry Vanlock Buckeye Cellulose
1) Do you sell?	Yes	No	Yes	Yes	No	Willing to sell but don't at present			Yes	Yes		
2) To whom?	Anyone			Locally		Anyone, Ga. Kraft soon to start buying			Anyone			
3) How much do you have available?			75 tons/ day									
4) How much do you sell?	5-6 loads/day (35-54 tons) of bark, sawdust, and shavings		None									
5) Would you sell 6-7 green tons/ day to Ga.Tech.?	Yes		Yes						Maybe			
6) Is the wood soft-wood. hardwood, or both?	Both		Hardwood									
7) Can hardwood and softwood be separated?	Yes		Yes									
8) What would be a) delivered cost to Ga. Tech.?	$45/load $6-6.43/ton			$10-20/load					$11.25¢ per yd.^{3}			
b) Wood cost?	$35/load $4-5/ton		$4/ton									
c) Transportation cost.	$10/load 10-14¢/ton mi.											

per ton for the chips ($25.00 per cord) plus 5¢ per ton mile for transportation. A chart in the attached data sheet displays the number of miles from which chips can be bought and transported to the plant in an economic fashion. Only 1.16% of the land in a 100 mile radius would have to be devoted to supporting the plant's softwood requirements or 2.32% of the land to support it's hardwood requirements.

A number of analyses were undertaken to estimate the resource potential for wood to ethanol plants in Georgia. One method involved calculating the amount of excess growth (excess growth in a commercial forest refers to growth above that which is removed or dead) in Georgia. Assuming all excess growth would be used to supply wood to ethanol plants there is enough at present to support 28,138 ODT per day of capacity, 70% of that capacity being supplied as softwood and 30% as hardwood. Various percentages of that total were taken to reflect the amount of excess growth that would be available to the plant. Because the type of wood used in the plant would be similar to that used in a pulp and paper plant, it was simply assumed that the percentage of present removals that is used for pulp and paper plants would be comparable to the percentage of excess growth that could be used as feed for a wood to ethanol plant. This approach, which is admittedly somewhat simplistic, indicated only 10,794 ODT per day of capacity. Recalculation, assuming that this type of plant could use wood suitable for miscellaneous purposes as well as pulpwood quality for feedstock, yielded an estimate of 14,948 ODT per day.

Another approach assumes feedstock composition of industrial wood processing wastes, in-forest wastes resulting from logging operations, rough trees, rotten, trees, and dead trees in some proportion. Two estimates have been generated by Georgia Tech indicating how much wood energy reasonably could be recovered from these sources: the low estimate is 120.6 x 10^{12} BTU and the high is 277.4 x 10^{12} BTU. The high estimate includes 25% of excess growth, which is subtracted to prevent double counting in comparison with the other cited methods, leaving 193.4 x 10^{12} BTU. When these estimates in BTU were converted to tonage it was determined that between 22,669 and 36,353 ODT per day of feedstock could be supplied, of which 26-34% would be supplied as softwood and the remainder as hardwood. When this quantity is added to the excess growth estimate, the maximum potential recoverable resource is between 50,807 and 64,491 ODT per day, of which 50% is supplied by each class of wood.

The actual recoverable amount, however, is likely to be a good deal less than this maximum. Competing demands for this wood resource exist. Some estimates indicate that removals will equal growth by 2001, and, therefore, there will be no excess growth after that time. Also, that part of the resource base that is composed of rough, rotten and dead timber, and wood wastes will have demands placed upon it for use as industrial boiler fuel, fuel for gasifiers, and rural residential uses. A range of capacities has been calculated and is displayed in the attached data sheet, for various assumed percentages reflecting more realistic recoverable amounts of the estimated maximum recoverable resource base. 100% of the lower maximum resource base estimate could supply fifty 1,000 ODT per day plants, twenty-five 2,000 ODT per day plants, or ten 5,000 ODT per day plants. A more practical guess would assume that only 10 to 33%

of the maximum recoverable resource base could be used to support wood to ethanol plants. Accordingly, this amount of wood could support five to sixteen 1,000 ODT per day plants, two to six 2,000 ODT per day plants, or one to two 5,000 per day plants.

A summary of resource requirements, cost, and availability of wood for ethanol production in Georgia is given in Table 2.2.

TABLE 2.2.

Summary of Resource Requirements, Cost, and Availability for Wood to Ethanol Plant in Georgia

I. Resource Requirements for a 1000 ODT/day*Plant

(1) 700,000 tons/year of wood needed to operate the plant

(2) Softwood
  (a) 233,333 acres would be required to continually supply the plant
  (b) 10.8 mile radius around the plant of nothing but softwood forest would contain this acreage

(3) Hardwood
  (a) 466,667 acres would be required to continually supply the plant
  (b) 15.2 mile radius around the plant of nothing but hardwood forest would contain this acreage

II. Economics of Resource Requirements

Assume

- Greenwood chips as input at 3800 BTU/lb
- $2.00/MBTU price ceiling for delivered wood
- 5¢/ton-mile transportation cost
- Current cost of green wood chips prior to transportation is $8-$15/ton with an average of about $10/ton

Chip Cost per ton prior to transportation	No. of miles from which chips can be economically hauled to plant
$ 8	144
$ 9	124
$10	104
$11	84
$12	64
$13	44
$14	24
$15	4

III. The Amount of Plant Capacity that Could be Supplied by the Resource Base in Georgia

(1) Potential based on 100% useage of excess growth
  (a) Softwood = 19,684 ODT/day (70% of total)
  (b) Hardwood = 8,454 ODT/day (30% of total)
  (c) Total = 28,138 ODT/day

*ODT = Oven dry ton

(2) Potential based on a percentage of excess growth equal to the percentage that pulpwood is of total removals

(a) Softwood = 9,198 ODT/day (85% of total)
(b) Hardwood = 1,596 ODT/day (15% of total)
(c) Total = 10,794 ODT/day

(3) Potential based on a percentage of excess growth equal to the percentage that puplwood removals and other removal are of total removal

(a) Softwood = 10,848 ODT/day (73% of total)
(b) Hardwood = 4,100 ODT/day (27% of total)
(c) Total = 14,948 ODT/day

(4) Potential based on the amount of rough, rotten, dead, in-forest waste, and process waste that could possibly be recovered for wood energy

(a) Softwood = 5,894-12,360 ODT/day (26-34% of total)
(b) Hardwood = 16,775-23,993 ODT/day (74-66% of total)
(c) Total = 22,669-36,353 ODT/day

(5) Potential based on 100% useage of excess growth plus recoverable rough, rotten, dead, in-forest waste, and process waste

(a) Softwood = 25,578-32,044 ODT/day (50% of total both cases)
(b) Hardwood = 25,229-32,447 ODT/day (50% of total both cases)
(c) Total = 50,807-64,491 ODT/day

(6) Potential based on a percentage of excess growth equal to the percentage that pulpwood removals is of total removals plus recoverable rough, rotten, dead, in-forest waste, and process waste

(a) Softwood = 15,092-21,558 ODT/day (45%-46% of total)
(b) Hardwood = 18,371-25,589 ODT/day (55%-54% of total)
(c) Total = 33,463-47,147 ODT/day

(7) Potential based on a percentage of excess growth equal to the percentage that pulpwood removals and other removals are of total removals plus recoverable rough, rotten, dead, in-forest, waste, and process waste.

(a) Softwood = 16,742-23,200 ODT/day (45% of total for both)
(b) Hardwood = 20,875-28,093 ODT/day (55% of total for both)
(c) Total = 37,617-51,293 ODT/day

(8) Potential based on 75%, 66%, 50%, 33%, 25%, and 10% of maximum recoverable potential estimated in item 5 (which was 100% of excess growth plus recoverable rough, rotten, dead, in-forest, waste, and process waste)

*ODT/Day Plant Potential Based on Percentage of Maximum Recoverable Amount

	Maximum Recoverable	75%	66%	50%	33%	25%	10%
Softwood							
High range	32,044	24,033	21,022	16,022	10,575	8,011	3,204
Low range	25,578	19,184	16,881	12,789	8,441	6,395	2,558
Hardwood							
High range	32,447	24,335	21,514	16,224	10,708	8,112	3,248
Low range	25,229	18,922	16,651	12,615	8,326	6,307	2,523
Total							
High range	64,491	48,368	42,564	32,246	21,282	16,123	6,449
Low range	50,807	38,105	33,533	25,404	16,766	12,702	5,081

*Softwood and Hardwood each compose approximately 50% of the total in all cases.

(9) Number of 1,000 or 2,000 or 5,000 ODT/Day plants that could be constructed in Georgia assuming various recoverable potentials based on percentages of the maximum recoverable amount (low range) as displayed in item 8.

Number of Plants Feasible to Construct
for Each Size Category
Based on Various Resource Base Estimate

	% of Maximum Recoverable Potential.						
Size of Plants in ODT/Day	100%	75%	66%	50%	33%	25%	10%
1,000	50	38	33	25	16	12	5
2,000	25	19	16	12	8	6	2
5,000	10	7	6	5	3	2	1

Comment: Strictly on an intuitive basis the feasible resource base potential for wood to enhance plants will likely be less than 50% of the maximum estimate because of competing demands for this wood. The demand would be for pulp and paper grade timber and saw timber from that portion of the resource base which is excess growth (approximately 55%). The other 45% of the resource base would have demands placed upon it for wood energy for industrial uses in boilers and gasifiers and rural residential use. A safe guess for practical plant potential is in the 5,000 - 16,000 ODT/Day range which is 10% - 33% of the estimated low range maximum.

Georgia does not have large producers of wheat straw or corn stover; however, apparently enough straw and stover is produced by many relative small farmers to meet the needs of PDU. Many telephone conversations were made to find sources and prices of wheat straw and corn stover and the results of these conversations are summarized below.

Current costs estimates for wheat straw delivered in Atlanta range from $40 to $80 per ton. Sixty dollars per ton appears to be a realistic estimate if the material is purchased when harvested. The cost of wheat straw is affected by weather which affect yields. The price of wheat this season influences the amount planted next season which affect the supply and therefore, the price of straw. The time of purchase affects the price, i.e., if the farmer does not have to store the wheat straw, then the price is cheaper.

Results of survey indicate that wheat straw is the most likely feed stock of this type. At this time sufficient quantities of rye, oat straw or sorghum residue have not been found. Sources indicate that wheat straw can be obtained from relative close counties of Newton, Henry, Fayette, Butts and Jackson.

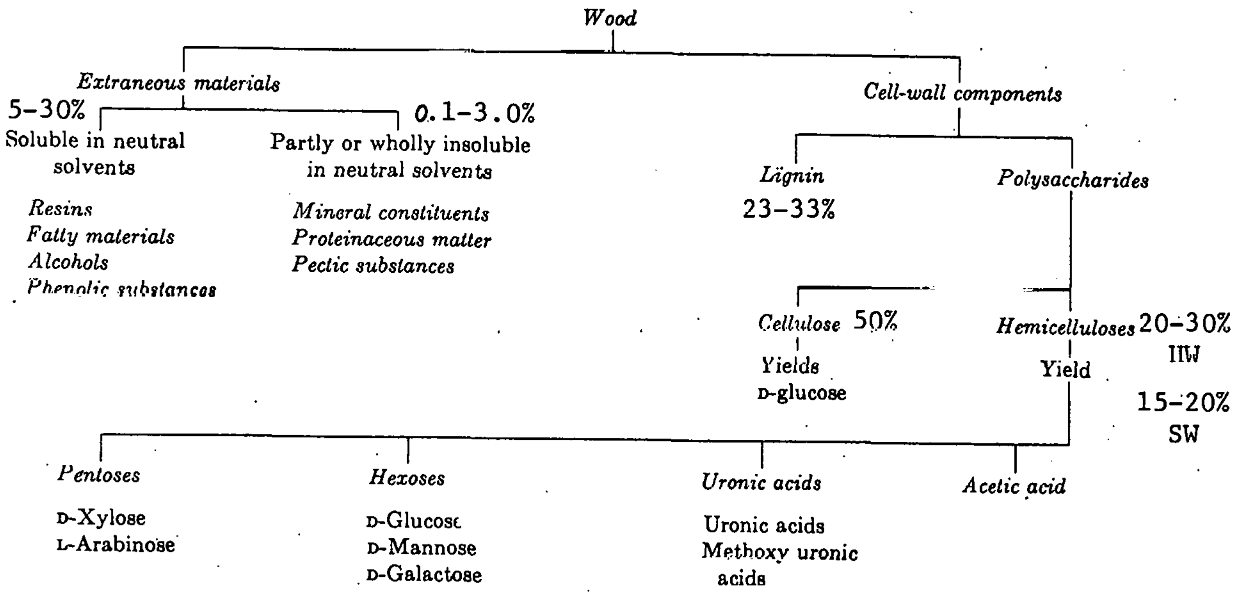
To determine the availability of corn stover (here it is called corn stubble) from the top 10 corn producing counties Laurens County was picked because it is closer to Atlanta and close to the Interstate. Cost of corn stubble estimated to be $45/ton plus delivery. The same factors which affect the price of corn since it is an annual crop. No problem is anticipated in being able to locate adequate supplies of corn stubble for the PDU operation. Appendix A summarizes a Biomass Feedstock Survey.

2.2. Feed-Stock Characteristics

Before investigation of any material, it is necessary to know something of its general nature and composition. The methods which can be devised for separation of components and for analysis must be applied with understanding of the behavior of the components sought and of the effects of other components which may interfere in the desired preparation or analytical procedure.

The woody tissue or xylem (i.e., wood) possesses in general, a characteristic composition. The same major components are present in all woods, although the proportions depend to some degree upon the species. Small variations are found from tree to tree and in different parts of the same tree. The kinds and amounts of certain minor components are determined to a greater extent by the species.

An idealized statement of wood composition is shown in the following outline form:



HW = Hard Wood
SW = Soft Wood

Table 2:3. The composition of wood.

The greater part of wood is made up of polysaccharides. The major component is <u>cellulose</u>. It is a linear polysaccharide built up from anhydroglucose units which are connected with each other by 1 → 4 β - glucosidic linkage and possess an orderly structure. It is distinguished from most of the other polysaccharides in that it yields only D-glucose upon hydrolysis. Cellulose is always accompanied by other polysaccharides, commonly called hemicelluloses. They comprise all non-cellulosic polysaccharides and related substances such as,

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[1] Methods of Wood Chemistry, Vol. 1 by Browning, B.L. Interscience Publishers, A Division of John Wiley & Sons. 1967, p.8.

for example, Uronic acids and their derivatives. These yield upon hydrolysis the hexoses: D-mannose, D-galactose, and D-glucose and the pentoses: D-xylose and L-arabinose. Together, these five sugars are present in the hydrolysates of all woods, and in their polymeric forms are characteristic components of wood. The relative amounts are variable, particularly in the case of D-Mannose, which is significant component in the hemicelluloses of soft woods but a minor one in hard woods. The polysaccharides that yield L-arabinose and D-galactose are associated particularly with the early stages of growth of the cell, and their relative proportions decreases as the cell matures.

Uronic anhydride groups are characteristically components of the hemicelluloses, and comprise anhydroglucuronic (mainly as the monomethyl ether) or anhydrogalacturonic acid.

Lignin is an important component of all woods. It is an aromatic amorphous substance. It is distinguished from the polysaccharides by its resistance to hydrolysis by acids, and by its relatively greater reactivity with oxidizing and other reagents. It contains a basic skeleton of 4 or more substituted phenyl propane units per molecule.

Finally, all woods contain extraneous components which are not considered essential parts of the cell wall. These include extractives which can be removed from wood with neutral solvents, and other extraneous materials such as proteins and pectic substances.

For wood hydrolysis the amount of fermentable sugars are important, whereas for the production of furfural, pentosan contents are important. Methoxyl groups play a role in the pyrolysis for the production of methanol, while the acetyl group determines the yield of acetic acid.

In the characterization of woods we will be faced by names given to the cellulose according to these methods used for its isolation from the other components.

1) <u>Cross and Bevan Cellulose</u>: The isolation is achieved by treatment with strong (17.5%) sodium hydroxide. The cellulose isolated still contains noncellulosic components which are beta and gamma cellulose and are included in the hemicellulose. This cellulose consists of α - cellulose which is the unchanged cellulose and the alkali resistant hemicelluloses (beta and gamma cellulose).

2) Holocellulose: It is unchanged α - cellulose plus hemicellulose and isolated by alternate treatment with acidic sodium chlorite and extraction with potassium hydroxide. If the holocellulose is treated with strong alkali (17.5% sodium hydroxide) solubilization of hemicellulose and low molecular weight celluloses is achieved leaving α - cellulose residue.

The following table lists the chemical composition of North America hard-and-softwoods:

Table 2.4. CHEMICAL COMPOSITION OF TEN SPECIES OF NORTH AMERICAN WOODS

	Wood species	α-Cellulose	α-Cellulose[b]	Lignin	Acetyl	Ash	Uronic anhydride	Galactan	Glucan	Mannan	Araban	Xylan
HARDWOODS	Trembling aspen (*Populus tremuloides*)	56.5	53.3	16.3	3.4	0.2	3.3	0.8	57.3	2.3	0.4	16.0
	Beech (*Fagus grandifolia*)	45.2	42.1	22.1	3.9	0.4	4.8	1.2	47.5	2.1	0.5	17.5
	White birch (*Betula papyrifera*)	44.5	41.0	18.9	4.4	0.2	4.6	0.6	44.7	1.5	0.5	24.6
	Red maple (*Acer rubrum*)	44.8	44.1	24.0	3.8	0.2	3.5	0.6	46.6	3.5	0.5	17.3
SOFTWOODS	Balsam fir (*Abies balsamea*)	47.7	44.8	29.4	1.5	0.2	3.4	1.0	46.8	12.4	0.5	4.8
	Eastern white cedar (*Thuja occidentalis*)	48.9	45.4	30.7	1.1	0.2	4.2	1.5	45.2	8.3	1.3	7.5
	Eastern hemlock (*Tsuga canadensis*)	45.2	42.4	32.5	1.7	0.2	3.3	1.2	45.3	11.2	0.6	4.0
	Jack pine (*Pinus banksiana*)	45.0	41.6	28.6	1.2	0.2	3.9	1.4	45.6	10.8	1.4	7.1
	White spruce (*Picea glauca*)	48.5	44.8	27.1	1.3	0.3	3.6	1.2	46.5	11.6	1.6	6.8
	Tamarack (*Larix laricina*)	47.8	43.9	28.6	1.5	0.2	2.9	2.3	46.1	13.1	1.0	4.3

[a] Percent based on extractive-free wood.

[b] Corrected for nonglucan material.

The hemicelluloses from hard woods contain more xylan (pentosan) than mannan (hexosan) while vice versa, the soft woods have more mannan than xylan.

The analytical data of acid chlorite holocellulose of two different species of soft-and-hardwoods are shown in the following table.

Table 2.5. Analytical Data of Acid Chlorite Holocellulose(3)

%	Softwood		Hardwood	
Composition	Western Hemlock	Southern Pine	Western Red Alden	Gum Wood
Soluble lignin of Holocellulose	4.2	3.9	3.6	4.6
Separated lignin and extractives	4.4	4.1	3.1	4.8
Holocellulose:	60.9	57.9	64.9	66.2
Cellulose	41.7	44.3	45.0	46.5
Hemicellulose residue:				
Galactose	1.3	1.1	0.9	0.9
Mannose	14.4	11.1	0.7	1.9
Arabinose	0.7	0.7	0.1	0.3
Xylose	2.9	6.8	19.2	16.6
4-O-Methyl-D-glucuronic acid	.4	1.	1.9	1.7

The principle component of softwood - hemicelluloses is again D-Mannose while the principle component of hard wood hemicelluloses is D-Xylose.

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[2] Timell, T., Tappi 40(17), 568 (1957).

[3] Ishikawa, H., Schubert, W.J. and Nord, F.F., Biochem. 338, 153 (1963).

Three well defined groups of hemicelluloses are recognized as single or collective components in all lignified plants.

1) The Xylan group present as arabinoxylan, glucuronoxylan or arabinoglucuronoxylan. In hard wood the principle component of the hemicellulose is 4-O-methylglucuronoxylan with a high ratio of D-xylose to 4-O-methylglucuronic acid. Small amounts of mannose, galactose and arabinose are also found. The main part of softwood hemicellulose consists of glucomannan, small amount of 4-O-methylglucuronoaraboxylan which has a lower ratio of D-xylose to 4-O-methyl-D-glucuronic acid than that in hard woods.

2) The mannan group present as glucomannan and galactomannan. Glucomannan from hard wood (birch) has a ratio of mannose to glucose 1:1.1, while those from other hard woods such a Maple, Beech, Poplar and Elm have ratios 1:1.5 to 1:2.4. Galactomannan of eastern hemlock (soft wood) contains glucose, galactose and mannan in the ratio of 1:1:3. A fundamental difference between glucomannans of hard and soft woods is the absence of galactose units in the former.

3) The Arabinogalactan group: It is relatively rare but found in relatively large amounts in hard species. It is a water-soluble polyose and its physical and chemical properties are similar to natural gum. The ratio of arabinose to galactose increases with increasing age of the tree from 1:5.4 for the outer heartwood of larix occidental is to 1:10.2 for the inner heartwood.

Arabinogalactin from larchwood can be used industrially as a gum,

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4. Timell, T., Svensk Papperstidn. 53(15), 472 (1960).

with a low viscosity and high dispersion capacity.

The amounts and distribution of polysaccharides of the major southern pines are listed in the following table which shows the three groups of hemicelluloses and their sugar residues:(5)

Table 2.6. *Cell wall polysaccharides in southern pine wood*

Name	Percent of extractive-free wood (approx.)	Sugar residues	Parts	Degree of polymerization (DP)	Solubility
Cellulose	43±2	β-D glucose	All	9000 ±1000	alkali metal complexes, e.g.,cuprammonium hydroxide
Hemicelluloses					
Galactoglucomannan	15±3	β-D mannose	3		
		β-D glucose	1	>150	[1]
		α-D galactose	0.1 or 1.0		
		O-acetyl	0.25		
Xylans	9±2	β-D xylose	10		
		4-O-methyl D-glucuronic acid	1.5	>150	dilute alkali
		L arabinose	0.75		
Arabinogalactan	small[2]	β-D galactose	11		
		L arabinose	1		water
Pectin	small	galacturonic acid galactose arabinose			hot water

[1] Galactoglucomannans with 0.1 part α-D galactose are soluble in alkali; those with 1.0 part α-D galactose are soluble in water.

[2] Usually removed with extractives.

The chemical composition of southern pine wood is listed in the following table.(6) The hemicellulose residues of these soft wood species have high fraction of mannose. The cellulose residues consists of

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5 Timell, T.E., Wood Hemicelluloses II. Advances in Carbohydrate Chem., 20:409-483 (1965).

6 Adams, G.A. "Wood Carbohydrates - Review of the Present Status of Hemicellulose Chemistry, Pulp & Paper Mag. Can. 65, 513-T24 (1964).

glucose.

Table 2.7. *Chemical composition of southern pine wood*

Components	Percent of ovendry extractive-free wood				
	Loblolly	Longleaf	Slash	Shortleaf	Sand
Total carbohydrate[1]	65–69	67–70	65–71	67–71	~70
Cellulose residues					
glucose	42–46	43–45	43–45	41–45	~43
Hemicellulose residues					
glucose	1–5	1–4	1–5		
mannose	10–11	~11	8–15		
xylose	~7	~7	~7		
arabinose	1–2	0.5–1.0	~1		
galactose	1.5–2.5	1–1.5	~1		
Lignin	27–30	27–30	25–30	27–29	~27
Uronic anhydride	1–3	1–3	2–4		
Acetyl	~1	~1	~1		
Ash	<0.5	<0.5	<0.5	~0.5	

[1] Based on sugar anhydride.

The composition of various woods carbohydrate portion is shown in the following table.(7) The noticeable difference in galactan, mannan and xylan contents in soft and hard woods are clearly apparent.

Table 2.8. COMPOSITION OF THE CARBOHYDRATE PORTION OF VARIOUS WOODS

Wood species	Botanical name	Glucosan (%)	Galactan (%)	Mannan (%)	Araban (%)	Xylan (%)
Spruce	*Picea excelsa*	95.5	6.0	16.0	3.5	9.0
White pine	*Pinus silvestris*	65.0	6.0	12.5	3.5	13.0
Larch	*Larix sibirica*	63.0	17.5	7.5	3.0	9.0
Poplar	*Populus tremula*	64.5	1.5	3.0	1.0	30.0
Birch	*Betula verrucosa*	58.5	1.5	0.5	0.5	39.0
Linden	*Tilia cordata*	58.5	1.5	3.5	2.0	34.5
Maple	*Acer platanoides*	60.5	2.0	4.0	1.0	32.5
Beech	*Fagus silvatica*	65.0	4.0	1.5	1.5	28.0
Oak	*Quercus excelsior*	68.5	2.5	2.0	1.0	26.0
Ash	*Fraxinus excelsior*	60.0	3.0	2.5	2.5	32.0
Willow	*Salix alba*	74.0	3.0	2.5	1.0	26.0
Elm	*Ulmus scabra*	68.5	2.5	2.0	1.0	27.0
Alder	*Alnus incana*	67.0	3.5	1.5	1.0	27.0

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7 The Chemical Technology of Wood, Herman, F.J. Wenzl Academic Press, New York and London, p. 158 (1970).

The average percent composition of soft and hard woods is summarized in the following table. These values are estimated from all the figures given in the tables mentioned before.

Table 2.9. Average Composition of Soft and Hard Woods

(%)	Hard wood	Soft wood
Cellulose	45.8	43.8
Hemicelluloses:		
Galactose	.9	1.4
Mannose	2.4	11.2
Arabinose	.5	1.1
Xylose	18.9	5.8
Uronic Anhydride	4.1	3.6
Acetyl	3.9	1.4
Lignin	20.3	29.5
Ash	.3	.2

Agricultural residues composition

Cellulose and hemicelluloses constitute 45 to 70% of the weight of the dried plant residue and will vary according to the age and maturity of the plant when harvested.

On a dry-basis, the aerial portion of the mature corn plant is 53 percent grain, 10 percent cob, 25 percent stalk, 6 percent leaf, and 6 percent husk. These data are expressed in more detail in the following table:

Table 2.10.

Compositional Analysis of the Corn Plant[8]

	% Dry Matter	% of Residues	Protein	Ash	Hemi-cellulose	Cellulose	Lignin	Fat and oil(esters)	Other soluble(a)
Grain	77	--	10.9	1.7	--	2.4(1)	--	4.7	80.3(b)
Leaf	82	11.7	7.0	13.7	24.8	22.0	5.1	2.4	25.0(c)
Husk	57	13.0	2.8	3.4	36.4	32.9	6.7	0.9	16.9(c)
Cob	56	21.3	2.8	1.4	37.3	34.9	7.4	0.4	15.8(c)
Stalk	34	53.9	3.7	4.7	23.7	34.4	10.5	1.7	21.3(c)

(a) Crude fiber 76.3 percent

(b) Starch

(c) Primarily sucrose

Source: Grain Composition adapted from C.E. Inglett, Corn Culture, Processing Products , AVI Publishing Co. 1970, Chapter 7 other data from R.L. Velter.

Carbohydrate content of corn stalks and wheat straw along with the lignin and protein content are shown in the following diagrams. About 20% of the carbohydrate in plant tissue is composed of sugars other than glucose. These sugars are released upon acid or enzymatic hydrolysis.

These data are compiled from the joint United States - Canadian tables of feed composition, publication 1232, National Academy of Science, National Research Council (1964).

Table 2.11. Composition of Agricultural Residues

	Corn Stalks(8)	Wheat Straw(9)
Total Carbohydrates %	56.8	69.2
Cellulose	29.3	40.0
Glucose	37.7	41.1
Arabinose	1.9	6.2
Xylose	15.5	21.0
Mannose	0.6	0.3
Galactose	1.1	0.6
Lignin	3.1	13.6
Protein	5.5	3.0
Ash	4.9	-

(8) Battelle Columbus Laboratories, Columbus, Ohio Teck 77, Final Report to ERDA Division/Solar Energy "System Study of Fuels from Sugarcane, Sweet Sorghum, Sugar Belts and Corn. March 31, 1977, p. 15 &59.

(9) Enzymatic Conversion of Cellutosic Materials, Technology & Applications, By Elmer L. Gaden, Jr. 1976: An interscience publication, John Wiley & Sons, New York, London, Sydney, Toronto. p.246.

3.0. PRETREATMENT PROCESSES (1,2,3,4,5,6)

Lignocellulosics in general are essentially immune to attack by cellulolytic enzymes. This resistance is apparently due to the close physical and/or chemical association between lignin and cellulose and possibly the crystallinity of the cellulose. In order to utilize the cellulose effectively some method of changing the nature of the cellulose and disrupting the physical association with lignin must be developed at a low cost.

A number of chemical pretreatments have been explored, however, they are not universally applicable with the exception of delignification. Purified wood pulps are an excellent source of dietary energy for ruminant animals and therefore excellent substrate for enzymatic hydrolysis or chemical hydrolysis. However, the cost in the range of $200 to $400 per ton* are much too high.

The mechanical pretreatment of ball-milling is a very good treatment for making the cellulose available for hydrolysis, however, just the power costs makes it too expensive,also. The use of two roll milling shows a good deal of promise and power costs are within the range of possibility.

The process which looks the most promising at this time both from an operating cost and equipment cost standpoint is the "steam explosion" process.** Operating costs are very low, equipment is simple and it has the added advantage of permitting almost total removal of the lignin. Baker showed that based on in vitro digestible that there is an appreciable difference between the response of hard woods and soft woods to delignification. Figure 1 taken from his study shows that with hard woods digestibility increases rapidly with delignification and then approaches plateau at about 90% as delignification approaches completion. Soft woods behave quite differently

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* See Appendix B for detailed "Cost Data".

** Three Processes: (1) Iotech, (2) Stake Technology, (3) GE the digestibility increases gradually with increasing delignification to 20-40% delignification. Following this induction stage the digestibility increases rapidly with further increases in delignification to a maximum digestibility of about 90% at complete delignification. Since the enzymatic hydrolysis of cellulose is essentially the same process as in vitro digestion it is logical to extrapolate this data to an expectation of results with enzymatic hydrolysis. Also, the fact that the cellulose is much more readily available for enzymatic reaction leads to the conclusion that it should be more readily available for chemical hydrolysis. Millett, et al, recalculated data obtained by Scarinin on birch and spruce pulps prepared by 10 different pulping techniques, to fit Baker's format. The results shown in figure 2 shows that it is the amount of delignification, not the delignification process, which controls the digestibility of the cellulose. Based on these observations, the effects of delignification, the steam explosion process takes on additional merit.

Tsao at Purdue has developed a unique process which takes a completely different approach to the processes previously described. The basis for Tsao's process is that if cellulose is dissolved and then precipitated the cellulose structure is separated from the lignin and changed from the crystalline form to more reactive amorphorous structure. Amorphorous cellulose is readily hydrolyzed to fermentable sugars by both acids and enzymes. To produce amorphorous cellulose from biomass Tsao proposes the following process. The biomass is first prehydrolyzed with dilute sulfuric acid to remove the hemicellulose. The remaining residue is washed and dried to a suitable moisture content and then dissolved in concentrated sulfuric acid. Other solvents have been proposed but the present choice is 70-80% sulfuric acid.

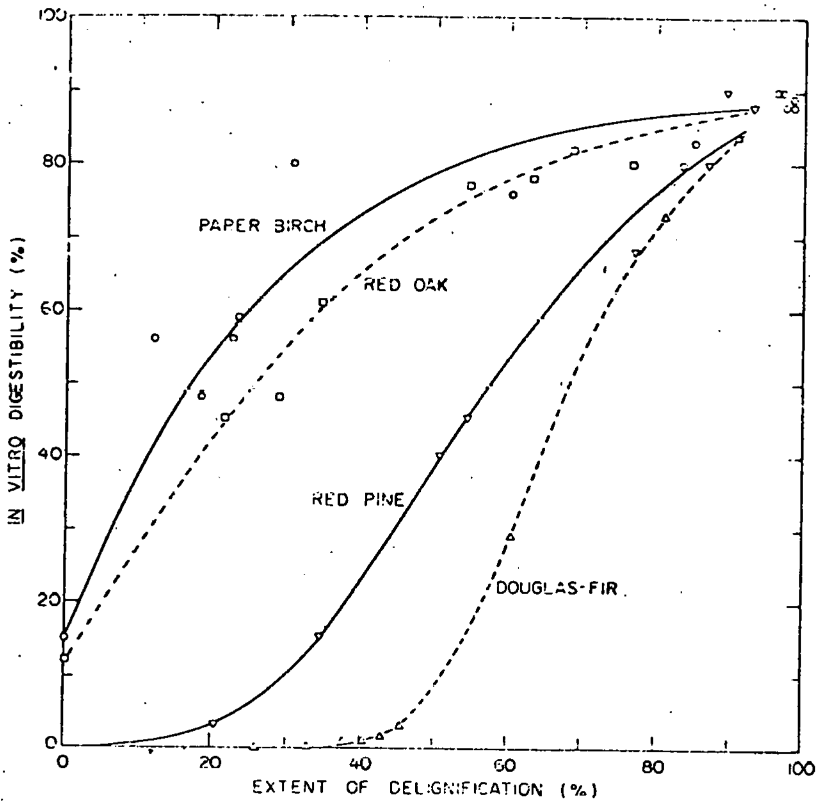

FIGURE 3.1 RELATIONSHIP BETWEEN IN VITRO DIGESTIBILITY AND EXTENT OF DELIGNIFICATION FOR KRAFT PULPS MADE FROM FOUR WOOD SPECIES.

* Baker, A.J., _J. Animal Sci._ _36_ (4) 768 (1973)

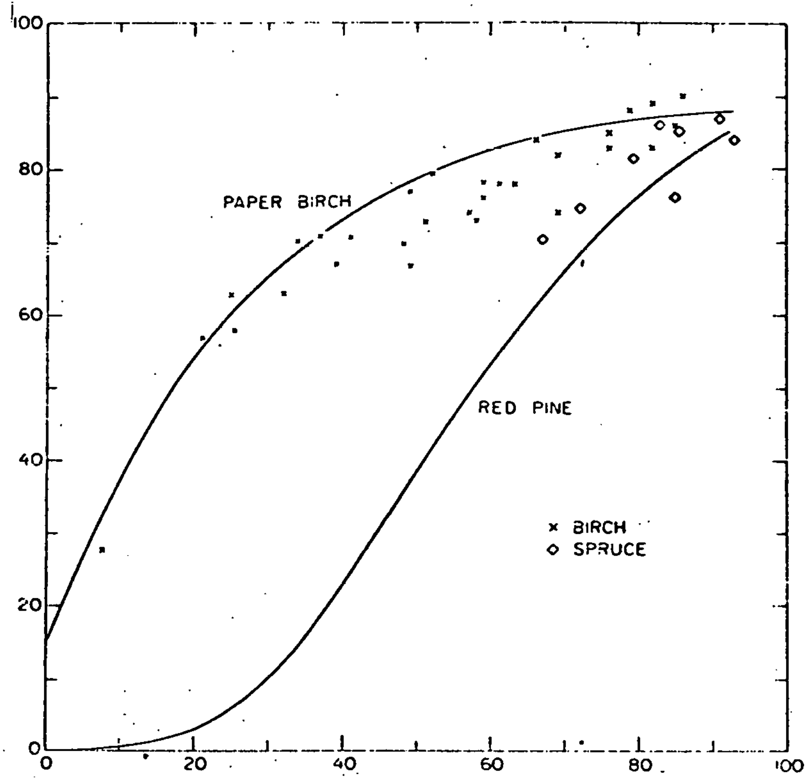

FIGURE 3.2.[**] RELATIONSHIP BETWEEN DIGESTIBILITY AND EXTENT OF DELIGNIFICATION FOR WOOD PULPS. (DATA POINTS FROM SAARINEN ET AL.* CURVES FROM FIG.)

* P. Saarinen, W.J. et al, <u>Acto Agr. Ferm.</u> <u>94</u> (1959)

** Millett, M. et al., <u>Biotechnol.</u> <u>&</u> <u>Bioeng</u>. Symp. No. 5, 205 (1975).

TABLE 3.1

ESTIMATED COST OF SELECTED PRETREATMENTS

Treatment	Power	Cost*
Ball Milling	(1) 1.4 kw-hr	4.9 ¢
2 Roll Milling	(2) .25 kw-hr	.9 ¢
	(4) .66 kw-hr	2.3 ¢
Steam Explosion	.7-1.3 lbs. steam	$.28-$.52

* Basis: 1 pound of wood

electric power cost @ 3.5¢/kw hr

steam costs $4.00/1000 lb.

(1) Nystrom, J., Bitech & Bioeng. Sym. No. 5 221-224 (1975)

(2) Spano, L. et.al., Second Annual Symp. of Fuels-from-Biomass

(3) Private communication with Stacke Tech Corp.

(4) Fuels-from-Biomass Newsletter, April, 1978, p. 4, Power required newspaper.

After dissolution the cellulose is rapidly precipitated by the addition of methanol. The precipitated cellulose along with the lignin is subsequently subjected to enzymatic or acid hydrolysis.

In addition to concentrated sulfuric acid many other "solvents" have been employed by Tsao and earlier investigators. These are summarized in Table 3.2.

There are a number of chemical pretreatments, in addition to pulping (see Appendix B), which have been explored for delignification of wood. A number of organic solvents, the appropriate reaction conditions, and the degree of delignification are presented in Table 3.3.

The various pretreatments which could be employed for lignocellulosics are summarized in Table 3.4.

Table 3.2. Cellulose "Solvents"

Metal Complex Solutions

Cuoxam or Cuam	$\{Cu(NH_3)_4\}\ (OH)_2$
Cupriethylenediamine, Cuene, or CED	$\{Cu(en)_2\}\ (OH)_2$
Cu:Biuret:Alkali	
Cooxene	$\{Co(en)_3\}\ (OH)_2$
Nioxam	$\{Ni(NH_3)_6\}\ (OH)_2$

Neutral Salts in Concentrated Aqueous Solution

$ZnCL_2$

$Ca(SCN)_2$

LiSCN, NaSCN, LiI, NaI, KI

$K_2\ \{HgI_4\}$

Strong Bases in Aqueous Solution

LiOH

NaOH

NaOH + ZnO

NaOH + BeO

Tetraethylammonium-hydroxide and some higher homologs

Trimethylbenzyl-ammoniumhydroxide ("Triton B"), Dimethyldibenzyl-ammoniumhydroxide ("Triton F")

Purdue/Tsao Solvents

"Cadoxen" (Ethylenediamine, Cadmium oxide, H_2O)

CMCS

Ethylene diamine

Sulfuric acid.

Table 3.3. Delignification of Wood Using Organic Solvents

Solvent System	Conditions of Extraction			% Delignification
	Temperature °C	Pressure psi	Duration hours	
Methyl Alcohol-H_2O	158	150	4	58.4
Ethanol - H_2O	165	150	4.5	67.4
n-Propanol - H_2O	172	150	4	76.4
Isopropanol - H_2O	162	150	4	62
n-Butanol - H_2O	174	150	4	87.2
Isobutyl Alcohol - H_2O	174	150	4	80.5
Tertiary Butyl Alcohol - H_2O	157	150	4	56
n-Amyl Alcohol - H_2O	177	150	4	82
IsoAmyl Alcohol - H_2O	177	150	4	84.1
Tertiary Amyl Alcohol - H_2O	159	150	4	60.7
Dioxane - H_2O	176	150	4	65.1
Acetone - NH_3	-	-	-	50
Cyclohexanone - NH_3	210	890	1.25	81.4
Methyl Ethyl Ketone - NH_3	210	860	2	76.08
Xylene Sulfonic Acid	100	15	1	80

Table 3.4. Pretreatments

I. Chemical

Swelling with Alkaline Agents

1) Sodium Hydroxide
2) Ammonia

Delignification

1) Pulping
2) ClO_2
3) Ammonium Bisulfate
4) SO_2
5) Sodium Chlorite
6) Organic Solvents

Cellulose Dissolution

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

II. Physical

1) Steam
    A) Iotech
    B) Stake Technology
    C) GE
    D) Autoclaving
2) Grinding
    A) Ball Milling
    B) Roll Milling
3) Irradiation
    A) Gamma
    B) UV
    C) Heat
4) Freezing
5) Pressure

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1. Tassinari, Thomas and Charles Macey, Differential Speed Two Roll Mill retreatment of Cellulosic Materials for Enzymatic Hydrolysis, Biotechnology and Bioengineering, 19 , 1321 (1977).

2. Nystrom, John, Biotechnology and Bioengineering Symposium No. 5, 221 (1975).

3. Millett, Merrill A. and Baker, Andrew J. Pretreatment to Enhance Chemical, Enzymatic and Microbiological Attack of Cellulosic Materials, Biotechnology and Bioengineering Symposium No. 5, 193 (1975).

4. DeLong, Edward, Iotech Corp. personal communication.

5. Ozechowsky, M.S., Stake Technology Ltd., personal communication.

6. Preliminary Engineering and Cost Analysis of Purdue/TSoo cellulose Hydrolysis (Solvent) Process, Arthur G. McKee & Company, October, 1978. HCP/T4641-01.

4.0. HYDROLYSIS

During this reporting period the various hydrolysis processes which have been developed were subjected to extensive review. The objective of this review is to determine the most promising process or processes for inclusion in the conceptual designs for the PDU designs and subsequently in the detailed engineering design. This work is described in two sections. Subsection 4.1 describes the important acid hydrolysis process and subsection 4.2 describes the work in enzymatic hydrolysis.

4.1. Acid Hydrolysis

Acid hydrolysis of wood is actually a simple chemical reaction. Either sulfuric acid or hydrochloric acid can be used as the catalyst for the hydrolysis of wood. The wood hydrolysis can easily be carried out quantitatively in the laboratory. But the economic industrialization on a commercial scale has proved to be a difficult problem. The primary problems have been the recovery of acid, the finding of suitable acid resistant materials, designing equipment, and the discovery of a simple way to refine sugar.

Concentrated sulfuric acid hydrolyzes wood quantitatively with little sugar degradation when sufficiently large quantities of acid are used. With concentrated hydrochloric acid the reaction reaches an equilibrium after a certain amount of time but the acid hydrolyzate is capable of continuing the hydrolysis if it contacts fresh wood. This fact has led to the development of a counter current system which produces solutions of up to 20% sugar.

The dilute sulfuric acid process was devised to overcome the difficulty of acid recovery. The processes using dilute acid had to be carried out at elevated temperatures which results in the reduction of yields due to the degradation of sugars.

4.1.1. Concentrated Acid Processes

4.1.1.1. Hokkaido Process

The process known as the Hokkaido process was developed in Japan in 1948 to hydrolyze wood with concentrated sulfuric acid. In this process wood chips are first prehydrolyzed under conditions that depend upon whether furfural or xylose is the desired product from the reaction. If xylose is desired then, the prehydrolysis consists of reacting the wood with 1.2-1.5% sulfuric acid at 140° to 150°C. Furfural is produced when the pentose formed from the pentosans is directly converted by dehydration by steam at 180 to 185°C. The prehydrolyzed wood is dried and crushed. Then the main hydrolysis is carried out by treating this crushed "wood" with 80% sulfuric acid at room temperature. The important prerequisite in concentrated sulfuric process is the maintenance of a low mixing ratio of acid to wood, without sacrificing sugar yield. To obtain the desired low mixing ratio a new mixing process was developed. In this process the dried powdered prehydrolyzed wood is mixed with acid of the correct concentration by spraying together in a thin film. The mixing requires only about 30 seconds and the product is immediately filtered under pressure and washed. The sugar yield is greater than 90% with a mix ratio of .9 and about 96% with mix ratio of 1. The concentration of the sulfuric acid from the combined fillrate and washing water is 30-40%. This acidified sugar solution is treated with a diffusion dialysis using an ion exchange resin membrane to recover 80% of the total sulfuric acid as a 25-35% solution. The acid is concentrated by evaporation to 80% and reused. The sugar solution contains 5 to 10% glucose polymer and 5 to 15% sulfuric acid. During this dialysis 1.8 to 2% of the total sugars are lost. The sugar solution after dialysis is post hydrolyzed by heating at 100°C for about 100 minutes. The hydrolysete is neutralized and the resultant calcium sulface removed by filtration. The pH of the neutralized sugar solution is adjusted to 2.5 to remove the calcium ions and then concentrated to 50%. The sugar is separated as a double-salt by adding the theoretical quantity of sodium chloride. After washing with cold water the glucose is isolated in crystalline form. An overall yield of 286-296 kg/ton wood which is 83-85% of theoretical is obtained.

J. Kobayashi has proposed a modification of the Hokkaido process called "the Thorough Drying Process". The primary advantage is that the large amount of power required to mix sulfuric acid and dry wood for the main hydrolysis is reduced. In this process wet prehydrolyzed wood is immersed in dilute sulfuric acid and after the acid has drained the wood is dried at 40-50°C. by blowing with dry air. The sulfuric acid in the wood becomes concentrated as the drying progresses and the main hydrolysis is completed. Simultaneously, unit power consumption should be reduced and construction costs should be lower with almost the same sugar yields as with the Hokkaido.

One other concentrated sulfuric acid process was developed by Nippon Mokuzai Kogaku Co. The main feature of his process is the sulfuric acid is not recovered but converted into gypsum which is marketed as a by-product. The other product from this process are crystaline glucose, crystalline xylose and refined molasses.

4.1.1.2. Bergius-Rheinau Process

Several processes have been developed which use concentrated hydrochloric acid to hydrolyze wood. The first commercial process is known as the Bergius-Rheinau process. In this process the wood is hydrolyzed by immersing in a 40% hydrochloric acid. The first cycle produces a 10% sugar solution. This acid solution containing sugar is reused several times for hydrolysis to obtain a sugar solution of about 40%. The 40% sugar solution is distilled under reduced pressure at 36°C. to recover hydrogen chloride gas. About 80% of hydrochloric acid is recovered. The solution leaving the vacuum distillation equipment contains about 55% sugar and a small quantity of hydrochloric acid. The sugar solution is spray dried with hot air to expel residual hydrochloric acid. The lignin remaining in the reactor is washed with water to recover sugar and hydrochloric acid. The most difficult technical problem encountered in the early stage of development was selections of suitable acid resistant materials for heaters and condensers. One difficulty lay in the transfer of heat for the evaporation of to recover hydrochloric acid. Metal could not be used because of the corrosiveness of the acid and ceramic linings were unacceptable because of their low heat conductivity. To solve the problem a mineral oil which remained liquid at the required temperatures, which did not react with the HCL, and which did not emulsify with the hydrolyzate, was used as a heat transfer medium. The hot oil in a fine spray was brought in contact ith acid hydrolyzate in a vacuum vessel. Thus, heat was transferred directly to the hydrolyzate. The vapors which consisted of hydrochloric acid and steam were removed and condensed to recover the acid. The remaining hydrolyzate was largely free of hydrochloric acid but mixed with oil which was removed by decantation for recycle.

4.1.1.3. Udic-Rheinau Process (new Rheinau Process)

The Rheinau process was improved in an attempt to make it economically feasible under peacetime conditions. The improved process is known as the new Rheinau Process. In this process crystalline glucose was the principal product. Two new processes of prehydrolysis and post hydrolysis were incorporated and chemical engineering studies were made of the hydrochloric acid recovery. In the improved process the wood was first immersed in 1% hydrochloric acid and then prehydrolyzed at 130°C. under pressure to remove the hemicellulose. The prehydrolyzed wood which contain lignin and cellulose is dried and converted to glucose and di, tri, and tetramer sugars with 41% hydrochloric acid in the main hydrolysis. The lignin which remains after hydrolysis and extraction is washed with hydrochloric acid solution and then water. Hydrochloric acid is recovered by vacuum distillation of the acidified sugar solution. The resultant solution is 60-65% sugar of which approximately one-half is dimer and trimer sugars. The solution is diluted to 10% sugar concentration and post-hydrolyzed. Since the primary product is crystalline glucose the sugar solution is deacidified and deionized with ion exchange resins, decolorized, refined and concentrated again to crystallize glucose. With the new Rheinau process the hydrochloric acid losses were reduced from over 18% in the Bergius-Rheinau process to 5-6%. Later it was found that no sugar was degraded if prehydrolysis was carried out at low temperatures with 35% hydrochloric acid. The new Rheinau process is now called the Udic-Rheinau process.

4.1.1.4. Hydrogen Chloride Gas Process

The use of hydrogen chloride gas for hydrolysis is essentially a concentrated acid process. The reason for using hydrogen chloride gas was to shift the hydrolysis reaction into the interior of the wood particles and to facilitate the recovery of the acid. In this process the wood is impregnated with a small quantity of highly concentrated hydrochloric acid and then the concentration is increased by passing hydrogen chloride gas into the wood. The acid can be recovered relatively simply by heating the wood.

4.1.1.5. Noguchi-Chisso Process

Historically the Prodor process was the first pilot process developed using hydrogen chloride gas.

In this process sawdust enters the mixer and is mixed with concentrated hydrochloric acid. A mixture consisting of 60 parts water, 46 parts hydrochloric acid and 100 parts dry sawdust is charged into the digester. The digester consists of 12 trays resembling a Herreshoft furnace. The mixture is swept alternately toward the center and the periphery of the trays by the rotation of blades where it falls to the next tray. Hydrogen chloride gas flows counter current to the flow of the sawdust acid mixture. After eight hours the hydrolyzed material comes off the bottom and is transferred to a drying section where the material is dried and the acid expelled by hot air. Because this process relies heavily on acid resistant structural materials which were not available the process was not successful.

A later process, the Darboven used a tank filled with carbon tetrachloride as the reactor instead of the tray type use in the Prodor. Wood chips are suspended in carbon tetrachloride and hydrogen chloride gas is blown into the vessel. Hydrolysis take place as the concentration of the hydrochloric acid in the wood flour increases. The hydrolyzed material is dried by hot air, after the carbon tetrachloride has been removed. The heat which is involved by the absorption of hydrogen chloride gas is removed by using the carbon tetrachloride as a heat exchange medium. The equipment required for their process is simpler than that required for the Prodor process.

A still later process was developed by A. Herneng and called the Hereng process. Wood chips, without any predrying are fed into the reaction column. The reaction column is a hexagonal column made of vinyl chloride having 40 inclined trays. The chips are mixed with 30% hydrochloric acid in the feeder where the acid concentration is reduced to 18-20% because of the moisture in the wood. The chips and hydrochloric acid solution flow down the slanting tray where prehydrolysis is completed in 45 minutes. Hydrochloric acid solution containing pentose is separated from the wood chips by means of a filter and a portion of the solution is recycled to the mixer at the top of the column. Sugar in the prehydrolysis solution is concentrated to 20-25% by the recycling operation. Prehydrolyzed material is drained and goes down the column with 30% hydrochloric acid at a temperature below 10°C. while hydrogen chloride gas is introduced at the bottom. The hydrochloric acid solution flowing down the column absorbs the hydrogen chloride gas and increases in concentration to 41-42% as the main hydrolysis occurs. The hydrolyzed material coming off the bottom of the column enters a drying chamber where it is dried by dry hydrogen chloride gas which has been washed and dried with concentrated calcium chloride solution. A mixture of sugar and lignin which is solid is obtained from the right end. The sugar is extracted with water and post hydrolyzed.

After considerable study initiated by the Noguchi Institute and the Shin Nippon Chisso Herija Co. a process known as the Noguchi Chisso process was developed. This process featured the handling of wood particles in their original form throughout and the conducting of the prehydrolysis and main hydrolysis in the interior of the wood particles. In particular the main hydrolysis is carried out with hydrogen chloride gas in a fluidized bed.

Wood flour produced by crushing logs or sawdust is used as a raw material. This material is permeated with 0.5-0.7 times the quantity of 3-5% hydrochloric acid. Prehydrolysis is carried out by introducing steam at 100-130°C. The prehydrolyzed wood is extracted by a counter current flow of water to get a sugar concentration of 10-15%. The prehydrolyzed wood is flash dried by hot air and then permeated with hydrochloric acid solution below 38% concentration. The material permeated with hydrochloric acid and containing sufficient water for the main hydrolysis, absorbs hydrogen chloride gas while being fluidized with cold hydrogen chloride gas. The acid concentration in the acid-permeated material reaches 42%. Hydrolysis does not take place up to this point.

The material which contains a high concentration of hydrochloric acid by low-temperature absorption (up to saturation) is rapidly heated to 40-45°C to complete hydrolysis while being fluidized with hot hydrogen chloride gas. Saccharification of wood cellulose proceeds almost quantitatively.

The material from the main hydrolysis is apparently solid. This is dried in hot hydrogen chloride gas to vaporize the permeated and absorbed hydrogen chloride. Sufficient hydrogen chloride is left in the sugar material to carry out post hydrolysis.

In a second test process, hydrogen chloride adsorption at low temperatures, and main hydrolysis by raising the temperature, are carried out while transporting acid-permeated material with hydrogen chloride gas by a pneumatic conveying method. Particles are carried through a deacidification process by means of pneumatic transport with high temperature hydrogen chloride gases. This process is called flash saccharification and if the ripening period of the process is omitted, the entire process of hydrochloric acid adsorption (cooling), heating, and hydrochloric acid recovery can be carried out in a few seconds. The yield of sugar by main hydrolysis is 95% and if the sugar decomposed in the acid recovery process is deducted the total yield is 90%.

4.1.2. Dilute Acid Processes

The dilute sulfuric acid processes were developed because economic recovery of acid is concentrated acid processes has not been achieved and yields are low with the use of small amounts of concentrated acids.

4.1.2.1. Scholler Process/Madison Process

In the early Scholler process 0.5-1% sulfuric acid is introduced continuously under pressure from the top of the Saccharification column, and the sachharified solution is continuously discharged from the bottom to remove the sugar from the reaction system as soon as possible to minimize the degradation of the sugar. Later the process was modified by introducing the acid intermittently. Final modification was the development of the cold shove process which increases the charge of wood in the reactor by compressing several times with high pressure steam.

The hydrolysis column in the Scholler process is called a percolator. The wood chips are packed in the percolator and then compressed with steam at about 3 atmospheres. More chips are added and compressed with steam. This procedure is repeated several times compressing the charge which results in an increase of the bulk density of the wood chip of two times the original. Acid for hydrolysis is introduced under pressure and then expelled by steam. Fresh acid is not introduced immediately after the saccharified solution has drain from the wood chips but the temperature in maintained by introduction of steam. Hydrolysis proceeds during this period by the acid which has permeated the wood. Acid is rapidly introduced again and the solution containing the sugar is expelled from the percolator. As a result of a pressure difference produced between the wood and the acid the saccharified solution in the pores of the wood is expelled. Thus, by this process the residence time of the sugar is shortened and therefore, the quantity of sugar decomposed is reduced.

The Madison process developed at the Forest Products Laboratory is a modification of the Scholler Process. In this process 0.5% sulfuric acid is fed continuously into the reactor at a fixed rate. The raw material wood is crushed as small as possible in order to increase the rate of permeation of the acid into the interior of the wood.

After prehydrolying at 135-150°C to remove the hemicellulose, the main hydrolysis is conducted by introducing 0.5% sulfuric under pressure at the top and continuously removing solution from the bottom. The reaction temperature during the 3 hour hydrolysis time is raised from 150°C to 190°C. When the sugar concentration reaches about 1% near the end of the reaction the saccharified solution is introduced to the next percolator and the sugar concentration maintained at about 5-6%. Sugar yield as high as 75% are expected.

The TVA process is a modification of the Madison process with the objectives of designing simpler equipment and producing a more concentrated sugar solution.

According to Russian investigations the hydrodynamic flow conditions in the vertical percolation process have not been sufficiently utilized. They have combined vertical percolation with horizontal flow with the advantage of assuring practically unlimited flow of hydrolyzate. The yield of reducing sugars has been increased by 15 to 20% with the increase flow of hydrolyzate.

4.1.2.2. Grethlein Process

Dr. Hans Grethlein at Dartmouth has proposed a continuous process for hydrolysis of wood using dilute sulfuric acid. He based his design on an analysis of the reaction kinetics to optimum the conversion to glucose and minimize the degradation products. The resultant reactor was determined to be plug flow isothermal with a residence time of 0.19 minutes at 230°C an acid concentration of 1%.

The specific design proposed is based on newsprint as a feed material. In this design the newsprint is prepared by a pulper which is used to repulp waste newsprint. The resulting slurry is pumped through a liquid cyclone to remove minor particulate foreign matter. Dewatering screws remove enough water to give a 13% slurry. This slurry is pumped to a preheater and then to the reactor. Sulfuric acid at 50% concentration is added and final heating is carried out with live steam. The live steam addition reduces the slurry concentration to a nominal 10%. The reaction time is stopped by a flash expansion of the material as it flows from the reactor to the flash tank. The flash liquid acid hydrolyzate is pumped to a neutralized tank where the acid is neutralized with lime. The unreacted lignin, cellulose and calcium sulfate are removed by a continuous centrifuge.

The advantage of this process is that equipment size can be greatly reduced since the reaction time is on the order of seconds instead of hours as with the previous described batch systems.

4.1.2.3. Purdue Process

George Tsao at Purdue University has developed a unique process for hydrolysis of wood using dilute sulfuric acid or enzymatic hydrolysis. The Purdue process consists of three main operations; first a dilute acid pretreatment, second, a solvation to modify the cellulose structure and last, a hydrolysis and separation of the hexose sugar.

A brief description of the proposed process follows. The feed material is first ground or chipped and then prehydrolyzed with dilute sulfuric acid. The prehydrolyzate is separated,neutralized and discharged for further processing. The residue is dried to 10% moisture in a low pH condition and then intimately mixed with concentrated sulfuric acid which dissolves the cellulose. The cellulose is then precipitated by the addition of methanol. The precipitated cellulose is amorphorus and is easily hydrolyzed by acid or enzyme to glucose.

4.1.2.4. Weak Acid Hydrolysis

Another process which deserves some attention is the weak acid or auto hydrolysis process described by Snyder in his patent. This process requires that the woody material be initially impregnated with an alkaline or buffer reagent and the subjected to elevated temperatures (250-300°C) and pressures (600-1250 psi) for a short period of time. The amount of alkali or buffer added is the amount necessary to keep the pH at the end of the reaction between 3.1 and 3.4. The reaction times varies from about 60 seconds to 5 minutes according to the pressure and the amount of alakli.

In this process approximately 30% pentoses are converted to furfural and with post hydrolysis approximately 80 to 90% of xylose and glucose can be recovered.

4.2. ENZYMATIC HYDROLYSIS

Cellulose is the most abundant and replenishable material. This natural resource can be utilized most efficiently if it can be hydrolyzed into its monomer, glucose, which can then be used as a starting material to produce a number of products. One of the most important products in which we are interested is ethanol.

Cellulose can be converted into glucose either by acid or enzymatic hydrolysis. The advantages of using enzymes to hydrolyze cellulose to produce glucose are summarized below. The cellulase enzymes are very specific to their substrates and do not react with other impurities. These are inactivated due to the presence of compounds toxic for their growth. A specific cellulase enzyme produces glucose only thus avoiding the other degradation products as observed in the hydrolyzate from the acid hydrolysis process. The glucose syrup produced enzymatically is purer and consistent in its composition as compared with the sugar syrup obtained from acid hydrolysis. The operating conditions in terms of pH, temperature and pressure are mild thus eliminating the need of special alloys for the hydrolyzing unit.

The development work on the various cellulase enzymes and enzymatic hydrolysis processes has been carried out in a large number of laboratories. Some of these cited in the literature are given below.

1. U.S. Army Natick Development Center, Natick, Mass.
2. University of California, Berkeley, CA
3. Indian Institute of Technology, New Delhi, India
4. General Electric and University of Pennsylvania
5. Massachusetts Institute of Technology, Cambridge, Mass.
6. Gulf Process
7. Rutgers University
8. Swedish Forest Product Laboratory
9. Faculty of Agriculture, Miyazaki, Japan

The cellulolytic enzymes have been isolated from a large number of organisms. The Natick, Berkeley,and Indian Institute of Technology groups are working with the strain of *Trichoderma viride*; the Japanese and Rutgers use mutants of *T. viride*; the Japanese also use *Aspergillus niger*. The General Electric and University of Pennsylvania group have worked with an *Actinomycetes* while the Swedish group is working with a fungus *Sporotrichum Pulverulentium*. The other organisms reported(5,6,7,8,9) to have significant level of cellulose activity are given below.

Cellvibrio Gilons
Basidiomycetes sp.
Penicillium pusillum
Aspergillus terreus
Fusarium moniliforme
Myrothecium Verrucarria

Polyporus sp.
Chryso sporium sp.
Aspergilli sp.
Bacillus sp.
Chaetomium sp.

Most of the data available on enzymatic hydrolysis of cellulose is from laboratory and pilot scale experiments. At present, there is no large scale plant in operation involving the enzymatic hydrolysis of cellulose to produce glucose. Some of the promising processes under development are briefly reviewed below.

4.2.1. Natick Process

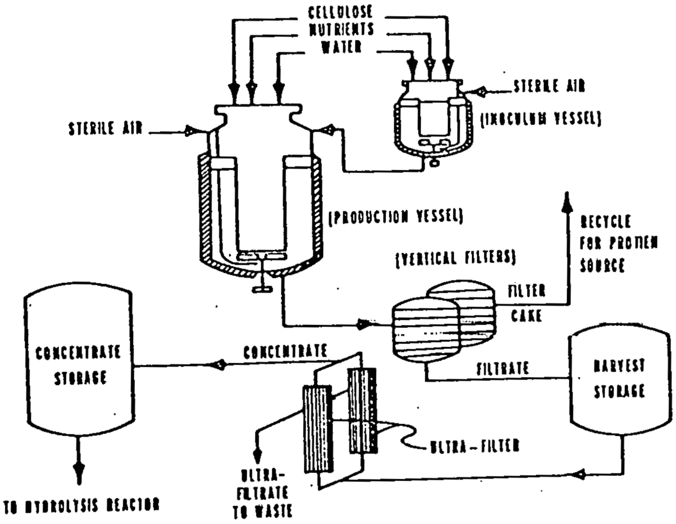
A schematic diagram of this process is shown in Fig. (4.1.). The production of ethanol by Natick Process involves four stages. 1) Pretreatment of lignocellulosic biomass 2) Production of active cellulose 3) Enzymatic saccharification of pretreated cellulosic substrate and 4) Fermentation of sugar solution to produce ethanol.

This process relies heavily on the energy intensive physical pretreatment(10,11) methods such as ball milling and differential speed two roll milling. The physical pretreatment of the substrate has the following advantages: a. This leads to increased surface area and decreased crystallinity of cellulose. b. This increases the bulk density of the substrate which allows the higher slurry concentration (up to 30%) in the hydrolyzer. The next step is the production of enzyme.(12,13,14) This has been accomplished by growing the fungus _T_. _Viride_ in a culture medium containing shredded cellulose and various nutrient salts. Following its growth, the fungus culture is filtered. The clear straw-colored filtrate is the enzyme solution that is used in the saccharification vessel.

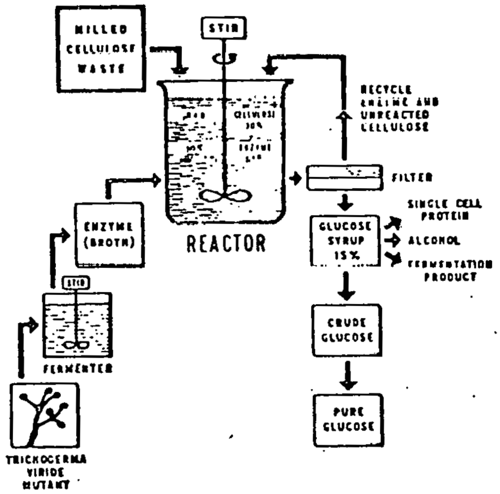
During the past few years, marked progress has been made in enzyme production(15) with a 30-fold increase in concentration of enzyme in the fermentation broth (0.50 to 15 filter paper cellulose units

FIGURE 4.1. NATICK PROCESS

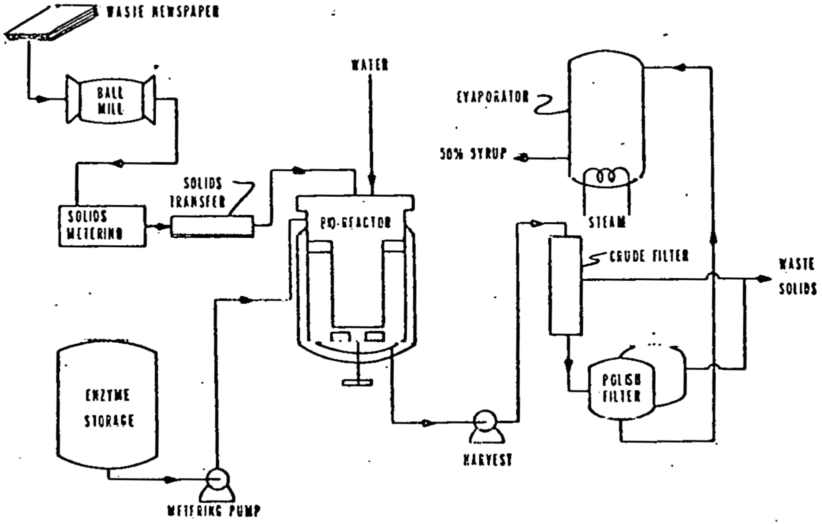
PILOT PLANT PROCESS FOR CELLULASE PRODUCTION



ENZYMATIC CONVERSION OF WASTE CELLULOSE TO GLUCOSE SUGAR



PILOT PLANT PROCESS FOR NEWSPAPER HYDROLYSIS



per ml) and a 24-fold increase in productivity (3.0 to 72 units per liter per hour). These advances were accomplished by strain selection(16) development of improved mutants(17,18) and optimization of fermentation conditions.

The next stage in the operation is saccharification(19,20,21) of pretreated substrate enzymatically. The milled cellulose is introduced into the enzyme solution and allowed to react with the cellulose to produce glucose. The saccharification takes place at 50°C and atmospheric pressure. The residual cellulose and enzyme are recycled and crude glucose syrup is filtered and prepared for the next stage to produce ethanol.

Before this process becomes economically viable the following aspects of this process will have to be resolved. The ball milling and two roll mill methods of pretreating the lignocellulosic biomass are energy intensive and therefore expensive. Thus there is a need for the development of a cost-effective pretreatment for cellulosic materials to make them readily susceptible to enzymatic hydrolysis. The enzymatic activity of the <u>Trichoderma</u> <u>cellulase</u> has to be increased several fold. <u>StrainRut</u> - <u>C-30</u>(22) appears promising but more work needs to be done.

Finally an assumption has been made that a 30% slurry of feed to the hydrolyzer can be pumped and mixed uniformly with cellulolytic enzymes which may not be trouble free in a commerical scale unit. Spano (23) from Natick laboratory presented the most recent economics of their process to produce 95% ethanol as shown in the table (4.1.).

From the cost figures presented it was clear that even the factory cost of the 95% ethanol produced by the Natick process is much

Table 4.1. Adjustment of the Factory Cost for Creditable Materials

Cellulosic Materials	Urban Waste	Wheat Straw	Poplar
* Factory cost (95% Ethanol)	$1.43	$1.52	$1.75
Estimated Credits	$0.54	$0.54	$0.54
Adjusted factory cost to produce 95% Ethanol	$0.89	$0.98	$1.21

Creditable Materials

1) Residual cellulose from hydrolysis plant; $0.36/gal. ethanol

   Based on combustion energy value, 6000 Btu/lb., $\$2.75/10^6$ Btu.

2) Cellular Biomass from ethanol plant; $0.18/gal. ethanol

   Based on $150/Ton as animal feed and/or fertilizer value.

* Market value of 95% ethanol = $1.12/gal.

more than the market price ($1.12/gal. 95% ethanol). One has to be a little careful in taking credits for the by products and a very extensive market research on the supply and demand should be conducted.

4.2.2. University of California(24,25)

Professor C.R. Wilke has conducted research and published a lot of his work. He hypothesized many process schemes based on his small scale laboratory work. He has used the cellulose enzyme from the strain of T. Viride as used in the Natick process. This process involves hydrolysis of cellulosic material in the presence of cellulase enzyme to produce a sugar solution and recovering from the hydrolysis products a major proportion of the cellulase enzyme used in the hydrolysis reaction for reuse. The required make up cellulase enzyme is produced in a two stage process wherein, in the first stage, the microorganisms are grown and in the second stage the cellulase enzyme formation is induced in the microorganisms containing culture medium by the addition of an appropriate inducer, such as a cellulosic material. The sugar solution recovered is concentrated and sent for fermentation to produce ethanol. Since the research used as a basis of the process design has only gone through bench scale development, many of the design assumptions have not been fully tested.

SRI(26) developed a preliminary design for the process on the basis of research concepts and publications by C.R. Wilke. The base case is for a 25 million ga./year plant for 95% ethanol from wheat straw. The preliminary design included material and energy balances and major equipment specification and sizing which in turn were used for estimating the required capital investment.

The process is divided into six operating sections: substrate pretreatment (milling and prehydrolysis), enzyme recovery, hydrolysis (5% feed slurry at 122°F) sugar solution concentration (4 to 10.7%) enzyme production and ethanol production. All operations are continuous except the ethanol fermentation stage.

According to SRI report the plant gate manufacturing cost for the production of 25 million gal/year of 95% ethanol is summarized below:

	$/gal.
Total material cost	2.04
Utilities cost	0.48
Capital cost	0.46
Labor cost, including overhead	0.36
	3.34

The major cost is for materials, which account for about 61% of the plant gate cost, with the agricultural waste accounting for about 12% and materials for enzyme production accounting for about 45%. Plant gate cost distribution for the various stages of operations are given below:

Plant section	%
Enzyme production	62
Substrate pretreatment	12
Hydrolysis	10
Enzyme recovery	2
Sugar solution concentration	4
Ethanol production	10
	100

FIGURE 4.2.

SRI DESIGN OF WILKE'S PROCESS

ETHANOL PRODUCTION FROM ENZYMATIC HYDRO
OF AGRICULTURAL WASTES (WHEAT STRAW)

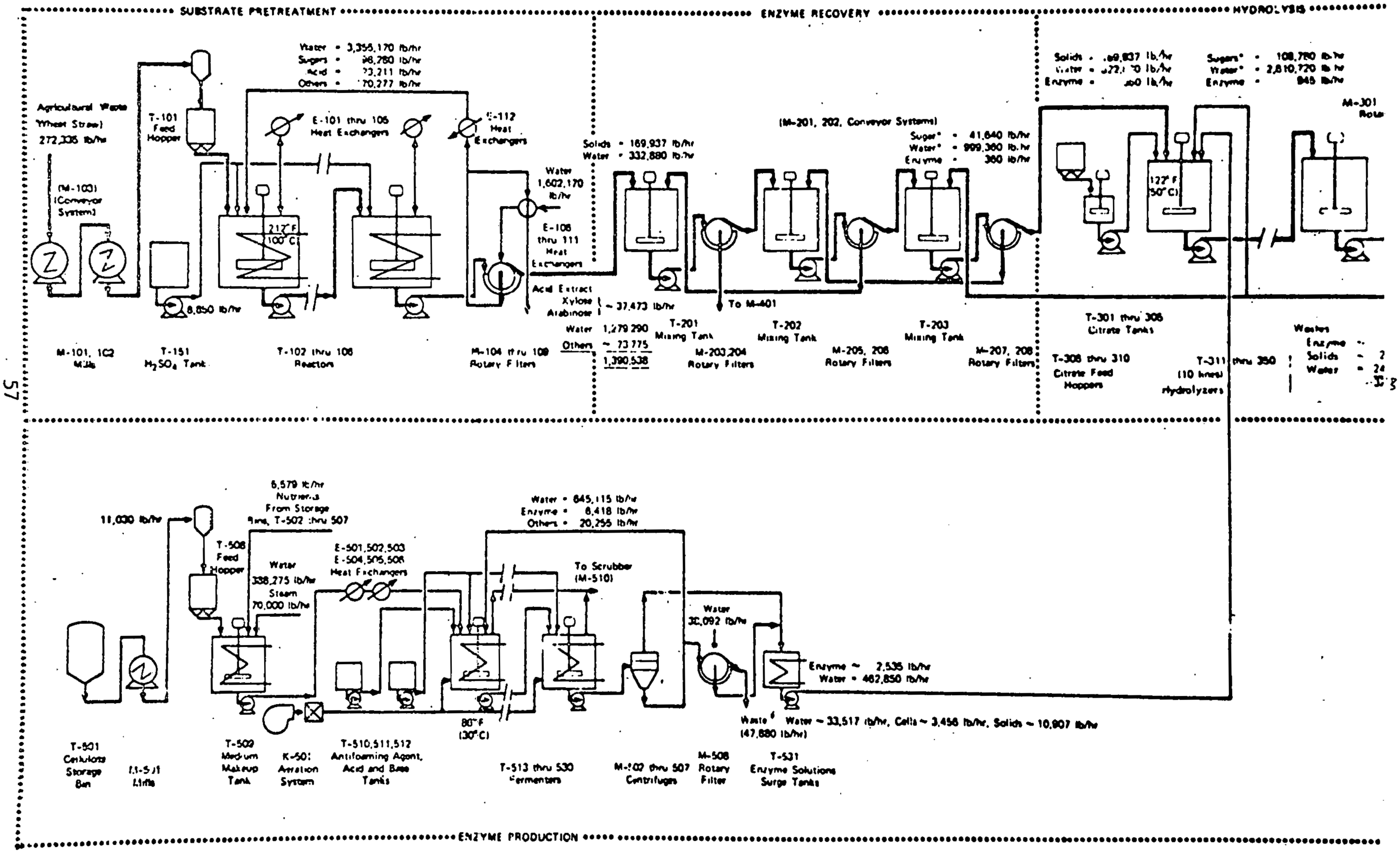
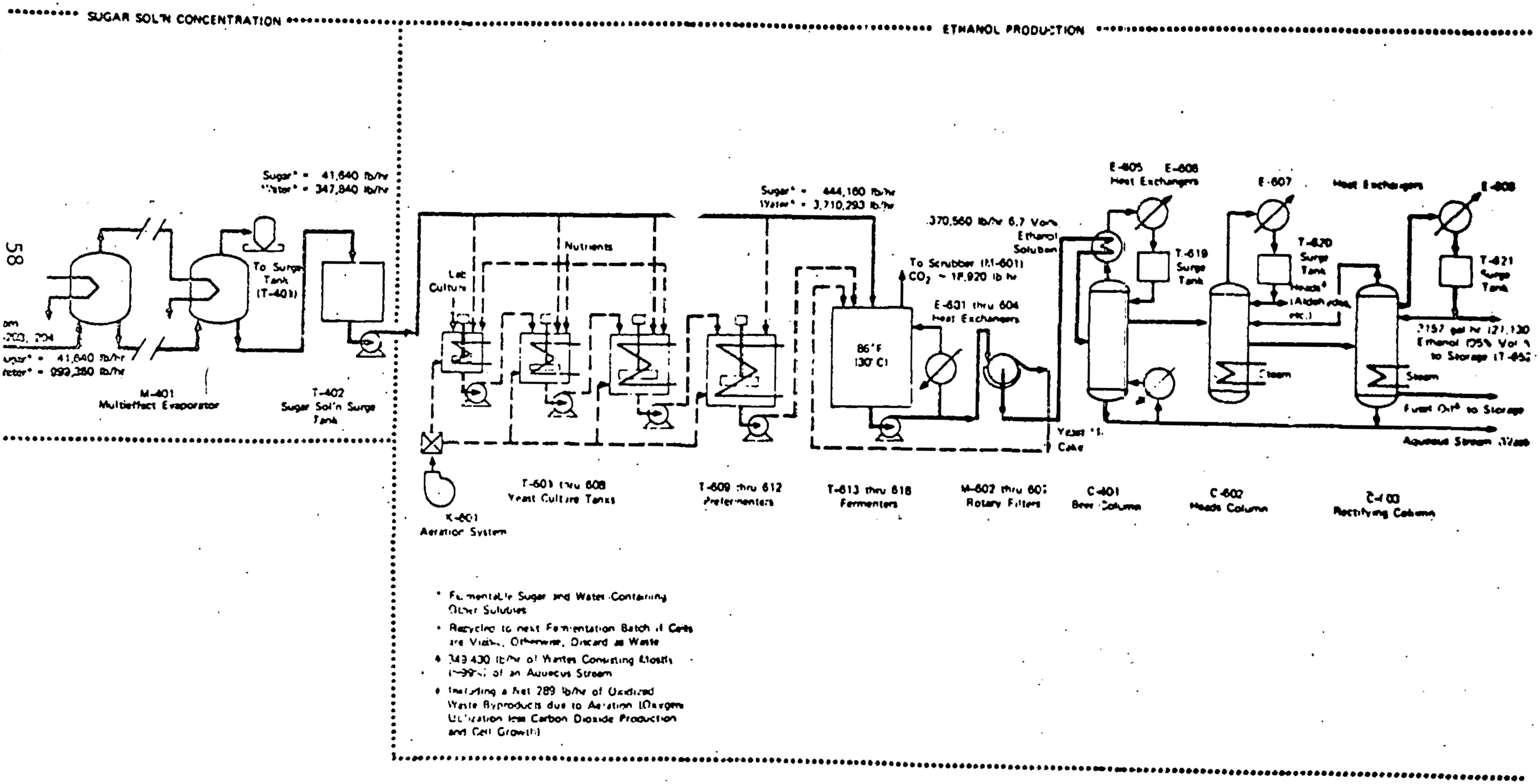


FIGURE 4.2. (cont'd).

SRI DESIGN OF WILKES PROCESS

ETHANOL PRODUCTION FROM ENZYMATIC HYDROL
OF AGRICULTURAL WASTES (WHEAT STRAW)



- * Fermentable Sugar and Water Containing Other Solutes
- • Recycled to next Fermentation Batch if Cells are Viable, Otherwise, Discard as Waste
- ♦ 343,430 lb/hr of Wastes Consisting Mostly (~99%) of an Aqueous Stream
- ♦ Including a Net 289 lb/hr of Oxidized Waste Byproducts due to Aeration (Oxygen Utilization less Carbon Dioxide Production and Cell Growth)

From the cost figures discussed above it appears that the production of ethanol from cellulosic substrate following the enzymatic hydrolysis route by Wilke's process is uneconomical. It is essential to find ways to solve the problems described below:

1. Revovery of enzyme lost with unhydrolyzed substrate so as to minimize the make up enzyme requirements.
2. Reduction of cellulose requirement for enzyme production, so as to reduce the material cost and the equipment cost in enzyme production.
3. Use of cheaper cellulosic substrate and inexpensive nutrients to reduce material cost.
4. Develop a strain of microorganisms that can produce the enzyme with relatively very high level of activity, can grow on cheaper substrates at a slightly elevated temperature and at a faster induction rate.

4.2.3. Indian Institute of Technology, New Delhi(27)

This process is a modification of Natick process. Scientists from I.I.T. have found ball milling to be the most successful technique of treatment. According to them it reduces crystallinity, increases both contact surface and bulk density such that highly concentrated (30% or more cellulose) suspensions can be handled without difficulty in continuously stirred reactors to obtain higher concentrations of glucose syrup. The product sugars can be recovered free of enzyme and cellulose in a membrane reactor. It should be possible to make a compromise between the cost of milling and concentration of cellulose suspension on the one hand and evaporation cost to concentrate the hydrysate and nearly 60% of the total cost attributed to enzyme make up on the other. A conceptual flow diagram of this process is shown in Fig. (4.3.).

FIGURE 4.3. CONCEPTUAL FLOW DIAGRAM OF THE PROCESS DEVELOPED BY INDIAN INSTITUTE OF TECHNOLOGY

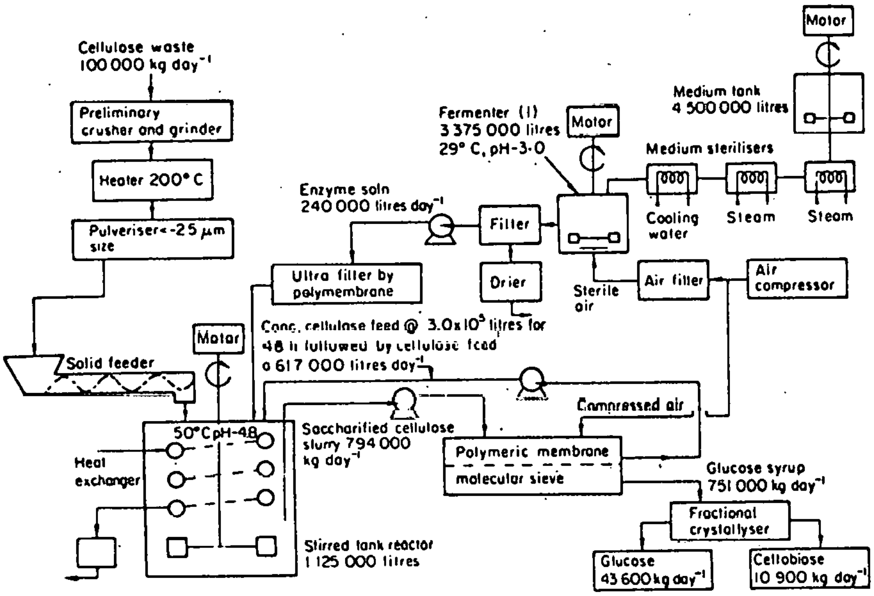


Figure 5a Process flow diagram for continuous enzymatic saccharification of cellulose

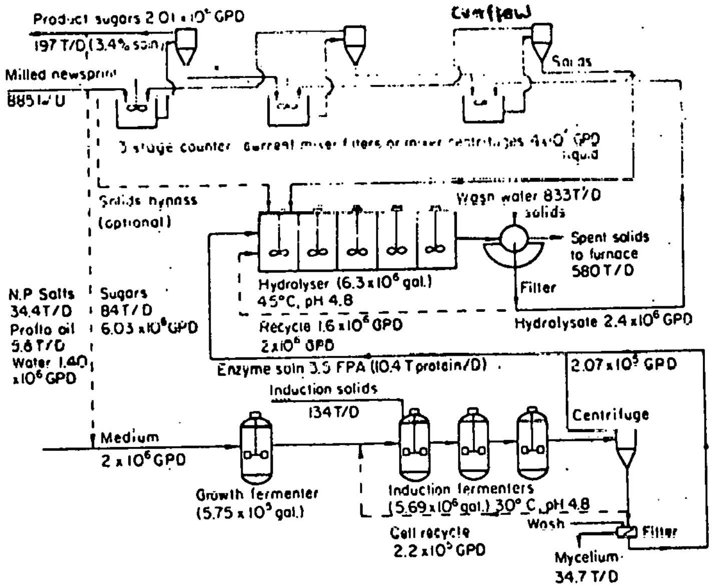


Figure 5b Flow diagram for hydrolysis of newsprint.

This process includes the following major steps:

1. Size reduction of cellulosic substrate (newspaper)
2. Treat an aqueous suspension of the substrate with the QM-9414 enzyme system (derived from T. viride).
3. Recover sugars by dialysis through a polymeric membrane
4. Followed by fractional crystallization to separate the one part of cellobiose from four parts of glucose produced.

The economics of this process are not published. This process would only be economically feasible if:

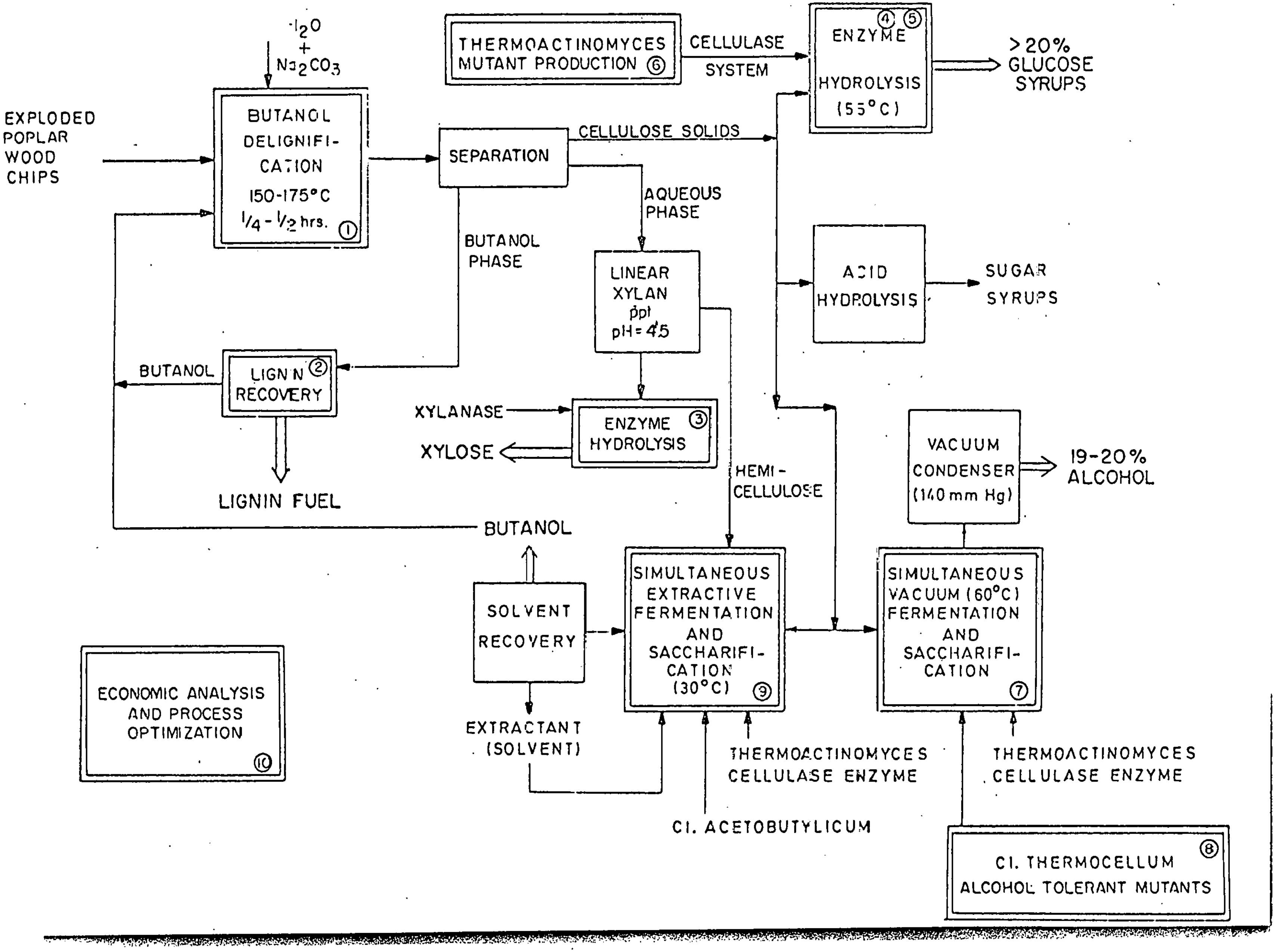
1. A less energy intensive substrate pretreatment method is formed.
2. A low cost membrane for use in the membrane reactor is developed for enzyme recovery, clean sugar production, high reactor loading and conservation of enzyme.
3. The equilibrium characteristics for the enzyme desorption process are ascertained for the repeated use of the most of the enzyme.

4.2.4. General Electric - University of Pennsylvania Process

This is a well thought process. Here two process schemes are presented. In the first process the delignified biomass is hydrolyzed using a cellulase isolated from Thermoactinomyces followed by a conventional fermentation to produce ethanol using a yeast. In the second process a very attractive scheme is presented. Here the delignification is carried out by using n-Butanol. The delignified biomass is subjected to a simultaneous saccharification by Thermoactinomyces and fermentation by the Cl. thermocellum. The alcohol is recovered under reduced pressure.

The advantage of this scheme over the two step process is the removal of glucose an inhibitor of the cellulase system which results

FIGURE 4.4. UNIVERSITY OF PENNSYLVANIA - FUELS FROM BIO-MASS PROCESS



in increased product yield. In this process the problems associated with the separate enzyme production stage are also eliminated. Since the process is anaerobic no aeration is required. The probability of contamination under anaerobic and thermophilic operating conditions are minimized. Instead of cooling, the extra heat energy may have to be supplied to maintain the fermenter under thermophilic temperature range. The vacuum system, compressor and H_2 circulation adds to the cost. Although the enzyme derived from the Thermoactinomyces degrades cellulose faster it deteriorates with prolonged exposure to the high temperature. Most of the work done in this process is at bench scale and the process scheme presented for simultaneous saccharification and fermentation is conceptual. Relatively lower(29) level of activity of enzyme and a low yield of ethanol make this process far from being adapted at commercial scale.

The manufacturing cost of 100% alcohol by GE-Penn process is estimated to be $0.703/gal. This does not included site preparation, feed stock pretreatment, sterilization equipment, nor the cost of enzyme preparation. Therefore no reliable cost figures are available for this process.

4.2.5. Massachusetts Institute of Technology, Cambridge, Mass.

The M.I.T. process (30) is being developed at bench scale. This involves simultaneous saccharification and fermentation of cellulose under thermophilic and anaerobic conditions using Closteridium thermocellum. At present the scientists are trying to produce a better strain of Cl. thermocellum for relatively higher enzymatic activity. Efforts are also being made to block the metabolic pathway of the organism to eliminate the production of Acetic acid thus giving ethanol only as the end product.

In this process the production of enzyme in a separate vessel is eliminated, problems associated with oxygen transfer do not exist and the probability of contamination is minimized.

Since this process is still in the early stage of its development, no reliable cost figures are available.

4.2.6. Gulf Process

This process is based on the enzymatic hydrolysis of cellulose and simultaneously its fermentation to produce ethanol.

The cellulases are prepared by growing the cellulolytic organism T. reesei in a submerged culture. The cellulases are added to the saccharification/fermentation as a whole culture innoculum. Filtration, centrifugation or concentration of enzymes is not involved before use.

The next stage in the process is simultaneous saccharification and fermentation (SSF). In this stage a 5% v/v yeast broth and T. reesei culture innoculum are added to a growth medium containing 10% w/v cellulose. The SSF is carried out at 40°C in the WSTR type vessel.

The advantages of this process over the conventional two stage system is that glucose is removed which is an inhibitor for cellulase system thus giving increased product yield. The ethanol concentration, because of the limitation of the cellulose concentration in feed slurry, never reaches a level which is inhibitory to the yeast or cellulases. Ethanol, being a volatile product, is also more easily recovered than glucose.

Another advantage of this process is that the yeast growth rapidly produces an anaerobic environment which eliminates the necessity for strict aseptic conditions.

The process is in its development stage and no cost figures are available.

4.2.7. Rutgers University

It is known that the sum of the factors contributing to the high cost of cellulose production are: (1) expensive culture medium ingredients, (2) high priced fermentors, (3) associated separation equipment, and (4) extremely low yield of enzyme.

Rutgers University(22) has made considerable advances in cellulase enzyme technology, thus, making a desirable contribution in improving the process economics related to enzyme production. The yields of cellulase from T. reesei have been increased substantially. The cellulase yields from the mutants Rut-NG-14 and Rut-C-30 grown in a fermenter are fifteen-fold greater than that obtained from the wild strain of QM6a in a flask culture. They have isolated catabolite repression mutants (eg. Rut-C-30) which allow the use of inexpensive ingredients in the growth medium; for example, the use of corn steep liquor, without any reduction in the yield of cellulase. They are also developing and evaluating the thermotolerant strain.

4.2.8. Swedish Forest Products Laboratory

This group has been experimenting with a white rot fungus. The enzymes from this organism decomposed not only cellulose and hemicellulose but also lignin. This work is in the early stages of experimentation and looks very promising on the long term basis.

4.2.9. Miyazaki University, Japan

Faculty members of this university have conducted research in the enzymatic hydrolysis of cellulose using enzymes derived from *T. viride* and *A. niger*. It was observed that delignified cellulosic residue would hydrolyse much more easily than the same substrate with lignin. They found peracetic acid as the best delignifying agent. The group found this process uneconomical and thus R & D efforts were halted.

4.3. Concluding Remarks on Enzymatic Hydrolysis Processes

Natick process is the only enzymatic hydrolysis process which has been developed at bench and pilot scale.

This process relies on the energy intensive physical pretreatment methods such as ball milling and differential speed two roll milling. More information is needed on the larger scale to evaluate the energy consumption by these methods. Thus, there is a need for the development of a cost effective pretreatment to make the substrate readily susceptible to enzymatic hydrolysis. In this process it has been assumed that a 30% feed slurry to the hydrolyzer would not cause any problem in pumping and in uniformly mixing it with enzymes in a commercial scale process vessel.

GE-Pennsylvania Process and Gulf process both appear to be commercially attractive and may have a better future for the following reasons:

These processes use the method of simultaneous saccharification and fermentation to produce ethanol from cellulose in the same vessel.

1. During the enzymatic hydrolysis of cellulose to glucose and its simultaneous fermentation to produce alcohol, the glucose an inhibitor for cellulase system, is removed to give higher yield of product whereas, in the two stage Natick process it is not possible.

2. The SSF processes are anaerobic and thermophilic in nature thus, eliminating the need of aeration and maintaining a strict asepsis in the system.

3. The separate stages for recovering and concentrating the enzyme is eliminated.

4. The separate vessels to conduct hydrolysis and fermentation are eliminated.

5. Ethanol concentration in the fermenting broth never reaches a concentration which may be inhibitory to yeast or cellulases.

No cost figures are available for treating the waste streams thus, no comparison of these processes can be made.

Comparing the factory cost of producing 95% ethanol using wheat straw as the substrate by Natick process ($1.52/gal) and by Wilkes process ($3.34/gal. calculated by SRI) with the market price of $1.12/gal., it appears that the enzymatic method to produce ethanol is economically less feasible.

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5.0. FERMENTATION

Wood hydrolyzates have been fermented rapidly and efficiently in pilot plant and industrial scale operations in several countries. The yields of alcohol, based on fermentable sugar present are similar to those obtained in the fermentation of other carbohydrate raw materials.

The toxic nature of the dilute acid hydrolyzate(1,2,3) has been reported in the past. Four potential sources of toxic substances have been cited. Namely carbohydrate decomposition, lignin decomposition, extraneous materials present in wood and metal ions from equipment corrosion.

The main soluble product of pentoses in the presence of acid under a wide variety of conditions is furfural and that of hexoses is hydroxymethylfurfural, which is readily converted to formic and levulinic acids. The second acid is relatively nontoxic. High pH at high temperature, during neutralization step can cause the formation of many acids, aldehydes and other compounds. Underkofler(4) has reported the work of Levers et al with reference to the concentration of various substances required to cause 25% inhibition in yeast propagation or in fermentation as shown in Table 5.1.

The toxicity of hydrolyzate may be reduced by the following conditions or methods(4): 1) steam distillation 2) acclimatization of the yeast 3) detoxification reactions brought about in the presence of yeast 4) treatment with lime 5) precipitation with proteins 6) adsorption on surface active materials 7) increasing the pH, filtering and readjusting the pH 8) use of large yeast inocula 9) adjustment of oxidation reduction potential, e.g., by the addition of sulfur dioxide 10) holding at high temperature or neutralization at high temperatures and 11) extraction or sulfide precipitation.

TABLE 5.1 TOXICITY OF VARIOUS COMPOUNDS FOR YEAST

Substance	*Concentration Causing 25% Inhibiting Effect* In yeast propagation g per 100 ml	 In yeast fermentation g per 100 ml
Furfural	0.110	0.0740
5-Hydroxymethylfurfural	0.140	0.2600
Menthol	0.011	0.0096
Borneol	0.033	0.0130
d-Pinene	0.002	0.0085
Pyrogallol	not tested	0.3700
Phloroglucin	not tested	1,3600
Gallic acid	not tested	0.2300
Tannin	not tested	0.0250
Terpineol	0.037	not tested
Vanillin	0.063	not tested
Eucalyptol	0.065	not tested

During the fermentation of wood sugars large yeast inocula or cell recycling system is essential other wise fermentation would proceed very slowly. The medium supports only a small amount of yeast multiplication and it would be much too expensive to grow and new inoculum for each batch of fermentation and this obviously would not work, without cell recycling, in the case of a continuous fermentation system. The fermentation proceeds normally when 1% yeast by volume is used. Yeast multiplication is regulated by the addition of .02% Urea and .006% monosodium phosphate by weight. The pH of the system should be maintained between 4.5-6 and the optimum fermentation temperature is between 27°C to 32°C. The time required for most fermentations with 1% yeast by volume is between 24 to 40 hours.

Yeast strains are selected to give fast and complete reaction and the metabolic heat must be removed continuously to prevent damaging temperature rise. It amounts to about 2.6×10^5 BTU per 1000 lbs. of sugars present. This can be absorbed on an internal cooling coils or by constantly circulating the liquor through an external heat exchanger, which under the conditions of turbulent flow can provide an overall heat transfer coefficient of about 300 $\mathrm{BTU/ft^2/OF}$. This represents one of the major uses of water in an industrial alcohol plant, which can summate to as much as 80 gallons of water per gallon ethanol produced.

The oxygen is necessary in the large amounts only during the early stages for the optimum reproduction of yeast cell but is not required for the production of alcohol, During fermentation, carbon dioxide is evolved and anaerobic conditions are soon established.

Based on 78% of the fermentable sugar the yield of alcohol can vary between 44-48.5%. Assuming a theoretical yield of 51.1%, the fermentation efficiency can fluctuate between 86 to 95%.

The yield of ethanol by various processes have been cited in the literature. By Scholler plant(5) 100 kgs of softwood yielded 51 parts of sugar, of which 41.3 parts or 81% were fermentable. This portion was converted to alcohol with 88% fermentation efficiency to yield 23.4 liters of alcohol. The plant losses reduced this to 22.7 liters as a maximum practicable yield.

The data on the Holzminden plant (6,7) showed that the best average yields, obtained during the second year of operation amounted to 19 liters per 100 kgs of wood. After the war the Swiss plant produced 21 liters of absolute ethanol per 100 kgs of wood.

Among the useful and valuable by-products collected would be carbon dioxide, three quarters of which can be recovered for sale as compressed liquid or dry ice. Yeast can be used as a source of protein and vitamin B complex and the remainder of the fluid after recovering ethanol can be utilized as animal feed supplement.

5.1. Review of Fermentation Alternatives

The following fermentation systems have been reviewed:

1. Open Vat Fermentation
2. Deep Vat Fermentation
3. Tower Fermentation
4. Vacuum Fermentation
5. Deep Jet Fermentation

5.1.1. Open Vat Fermentation

This system cannot be considered for commercial scale operations to produce ethanol for the reasons given below:

1. Contamination of the fermenting medium can be a problem.
2. There may exist a temperature gradient in the system due to the heat losses from the surface.
3. Depending upon the temperature of the fermenting medium and its ethanol concentration a fraction of alcohol would be lost which is undesirable.

5.1.2. Deep Vat Fermentation

The fermenters for this operation are stirred tank reactors with the ratio of volume of fluid to the surface area being at least 20.

These are agitated from the top with extra mixing provided by recycling the liquid using a pump. The pump should be such as to avoid damage to the yeast cells contained in the liquid passing through it. It is desirable to effect the thorough mixing of the yeast and the medium by combining the effect of the pumping with the positive mixing by agitator during the fermentation process. Efficient mixing is desirable to prevent settling and to insure isothermal, homogeneous conditions.

Use of baffles in the tank avoids the formation of a vortex in the system. The mixing action also prevents build up of stagnant film on the sides of the tank.

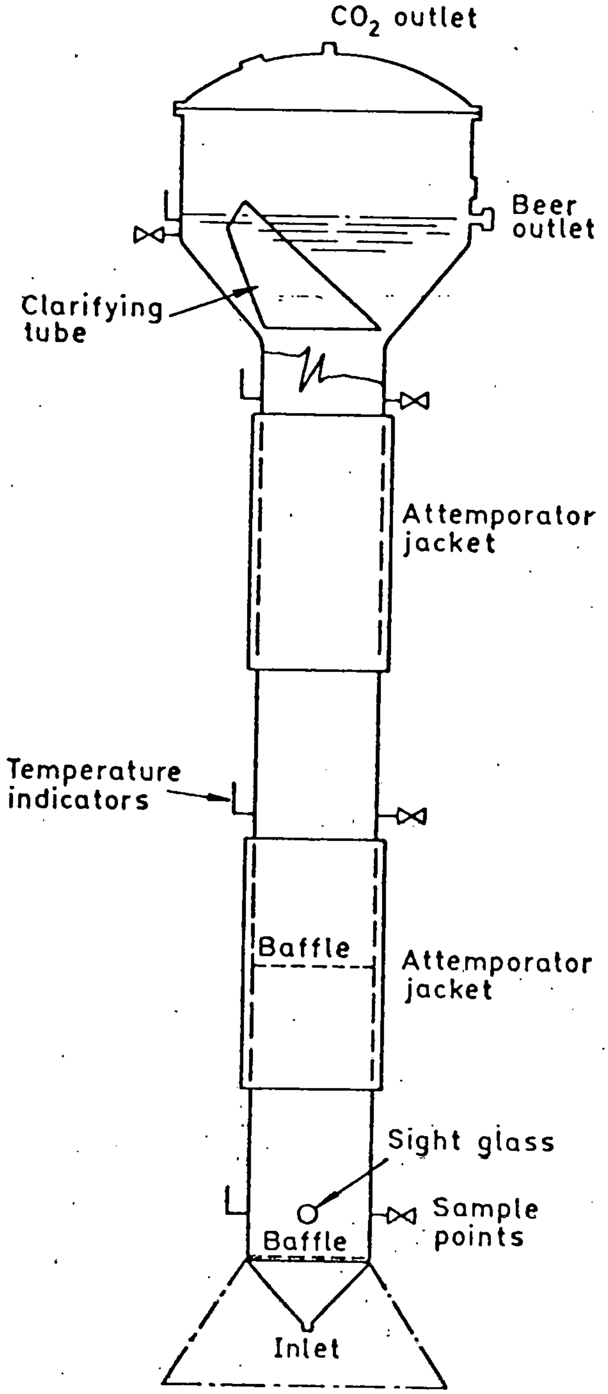
This process provides for a given volume of liquid to produce a dense foam confined within a small surface area, thus increasing the depth to volume ratio of the foam and facilitating its removal with minimum disturbance to the foam-liquid interface. The foam layer can be removed leaving a minimum residual foam that is desirable for the purpose of retaining surface characteristics favoring entrapment of solids which collect on the surfaces of the rising bubbles and preventing reentry of the solids into the liquid. Hence, the deep fermenter design provides an effective foam cover at minimum foam volume per liquid volume.

5.1.3. Tower Fermentation System

Tower fermenters have been used in U.K. for commercial operations to produce beer and vinegar. A number of British patents(8,9,10,11,12,13) have been issued for the application of this system mainly to produce beer.

The fermenter(14) consists of a vertical, cylindrical tower with a conical bottom (Fig.5.1.). Above the tower section the vessel opens into a large settling-zone, which contains a form of yeast separator. Generally an overall aspect ratio of 10:1 with aspect of 6:1 on the tubular section is used. The separator which can be of different forms, provides a volume in the tower free from rising gas thus allowing yeast to settle and return to the main body of tower and clear beer can be collected. To avoid the wash out of yeast a flocculent type must be selected. It is reported that a continuous tower fermentation for the production of alcoholic liquids is feasible with a considerable increase in the efficiency. Fermentation times as low as 2.4 hours (volumetric efficiency of 10) as compared with the batch fermentation time of 3-5 days (volumetric efficiency of 0.3-0.2) are reported. This information makes the tower fermenter very attractive. So far the design equations for tower fermenters are not fully developed and as a

FIGURE 5.1. SCHEMATIC DIAGRAM OF THE APV TOWER FERMENTER



result the experience would play a very important role as compared to the science in designing tower fermenter. No cost data is available for the capital cost of the tower fermenter and the operating and maintenance cost of such unit.

5.1.4. Vacuum Fermentation

In the Vacuferm process(16) full strength clarified molasses can be fed continuously to the fermenter still along with a recycled cell cream of aerobically grown yeast. The heat of fermentation in this process may be just enough to distill off ethanol whereas in the conventional fermentation system the excess heat generator must be removed with a cooling system. In the Vacuferm process a three-fold higher sugar concentration can be fermented or one-third of the time needed in a conventional process is possible. Therefore, a considerable reduction in the size of fermenter would be achieved.

The vacuum fermentation process appears to be uneconomical for the PDU process scheme for the following reasons:

1. The sugar concentration of the wood hydrolyzate produced would be between 4-8% depending on the pretreatment method, mode of hydrolysis and the operating conditions used. In order to adapt the vacuum fermentation the sugar solution will have to be concentrated to 20 +% w/w level. This would mean the inclusion of an energy intensive process step and extra capital for the larger and more efficient equipment for this stage.
2. With elapse of time there would be a considerable build up of substances in the fermenter that may be either directly inhibitory

to the yeast or may cause a considerable increase in the osmotic pressure of the fermenting medium thus inhibiting the metabolism of nutrients and salts by microorganisms and drastically reducing the yield of ethanol. Interestingly no scientist has investigated this aspect of vacuum fermentation.

3. No one has reported the detailed energy balances for the fermenter and vacuum system (since a lot of CO_2 will have to be removed too) in comparison with the conventional system.

4. The overall economics for the vacuum fermentation system does not appear to be better than conventional system (if 1, 2, & 3 mentioned above are evaluated realistically).

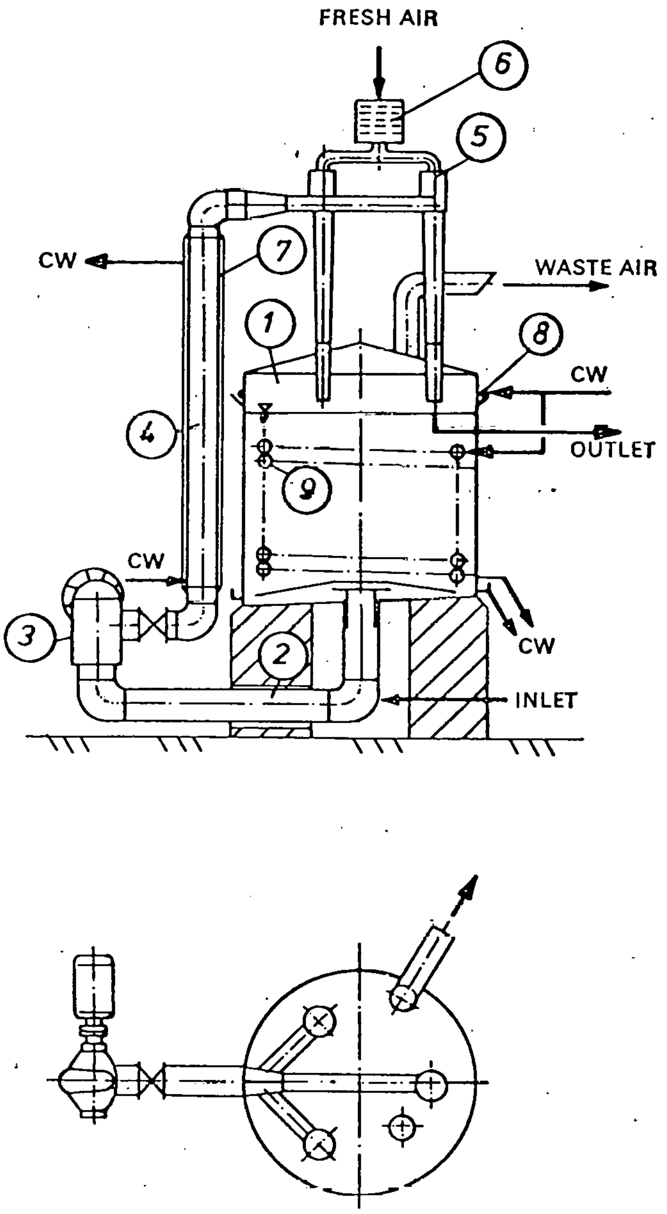
5.1.5. Deep Jet Fermentation Process(17)

The process and equipment are developed by Vogelbusch, an Austrian company. The deep jet fermentation is an aerobic process. It is very efficient and effective for:

1. The production of single cell protein from carbohydrates (hydrolyzed substances, slops from alcohol production and from agricultural waste products).
2. Microbiological fermentation to produce enzymes and organic acids.
3. Biological treatment of process effluent streams.

The Figure (5.2.) shows the basic design of the Deep Jet Aeration Process. The aeration of the liquid by means of a deep jet is done by recirculation of the entire fermenter contents through a simple external piping. The medium to be aerated comes through a properly designed suction line to a specially modified

FIGURE 5.2. DEEP JET FERMENTATION SYSTEM



1. FERMENTER
2. SUCTION LINE
3. SPECIAL PUMP
4. PRESSURE LINE
5. OVERFLOW SHAFT
6. AIR FILTER
7. JACKET COOLING
8. EXTERNAL COOLING
9. COOLING COILS

centrifugal pump. It is suitable for liquids with high contents of dispersed air which transports the liquid through the pressure line to the top of the aeration equipment. From there the liquid falls down to the reactor. The aeration equipment, called the overflow shaft, is a vertically mounted conical tube. By a proper design the recirculated liquid falls down from the top of the overflow shaft as an annular stream in a free fall into the medium to be aerated, self priming the necessary air quantity. In the lower part of the shaft the annular stream is accumulating with the aspirated air to a homogenous two phase jet with very finely dispersed air in the liquid leaving the shaft. The impulse of that jet is chosen high enough to make the jet pass through the liquid volume down to the bottom of the fermenter. In this system high turbulence, thorough gas dispersion, long residence time of the gas in the liquid and optimum homogeneity are achieved. For the removal of heat generated during the fermentation a cooling system can be introduced. The only mechanically moving parts of the system are recirculation pump. The demand for defoaming agent is low since the deep jet is entraining the foam too. The important features of the deep jet fermentation system are: 1. high oxygen transfer rates (12 kgs O_2/cu.M.hr.), 2. highest productivity per fermenter volume, 3. high turbulence leading to an entirely homogeneous system, 4. short residence time or high throughput rate, 5. low specific energy demand for the oxygen transfer, 6. low investment and low maintenance cost, 7. low consumption of defoaming agent.

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6.0. RECOVERY OF ETHANOL

The filtered liquor after fermentation contains not only ethanol and water, but also small quantities of many other relatively volatile components, including low boiling-point acetaldehyde and esters and a complex mixture generally known as fusel oil. This has a higher boiling point than ethanol or its aqueous azeotrope and contains many higher alcohols including amyl, isopropyl and butyl, together with their esters. It is impossible to obtain pure ethanol in a single simple fractionation, but it can be obtained as the azeotrope containing 4.4% water. The complete operation is usually split into several stages:

1. The beer is stripped with steam to yield a dilute ethanol which still contains part of the unwanted volatiles.

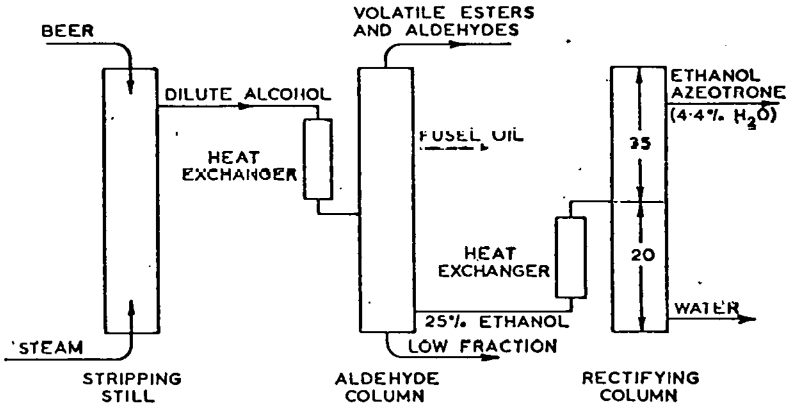
2. This is fed through a heat exchanger to a distillation column, from which separate fractions can be taken off including:

(a) Volatile esters and aldehydes (b) fusel oil (c) ethanol-water mixture containing about 25% ethanol (d) low fraction, mainly surplus water.

3. The dilute ethanol is again taken through a heat exchanger into another column from which the azeotrope can be taken off near the top and water from the bottom. This gives an extra opportunity for removal of last traces of other volatiles. These stages are shown in the Figure 6.1. A number of methods for producing absolute ethanol from the azeotrope have been reviewed. These are briefly mentioned below:

1. Absorption of water on a mixture of sodium and potassium acetates.
2. Azeotropic distillation
3. Extractive distillation
4. Industrial proprietary distillation methods

FIGURE 6.1. DIAGRAM OF THREE COLUMN SYSTEM OF DISTILLING ETHANOL AZEOTROPE FROM FERMENTED MEDIUM



Vulcan Cincinnati

Vogelbusch Process

ACR Process

5. Vacuum Distillation
6. Freeze concentration
7. Solvent Extraction
8. Membrane Separation
9. Ion Exchange and Molecular Sieve

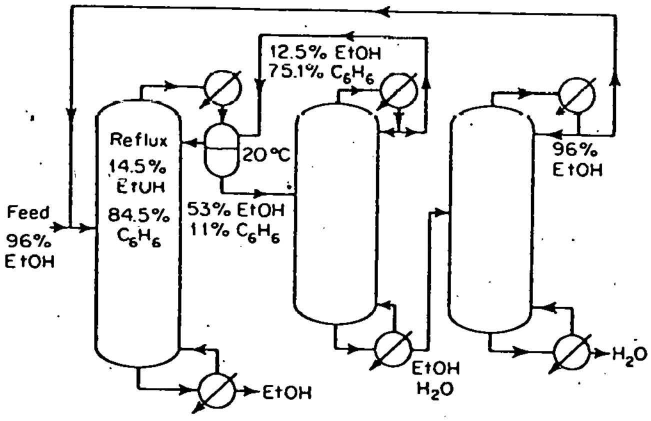
6.1. Absorption of Water on Salts

This method is one of the earlier methods of removing the residual water by absorbing it as water of crystallization on a mixture of sodium and potassium acetates. These salts are mixed in proportions giving the lowest melting point in anhydrous conditions and the salt mixture is circulated counter currently through the distillation column. The mixture is then dehydrated by heating with indirect high pressure steam. This method has been displaced by the azeotropic distillation technique.

6.2. Azeotropic Distillation(1,2,3,4)

In this process ethanol containing water is dehydrated by the addition of benzene as an entrainer. Here benzene forms a ternary azeotrope with ethanol and water which has a higher ratio of water to ethanol than ethanol - water azeotrope. The flow diagram of this process is shown in the Fig. 6.2. This azeotropic process utilizes the two-liquid phase separation at 20°C in the decanter to concentrate the benzene entrainer in the reflux to the primary column. Here the bottoms product is essentially pure ethanol containing no entrainer. The entrainers which have been used in commercial scale systems are Benzene,

FIGURE 6.2. AZEOTROPIC DISTILLATION - ETHANOL DEHYDRATION WITH BENZENE



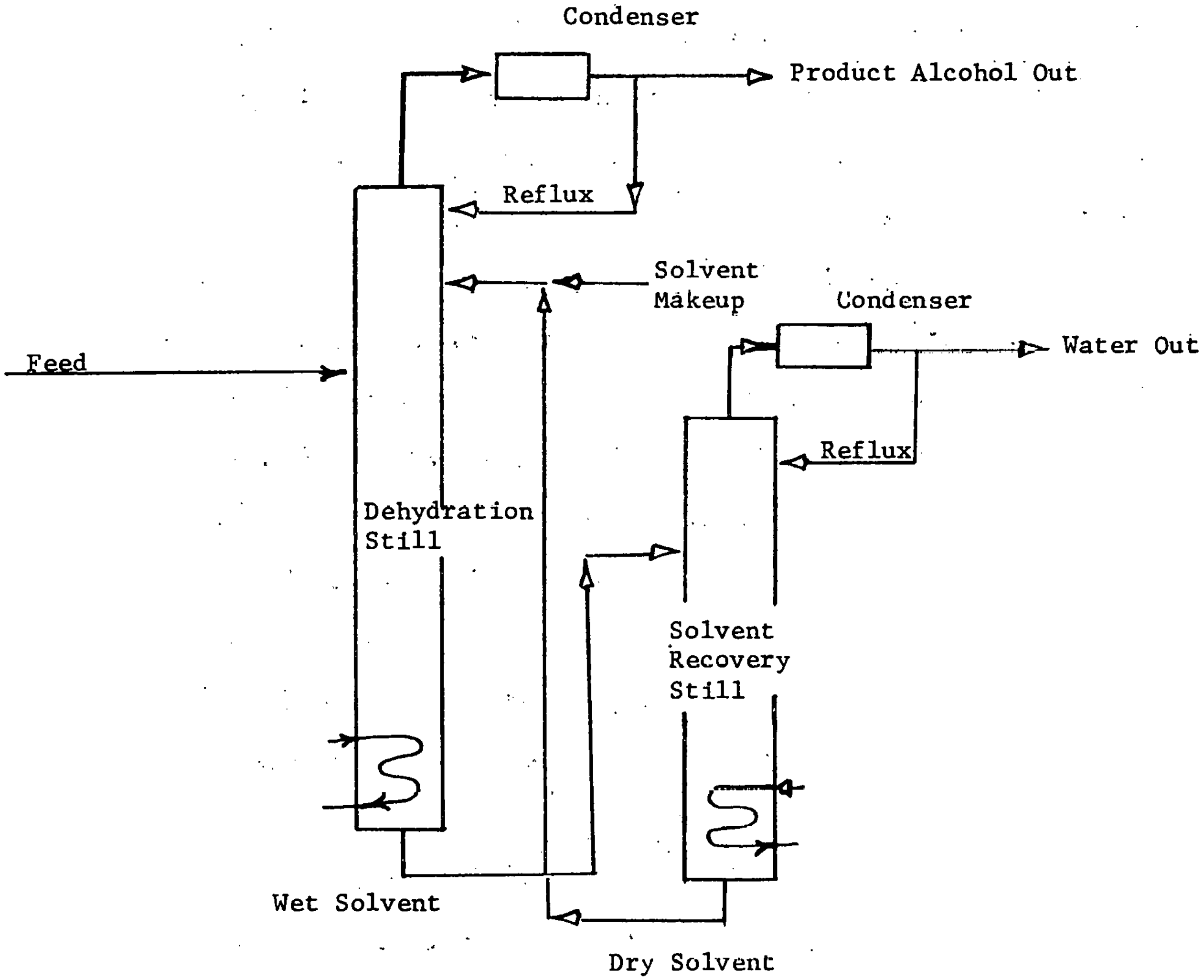
T.C.E., n-Pentane, cyclohexane, Ethyl Acetate etc. The disadvantages of using azeotropic distillation method to produce absolute ethanol, are that entrainers can be very toxic, and flammable. Fraction of volatile solvents are lost through the vents. Since a large quantity of steam is utilized, the azeotropic distillation is energy intensive and thus expensive.

6.3. Extractive Distillation(5,6)

In extractive distillation the third component or solvent which is added must not form an azeotrope with either of the components of the mixture to be separated. It must also be less volatile than either of the components and it must have a different effect on the partial pressures of each of these components in solution at a given concentration. Thus the basic phenomenon upon which this process depends, is the difference in the deviations from ideality which is manifest by non ideal solutions. A general flow scheme of an extractive distillation system is shown in Fig. 6.3.

A number of solvents have been recommended for this system. Some of these are Glycerine, Ethylene Glycol, Propylene Glycol, etc. In this process solvents used are non toxic with high flash point. There are no vent losses of the solvent. The disadvantages of this system are that since ethanol is recovered from the top, the equipment needed is generally larger in size. The reboiler heat load is much larger and as a result of that the cooling load on the condenser would be much larger. Another negative aspect is that the solvents when subjected to higher temperature can get degraded. It appears that less capital cost may be involved in the azeotropic distillation operation, but a

FIGURE 6.3. A GENERAL FLOW DIAGRAM OF EXTRACTIVE DISTILLATION



detailed cost benefit analysis needs to be conducted for azeotropic and extractive distillation system before giving any concluding remark.

6.4. Industrial Proprietary Distillation Processes *

Contacts were made with some companies to learn more about their proprietary processes for the recovery of absolute ethanol by distillation. The information received from two of these companies is summarized below.

6.4.1. Vogelbusch System(7)

This company has developed two distillation processes namely: 1) the combined distillation-rectification process 2) distillation-evaporation process. These processes use cyclohexane as an entrainer. The first process allows the utilization of rust-proof and acid-resisting material for the manufacture of columns, condenser piping, etc. Thus, attaining longer durability and higher reliability. The plant according to this process essentially consists of the same column units as the conventional process and differs from the same by the special heat economy and the favorable construction of the column plates. By an extended utilization of the heat employed for the rectification, a decisive decrease of the figures of steam consumption can be attained. The amount of steam consumption in this process can vary between 28.3 lbs. to 32.5 lbs. per gallon of absolute ethanol as compared with the consumption of 42-50 lbs. of steam per gallon of absolute ethanol produced by a conventional method.*

The amount of steam consumed in the second process (i.e., distillation - evaporation) is given as 20.8 lbs. of steam per

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* Vulcan Cincinnatti claims a proprietary distillation process which consumes 21.5 lbs of steam per gallon of anhydrous ethanol as compared to a conventional steam consumption of 44 lbs.

gallon of absolute ethanol produced. As far as the utilization of vapor compression system is concerned a much higher initial capital investment is needed as compared with the five stage swept surface type evaporator. Although there may be a saving in the consumption of steam more electrical energy would be utilized. Therefore unless a cheap, source of electrical energy is available, a thorough cost benefit analysis should be conducted before installing a vapor compression system.

6.4.2. A.C.R. Process(8)

A.C.R. Process Corporation of Urbana, Illinois has developed a proprietary distillation process to produce absolute ethanol while maintaining a very low consumption of steam.

Their integrated process uses gasoline as an entrainer which can be advantageous since any loss of entrainer would be added to the final volume of gasohol. The total steam required for the integrated system, which includes preprocessing, preheating and drying of the product, is 32 lbs. of steam per gallon of absolute ethanol. These figures are comparable with the other systems mentioned earlier.

6.5. Vacuum Distillation

Vacuum Distillation is one of the methods to change the composition and the boiling point of the azeotropic mixture. In some cases, changing the system pressure can eliminate the azeotropism altogether. Ethanol-water azeotrope (89.4 mole percent ethanol) occurs at 1 atmosphere and 78.2°C. It has been reported(9) that this azeotropism disappears altogether at pressure below 77_{mm}Hg.

From a practical standpoint, one may need a large number of theoretical stages which may lead to high initial capital investment.

6.6. Freeze Concentration

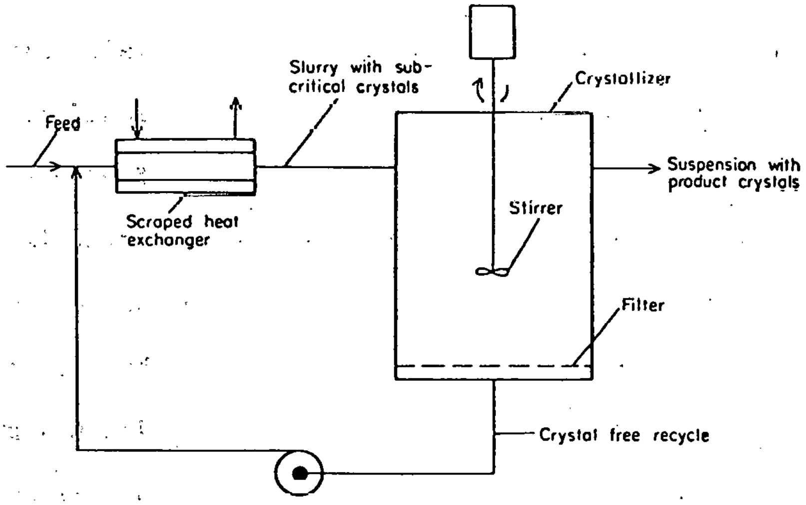
In freeze concentration water is first segregated from the aqueous solution by crystallization. There upon the concentrated liquid is separated from the ice (Fig. 6.4). In fact, this process is well developed and understood for the concentration of heat sensitive liquid foods containing volatile aromas. Since water is essentially withdrawn from the solution by the phase transformation from the liquid to crystal, losses of solvent or aroma can be completely avoided. If high local supercoolings in the crystallizer are prevented the ice crystals of high purity can be collected. The clearness of separation, and especially the capacity of ice-liquid separators, increase sharply with decreasing surface area of the crystals. Crystallizer design and process conditions in the crystallizer must therefore be directed towards the formation of large, and spherical crystals. This method of removing water is relatively well developed. It is suitable for the heat sensitive liquids. This process of dehydrating an aqueous solution can be used on its own or as a part of the overall scheme.

6.7. Solvent Extraction

It is known that water is insoluble in most organic solvents of high molecular weights for example, gasoline and kerosine, whereas ethanol is soluble in many organic solvents.

Therefore, it might be possible to remove ethanol selectively from an aqueous mixture by contacting it with an organic solvent (possibly gasoline, or kerosene).

FIGURE 6.4. SCHEMATIC REPRESENTATION OF CRYSTALLIZERS EXTERNALLY COOLED BY SUBCRITICAL CRYSTALS.



Thus, if the above process is developed a considerable amount of thermal energy can be saved. This method of dehydrating alcohol is definitely suitable for the production of gasohol since the amount of solvent lost with alcohol would not have to be recovered.Another advantage of using this process would be that the ethanol produced would simultaneously be denatured too.

6.8. Membrane Separation

This method is in a developing stage. The philosophy behind this method is to remove water or ethanol selectively from an aqueous solution of ethanol to produce highly concentrated or absolute ethanol as an end product. This can be a multistage process where the degree of dehydration of ethanol would control the number of stages needed.

Prof. H. Gregor of Columbia University is doing some work in developing membranes to remove concentrated HCl from the hydrolysis stage. Similarly, some work needs to be done in developing membranes to selectively remove ethanol.

6.9. By Using Chemical and Physical Adsorption

Drying by adsorption is used in industry because it typically produces a drier liquid or gas than can be obtained by other commercial methods. However, not all adsorbents can dry liquids to the same degree.

Molecular sieves are outstanding in their ability to produce low effluent water concentration. They are the ideal adsorbent to use where-ever extremely dry streams are required. Water concentrations as low as 35 parts per billion are obtainable in dynamic drying service over a wide range of operating conditions.

Not only will molecular sieves separate molecules based on size and configuration, but they will also adsorb preferentially based on polarity or degree of saturation. In a mixture of molecules small enough to enter the pores, the less volatile, the more polar or the more unsaturated a molecule, the more tightly it is held within the crystal. Aqueous ethanol mixtures have been concentrated to absolute ethanol by ion exchange with zeolites.(10) Union Carbide Corporation claims to have appropriate commercial adsorbents.

Therefore, use of this method can actually eliminate the energy required for distillation and dehydration of alcohol.

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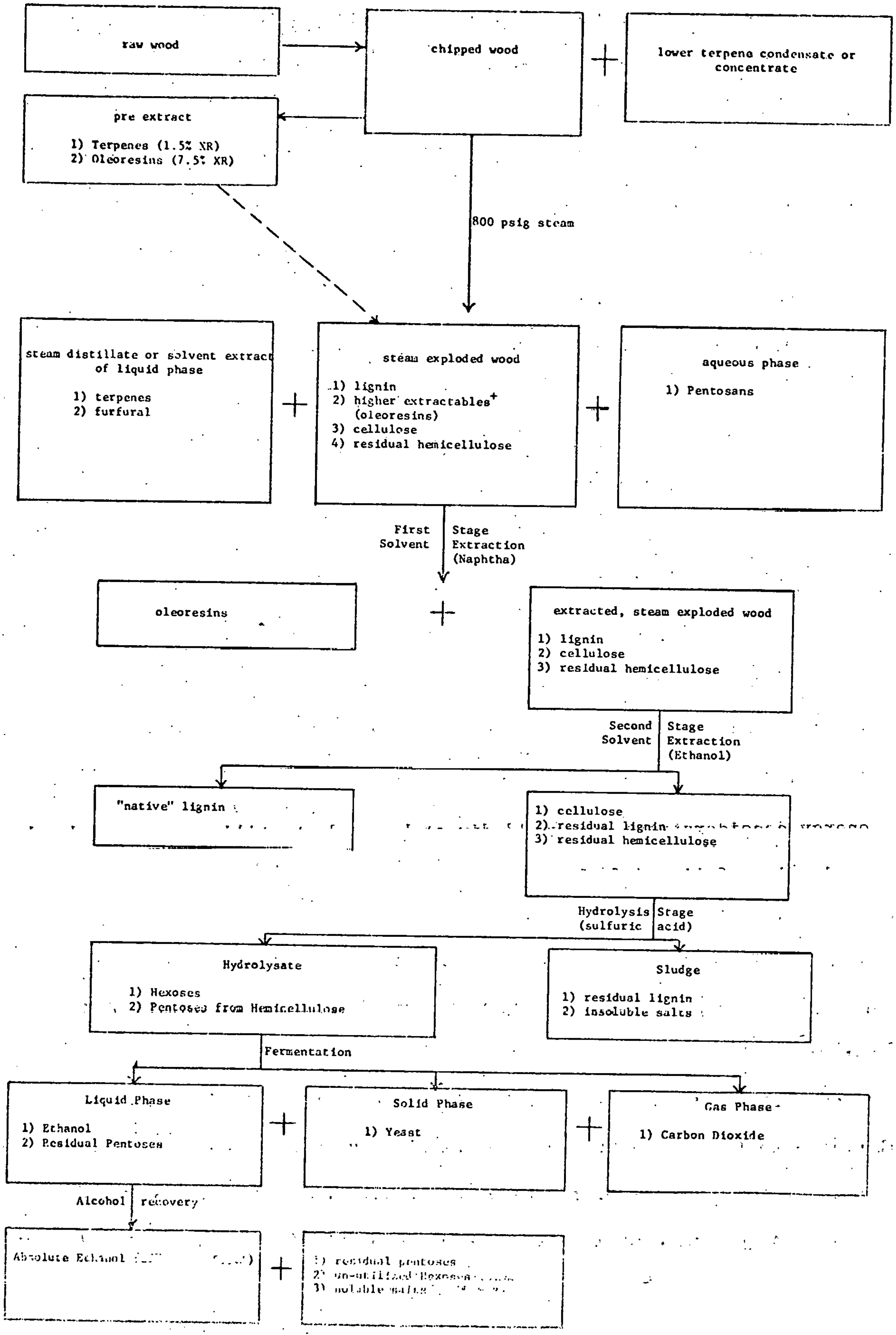
7.0. BY-PRODUCT UTILIZATION

It must be recognized that by-product recovery and utilization, while essential to the ultimate success of the project, must never become the "tail that wags the dog". Accordingly the central theme of the PDU process will always be to maximize the production of ethanol from the biomass in an energetically and economically effective manner. Only when such a process has been clearly defined, can a realistic consideration of by-product utilization be presented. Nevertheless, it is appropriate to discuss some of the underlying principles related to by-product recovery since a great deal is already known about those biomass fractions which are not particularly well-suited for conversion to ethanol.

Two basic approaches, both sound, can be invoked regarding the general utilization of by-products in the Georgia Tech fuels-from-biomass program. The first of these is based purely upon economic considerations and would direct the utilization of by-products towards the most profitable products, e.g., single-cell protein from the hemicelluloses and phenolic monomers from lignin. The second fundamentally different approach is based solely upon energy considerations and would direct by-product utilization towards the production of liquid fuels. In this case hemicelluloses would be converted to acetone and butanol while the lignin could be burned or converted to provide a hi-octane aromatic fraction. While both approaches will be considered in this section in order to provide a clear-cut definition of choices, the final process selection will undoubtedly represent a hybrid of the two basic choices. In both cases, the initial steam explosion treatment confers a special advantage to the PDU process in that it brings the raw materials to a state of maximum surface exposure while volatilizing the steam-distillable extracts and solubilizing the hemicellulose fraction.

FIGURE 7-1.

POINTS OF BY-PRODUCT RECOVERY



Furthermore, the lignin and other non-volatile extractables tend to phase-separate from the cellulose so that they can be more readily removed in subsequent steps.

Among the general principles to be considered in any by-product recovery scheme are the following:

1. At what point in the process should the recovery be made?
2. What is to be done with the recovered material?
3. Anything not recovered is waste and will have to be disposed of in an environmentally acceptable manner.
4. The overall energy balance should be as favorable as possible.
5. The overall economics should be as favorable as possible.

7.1. By-Product Streams

Each of the above points will be discussed in this and other subsections which follow. The first of these is the question regarding the point within a process at which a by-product stream is to be removed. Since a number of potential processes are under consideration, lengthy discussions of each with regard to by-product utilization would seem to be a poor use of resources. Therefore, only one complete scheme will be considered as an illustrative example. This example corresponds most nearly to the modified Madison Process discussed in another section. This scheme is outlined in Figure 7.1. The points of recovery will be described in the following paragraphs:

Lower terpenes in particular and the terpene fraction in general are vulnerable to losses due to their relatively high volatility. Recovery at an early stage would therefore, have the effect of increasing the yield as well as reducing the contribution made by such materials to the air pollution problems associated with the process. It is therefore, suggested that since the chipping operation generates a modest amount of heat while at the same time greatly increasing the available surface area that the trapping of volatile lower terpenes at this point be considered. Yield information is not presented because this fraction is normally lost and it is therefore, difficult to estimate the significance.

The next opportunity for by-product recovery can be realized either as a separate step immediately following the chipping operation or as an integral part of the steam explosion process. Terpenes and oleoresins are the by-products to be recovered and might be removed either as a liquid-liquid extract in which case a separation from solvent is required. Both terpenes and oleoresins are generated. If steam explosion were to be carried out without pre-extraction, the terpenes could be expected to show up in the spent steam condensate along with whatever furfural might have been created in the steam explosion process. The oleoresins, being less volatile, should remain with the wood. Post-explosion recovery might require only a phase separation although the need for a solvent extraction cannot be entirely ruled out.

Since the hemicellulose fraction can be expected to be readily hydrolyzable, all or part of this material may be converted to pentosans during the steam explosion process and thus, become extracted into the aqueous phase. In this case a negative adjustment to the yield figures must be made to allow for the conversion of pentosans to furfural. A residual amount of hemicellulosic material may remain with the exploded wood.

The first stage, post-explosion solvent extraction provides another opportunity to recover the oleoresins, leaving behind the lignin, cellulose and residual hemicellulose. If this option is exercised in preference to the previously described pre-extraction, the oleoresins thus obtained might be relatively free from other materials.

A second stage solvent extraction affords the opportunity to achieve delignification under unusually mild conditions. In this case, preliminary evidence suggests that the recovery factor will be about 90%. The solid phase can be expected to contain the residual lignin along with the residual hemicellulose and the cellulose.

Hydrolysis of this solid material provides a hydrolysate containing hexoses and pentoses. It may be desirable to add the pentosan-containing hemicellulose hydrolysate to this reaction mixture so that full advantage can be taken of the hexose component within the hemicellulose units. This contribution accounts for the apparently inflated yield information. The sludge remaining behind after this step contains residual lignin (probably highly condensed) and insoluble salts. It is not certain at this time whether these materials represent opportunities for by-product recovery and use as process fuel or should be regarded as waste disposal problems.

Fermentation of the hydrolysate in addition to producing the desired ethanol also affords the opportunity to recover carbon dioxide in the off-gases and surplus yeast cells as a solid phase. Following the recovery of the alcohol, the remaining liquid phase would contain the residual pentoses together with the un-utilized hexoses and the soluble salts. This fraction would represent the final by-product input stream.

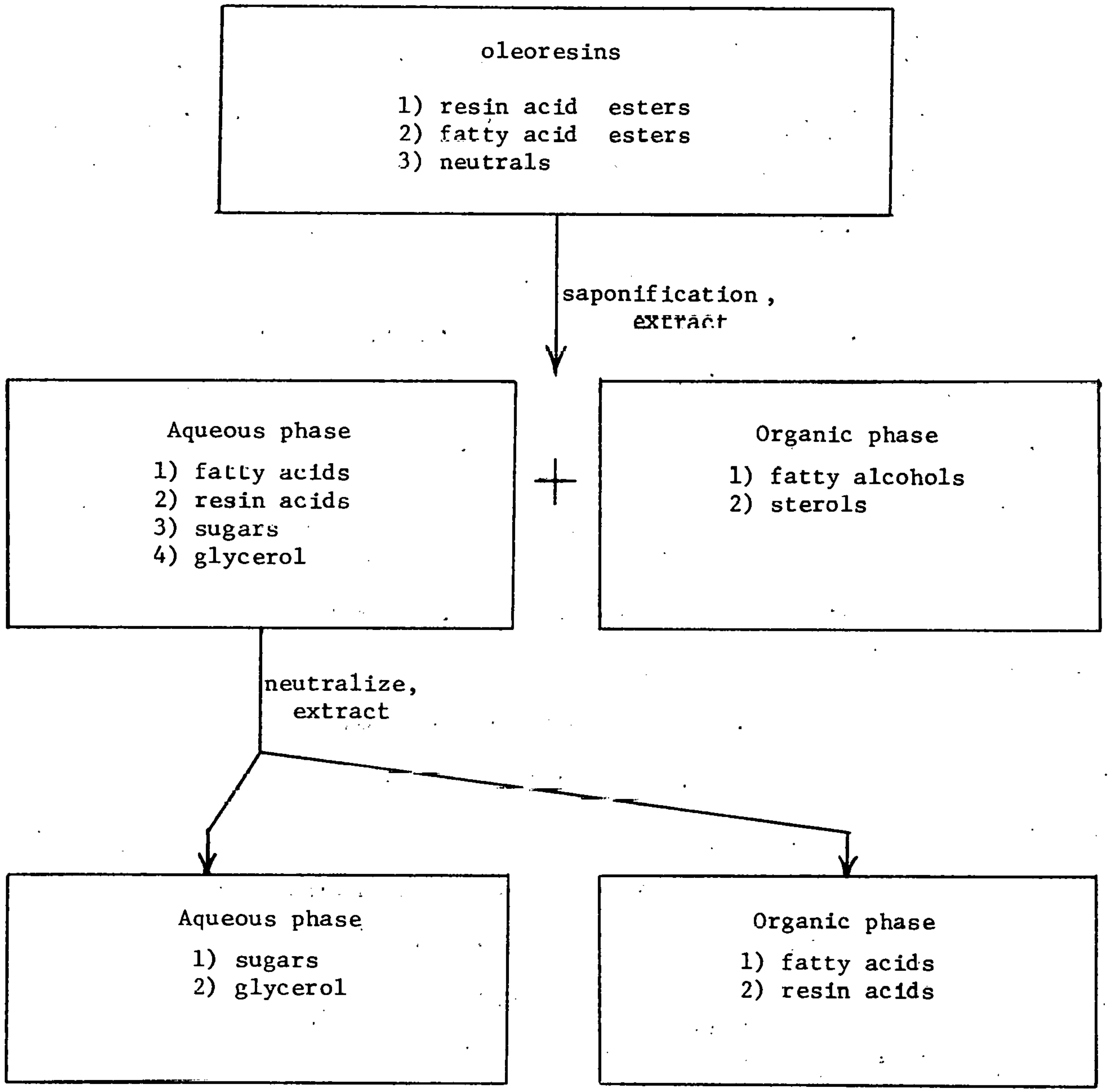
Georgia Tech intends to keep a close watch on material balances not only as indicators of process success, but as indicators of by-product recovery opportunities and/or points of pollutant release.

7.2. In addition to establishing the point of recovery, due consideration must be given to what must be done with the recovered material. In this case, the actual point of origin of the material is less important than its ultimate fate. Therefore, this aspect of by-product utilization can be discussed with a greater degree of independence from the overall scheme employed to generate the alcohol. It is not to be implied, however, that the nature of the by-product is totally independent of its origin.

Although the terpene fractions could be utilized directly as liquid fuel, their unsaturated nature would suggest that direct sale as a chemical intermediate would be a more worthwhile avenue to explore. Only minimal, "clean up" activities would be required to finish this product for sale. Therefore, a process diagram has not been included.

The oleoresin fraction will probably require some upgrading to a material having either a higher fuel value or a greater economic value since the influx of large quantities of this material might seriously degrade its value as a commodity in itself. Saponification of this extractive material can be expected to be a useful first step in the separation of this material into more valuable products. The aqueous phase following saponification could be extracted immediately to remove fatty alcohols and sterols both of which are high value products. Neutralization of the aqueous phase followed by a second extraction would leave the sugars and glycerol behind in the water while

FIGURE 7-2.
RELATIONSHIPS OF OLEORESIN PRODUCTS

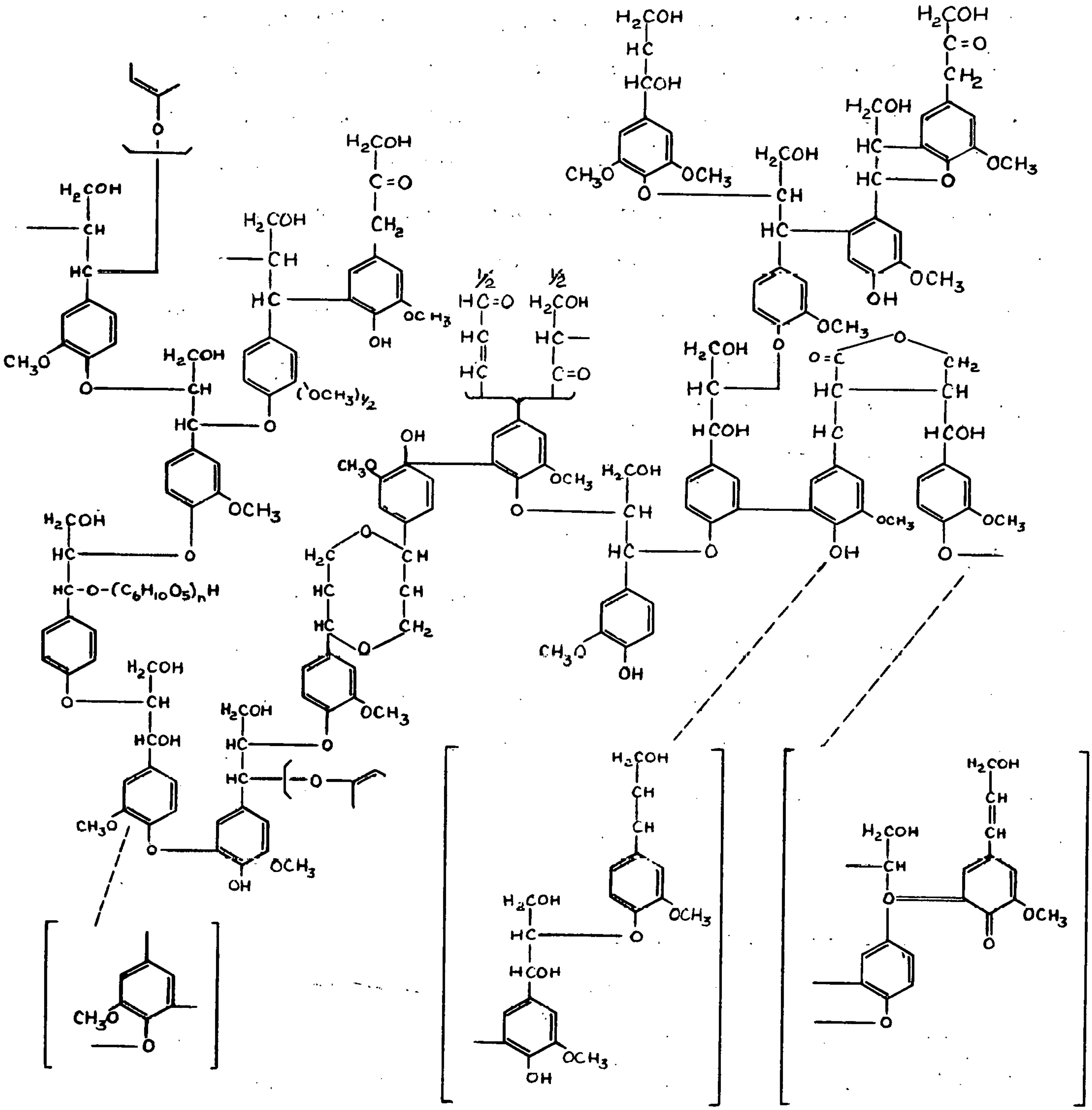


removing the fatty acids and resin acids. Direct fermentation of this solution could destroy the sugars and convert the glycerol to trimethylene glycol. Otherwise, the sugar solution might be returned to the fermentor for eventual conversion to ethanol. Isolation of the glycerol in sufficient quantities could provide a raw material for the manufacture of acrolein or alkyd resins. The fatty acids have a value of their own as chemical intermediates. The resin acid fraction may be the problem by-product of this group. New uses, or further processing may be required. The relationship of each of the potential oleoresin products to the others is shown in Figure 7.2. The proportions of some of these materials is highly source-dependent. Accordingly, it may be desirable to recover or not recover an individual product depending on the type of biomass being processed.

Lignin is the next major by-product to be considered in the Georgia Tech by-product utilization plan. Since lignin is a major component of wood, it is clear that any successful process for the production of liquid fuels from biomass of this type must successfully utilize this by-product. Lignin, in itself, has a considerable economic value as a feedstock in the manufacture of resins. Its usefulness for this purpose is directly related to the reactivity of its free phenolic functions. The fact that the Georgia Tech process begins with steam exploded wood from which the lignin is extracted under extremely mild conditions assures that the lignin so generated would always command a premium price for direct sale. So called "native" lignin, a representative structure of which is shown in Figure 7.3. indicates a truly exciting potential for liquid fuel production or for the production of valuable intermediates. Once again, the mild conditions employed for the isolation of this material greatly reduce the opportunity for the formation of new aromatic carbon-carbon bonds through coupling reactions. This is an important

FIGURE 7-3.

PARTIAL STRUCTURE OF LIGNIN (FROM FREUDENBERG, 1965)



factor to consider if one is concerned with the suitability of lignin as a substrate for the production of fuel and/or chemical intermediates. Fortunately, for the success of the utilization scheme, most of the linkages in "native" lignin do not involve aromatic carbon-carbon bonds and can therefore, be broken with relative ease in the presence of hydrogen and a sufficiently active catalyst. Completely new technology will not be required. While the processes developed to date have generally been directed towards the production of monophenols and phenol itself, it was noted almost immediately that a partially deactivated catalyst was required to avoid the complete stripping of functional groups and the subsequent generation of aromatic hydrocarbons. Since such materials commonly have octane ratings in excess of 100, they can not only serve as liquid fuels, but can be used to upgrade the octane ratings of less-desirable petroleum derived fractions further stretching the supplies of the very resource the process is designed to conserve. The overall yield of liquid aromatic hydrocarbon fuels on a dry wood basis might approach 12%. Since the only condition rquiring change in order to shift the process to the more economically valuable phenols is the activity of the catalyst, this process is close to ideal in flexibility. Furthermore, material balances approach 100% meaning that virtually nothing is wasted or lost.

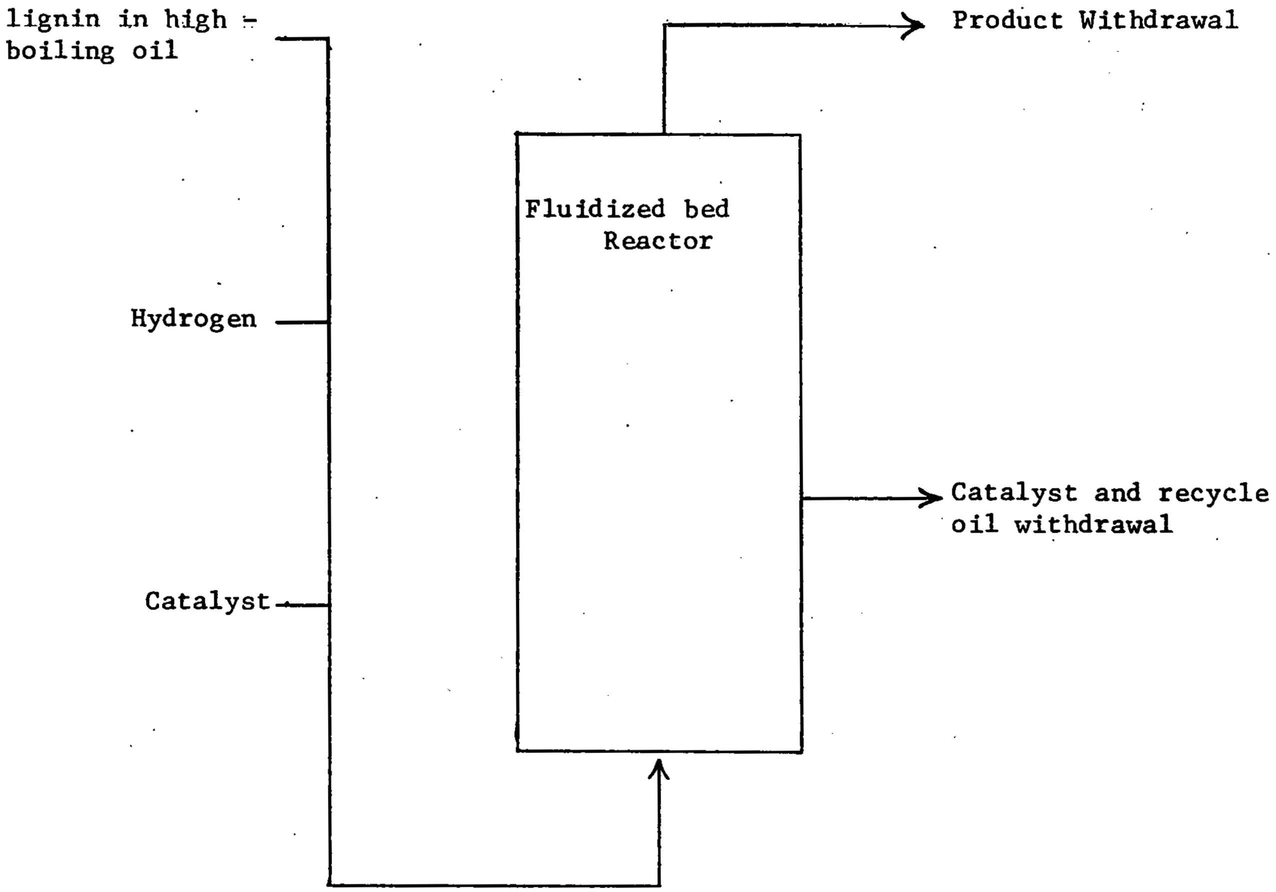
A fluidized bed reactor is recommended with provision for continuous catalyst addition and withdrawal so that performance can be regulated even though a polymeric material (lignin) will constitute the feed. The lignin may be introduced as a solution or suspension in a heavy oil so that it can be conducted through the bed with a higher degree of uniformity. The process is more than self sustaining in carrier, the excess of which can be burned to help meet the heating requirements of the hydrogenation unit. The products, being more volatile than either the vehicle or the feed are relatively easy to collect. A process diagram is presented in Figure 7.4. The use of a strong catalyst might be expected to yield about 4-6% carbon monoxide, 0-2% carbon dioxide, 20-30% alkanes (from the dealkylation of side chains), 20-25% water, 45-55% lower aromatics, 4-6% higher aromatics and about 3% of a recycle oil. A weaker catalyst might provide 3-4% carbon monoxide, 1-2% carbon dioxide, 15-20% alkanes, 15-20% water, 5-10% lower aromatics, 4-6% higher aromatics, 35-45% mono phenols, 8-10% diphenols, and about 2% of recycle oil.

Alternately, the lignin stream may be more usefully and economically employed as a fuel for the total ethanol process. Its application is under analysis.

Another major constituent of biomass, the hemicelluloses should be put to profitable use in a successful process. Hemicellulose is a mixture of pentoses (such as xylose and arabinose) and hexoses (such as glucose, mannose and galactose) together with glucuronic acid. In keeping with the major-product orientation of this work, it should be noted that the hexose fractions derived from hemicellulose are added to the principal fermentation unit and eventually wind up as ethanol. The pentoses or pentosans derived from the hemicellulosic material are a true by-product and may be directed towards a variety of products. The percentage distribution between the pentoses and hexoses within a given hemicellulose is highly dependent upon the source. Therefore, the relative success of a pentose utilization scheme would also depend on the source. For illustrative purposes we have assumed a 13% pentose content for the biomass utilization plan outlined in Figure 7.1.

Furfural is presently produced from pentosans in a commercial process. The chemical reactions leading to furfural involve the dehydration of pentose units, a reaction which might be expected to occur during steam explosion, particularly if encouraged by using a pre-soak to control pH during the

FIGURE 7-4.
HYDROGENOLYSIS OF LIGNIN REACTOR



Fuel-oriented Process	
Carbon Monoxide	4-6%
Lower Alkanes	20-30%
Lower Aromatics	45-55%
Higher Aromatics	4-6%
Recycle oil	2%

Monophenol-oriented Process	
Carbon Monoxide	3-4%
Lower Alkanes	15-20%
Lower Aromatics	5-10%
Higher Aromatics	4-6%
Monophenols	35-45%
Higher Phenols	8-10%
Recycle Oil	2%

explosion process. This possibility has been shown in Figure 7.1. as well as in the process diagrams presented in other sections. The reduction in weight plus the fact that the hemicelluloses contain significant amounts of other sugars accounts for the apparently low yield representing about 7% of the dry wood input. While this material has fuel value, it has a tendency to polymerize which could cause problems if it is to be used as a liquid fuel.

Since this property is an advantage for use as a chemical intermediate, it is suggested that economic considerations be allowed to rule in this case. Furfural should be regarded as a high-value product.

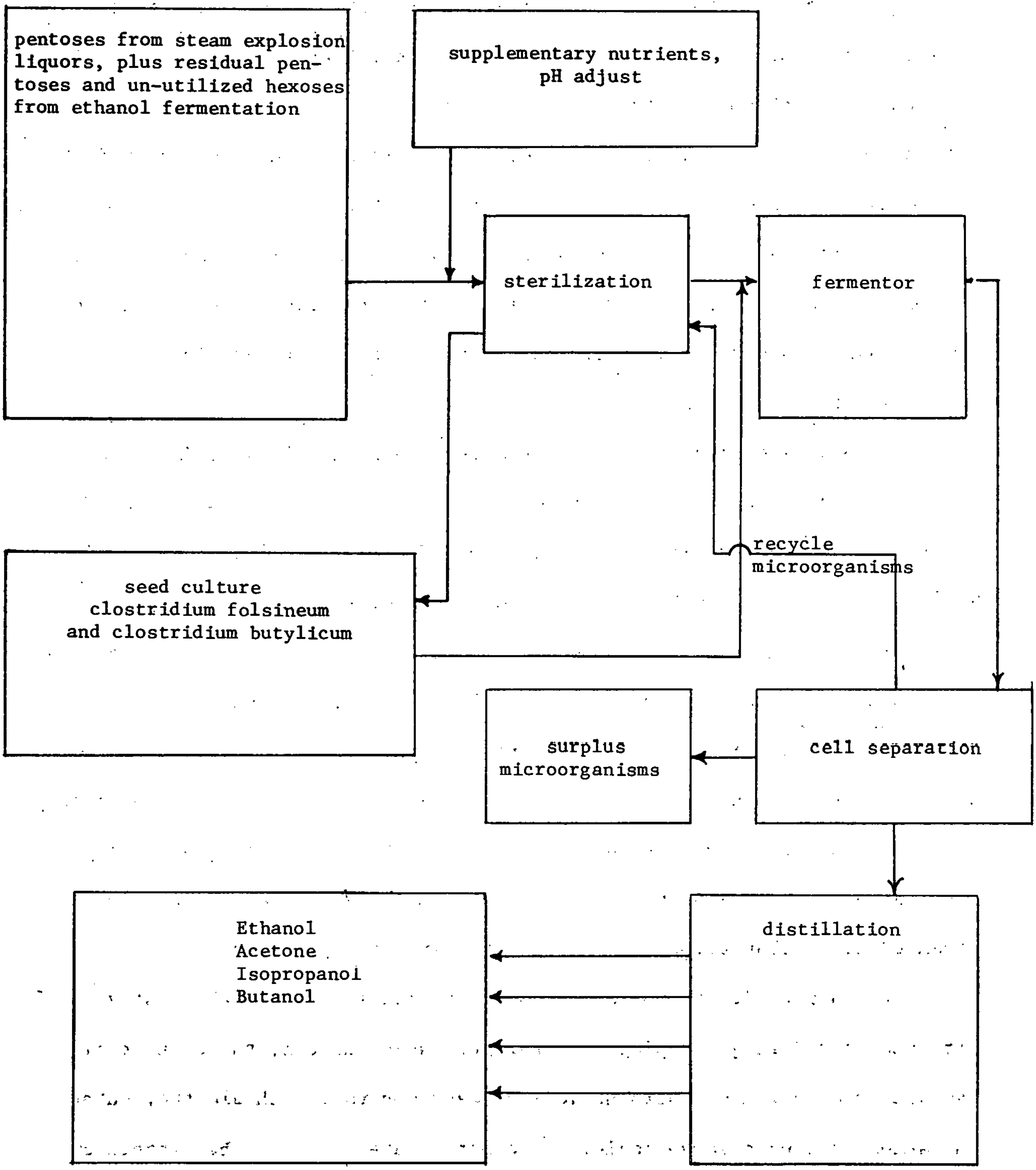
Since removal of hemicellulose prior to acid hydrolysis of the cellulose would reduce the opportunity for conversion of pentosans to toxic chemical compounds which could subsequently inhibit the conversion of glucose to ethanol, it may be desirable to ferment the hemicellulose hydrolysate separately with organisms such as Clostridium felsineum and Clostridium butylicum resulting in the following product distributions (yields based on sugar conversion):

Product	C. Felsineum	C. butylicum
Butanol	57	60
Ethanol	18	8
Acetone	24	4
Isopropanol	--	25

Since such organisms utilize both hexoses and pentoses, separation of the mixed sugars would not be required. In the case of the process shown in Figure 7.1. , the overall yield on a dry wood basis would be about 15-20%. Once again, all of the products can be used as liquid fuels, although a higher economic value might be realized if the uses were directed towards chemical intermediates or solvents. A block diagram is presented in Figure 7.5.

FIGURE 7 -5.

BLOCK DIAGRAM OF BUTANOL-ACETONE UNIT



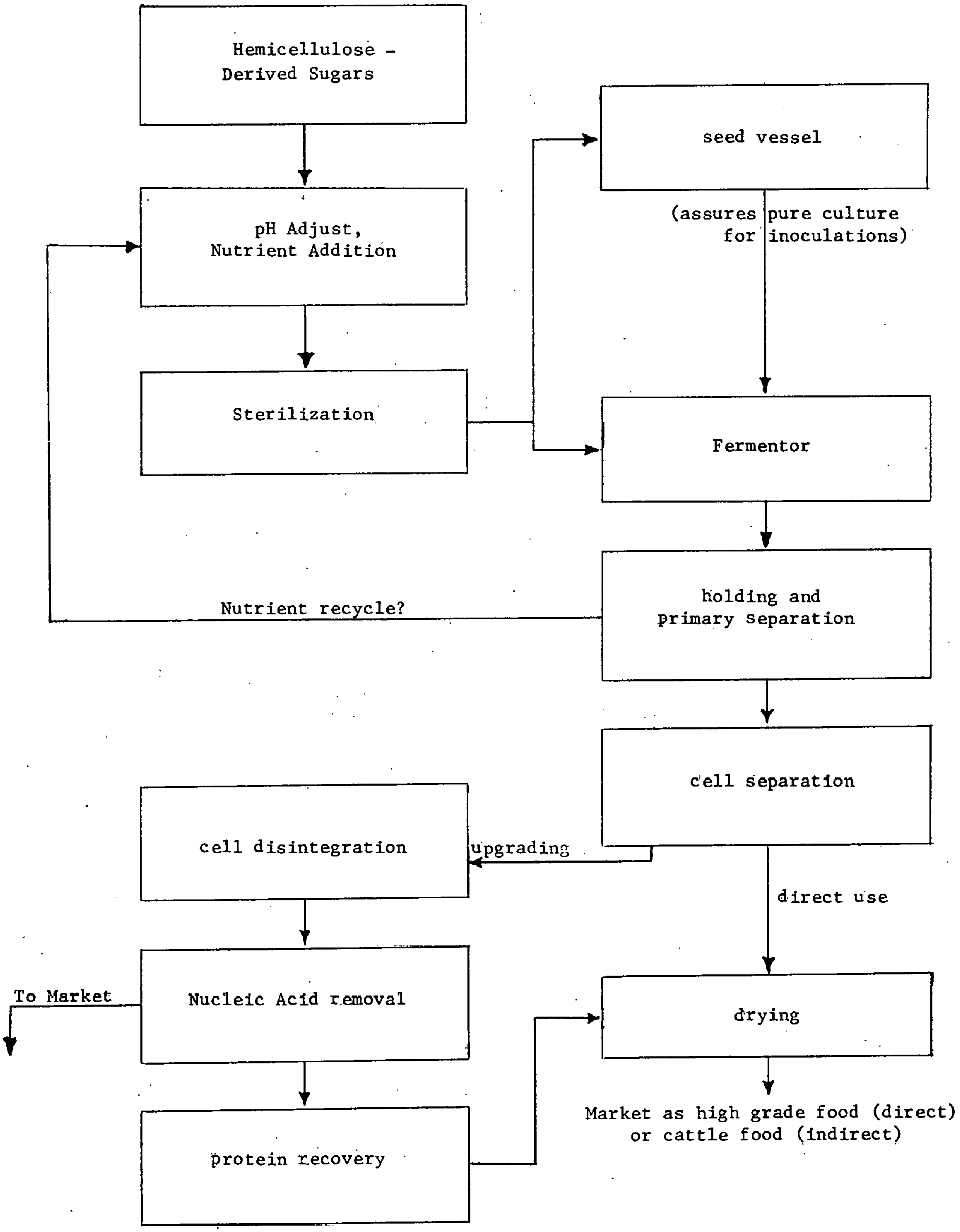
If a product of higher economic value is desired, the conversion of hemicellulose to single cell protein can be envisioned as shown in Figure 7.6. Continuous commercial processes for the growth of Torula and other desirable strains of yeast are currently in production. The current value of Torula is $300.00 per ton. Yields in the 20-25% range based on sugar content can be expected. On a dry wood basis, this amounts to about 4%. Furthermore, this material might be combined with the surplus yeast generated by the fermentation of the hexoses to ethanol and targeted towards a common outlet. If the process is carried beyond cell separation, the final products could be upgraded to nucleic acids and single-cell protein. These are also high-value products.

Carbon dioxide should be regarded as an economically useful by-product only if it can be passed along to a nearby user in the gaseous state. The capital costs involved in the compression and transport of this material would otherwise seem to be inappropriate to an energy production system.

7.3. In addition to economic and energy related questions which must be considered in making decisions about by-product recovery, it must not be forgotten that all materials not consumed or recovered in the various subprocesses are wastes and therefore must be disposed of in an environmentally acceptable manner. Thus, even in cases in which the economics or energy requirements are unfavorable, it may still be necessary to recover a by-product rather than allow it to leave the site as a pollutant.

For example, it may not otherwise be desirable to trap the most volatile terpenes lost during chipping and storage. Nevertheless, these materials can act as a source of photochemical oxidant generation should they enter the atmosphere on a large scale. If controls are likely to be imposed on

FIGURE 7-6. SINGLE-CELL PROTEIN FROM HEMICELLULOSE



such emissions, then recovery may have to be considered even if the value of the recovered material does not fully offset the cost of the recovery operation.

The ash content of the original biomass plus other inorganic salts added as a consequence of treatment represent another low-value material which may have to be recovered and sold as a by-product rather than being allowed to enter the environment. If the ash content of the biomass could be transformed to a more readily assimilated form, it might be returned to the land as a low-grade fertilizer. Once again, the economics are highly unfavorable and such a recovery scheme would only be considered if regulations do not permit these materials to be discharged as a process effluent.

Dilute streams of organic materials promise to be another waste disposal problem which will force the adoption of recovery schemes which are energetically and/or economically unattractive. Since most of these can be expected to be relatively high in biochemical oxygen demand (BOD), degradation by microorganisms would seem to be the most attractive form of disposal/recovery. It will be a real test of ingenuity to devise schemes which involve extremely low capital costs yet which will still afford some recovery of either energy or capital and which will furthermore also be effective in removing dilute organic materials from large volumes of water. The growth of fungi in plastic-lined pits is an example of a process which would involve very low capital costs and which would remove such things as pentoses and hexoses from solution in the form of a marketable product. If the growth medium is maintained at a sufficiently acid pH, the growth of competitive organisms will be inhibited. Thermophilic anaerobic digestion of organic wastes might be another means of removing dilute wastes while generating a small energy credit to partially offset the costs of treatment. In this case, however, process control would be more difficult to maintain and capital costs would be greater. Waste disposal and pollution control problems are bound to be a part of any process which is employed for the conversion of biomass to liquid fuels. The costs associated with the resolution of these problems may, in many cases, be partially offset by by-product recovery operations.

It will probably be wise to defer a more detailed consideration of this item until more is known about the nature of the waste streams and the environmental constraints which will be placed on the process.

In conclusion, it is evident that by-product recovery must be supportive of the overall process in order to be seriously considered. This support must take the form of an energy credit (i.e., the by-product is also a liquid fuel), an economic credit (i.e., the by-product must command a high price) or an environmental credit in which case the by-product although not necessarily having a high value in itself must offset the costs of treating a waste material. Since lignocellulosic materials contain significant quantities of biochemical raw materials which cannot be converted to ethanol, it is further evident that some by-product utilization will be required. Therefore, it is philosophically important to note that several of the major by-products suggested in this section can also serve as liquid fuels and that the utilization of such materials is fully consistent with the overall project goals. In fact, an on-site blending of the aromatic hydrocarbon by-product stream with the primary product could provide a liquid fuel which is more highly suited for eventual addition to gasoline than might be the ethanol alone.

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8.0. PROCESS ECONOMICS

Of fundamental importance to ethanol fermentation is the cost of the fermentable sugar. There are a number of sources of sugar including sugar crops, grain crops (starch), and cellulosic materials. In each case, there are two unit costs involved: (1) the cost of the raw material itself, and (2) the cost of converting the raw material to a sugar solution. For the sugar and grain crops the conversion cost is relatively low as compared to that of the cellulosic materials.

The price of raw sugar has varied widely over the last few years ranging from $0.01 to $0.65 per pound of raw sugar (1). 1977 costs for sugar in molasses and in cane juice were reported to be $0.05 and $0.06 per pound of sugar respectively (2).

Grains, such as corn, contain starch which is easily hydrolyzed to sugar solutions. The effect of corn price on the raw material cost of hexose from corn starch is shown in Table 8.1. (3).

The cost of converting the corn into hexose would be a nominal $.01 per pound of hexose.

Cellulosic materials are much more difficult to hydrolyze than is starch. There are two general methods of hydrolyzing cellulose, enzymatic and acidic. Neither method currently produces a 100 per cent conversion of cellulose to hexose. Recent publications describing enzymatic hydrolysis processes use a yield of 0.45 pound of hexose per pound of cellulose (41% of theory) with 0.55 pounds of cellulose remaining unhydrolyzed (4,5,6). Similarly various acid hydrolysis processes use yields of 0.6 pounds of hexose per pound of cellulose (55% of theory) with a varying portion of the unaccounted for cellulose being degraded into chemical by-products (7,8). A solvent

Table 8.1. Effect of Corn Price on Raw Material Cost of Hexose from Corn Starch*

	Corn Starch				
Price of Corn $/Bushel	1.5	2.	2.5	3.0	3.5
$/Ton	54	71	89	108	125
Raw Material Cost, $/lb of Hexose	.036	.049	.061	.073	.086

* GT calculations based on Reference (3).

acid hydrolysis process is described as converting 97% of the cellulose into hexose (9,10). Obviously not only the unit cost of the raw material but also the yield will dramatically effect the unit cost of the hexose produced.

The effect of corn stover price and yield on the raw material cost is shown in Table 8.2. The corn stover is assumed to be 40 percent cellulosic (hexsans only) materials on a dry basis (1). The effect of wheat straw price and yield on the raw material cost is shown in Table 8.3. The wheat straw is assumed to be 34 percent cellulosic (hexosans only) material (5).

The effect of wood chips price and yield on the raw material cost is shown in Table 8.4. The wood chips are assumed to be 55% cellulosic materials and 25% lignin.

There have been a number of processes proposed to convert cellulose to hexose. Wilke, Yang and van Stochar (1977) at Berkeley estimated that an enzymatic plant with a feed of 885 ton per day of newsprint would produce hexose for a conversion cost of $0.052 per pound of hexose (yield of 0.35 lb. hexose per pound cellulosic materials) (4). Recently Spano _et al_ (1978) at Natick estimated a similar process to treat 230 ton of cellulose per day from urban waste, wheat straw, or poplar would produce hexose for a conversion cost of $0.054 per pound of hexose (yield of 0.45 lb. hexose per pound cellulose) (5). With a design based on data from Berkeley and Natick SRI calculated a conversion cost of $0.19 per lb. of hexose for a facility to treat 3300 ton wheat straw per day (yield of .45 lb. hexose per pound hexsan) (5). Grethlein (1978) estimated a conversion cost of between $0.018 to $0.025 per pound of hexose for a continuous acid hydrolysis facility (yield of 0.47 pound of hexose per pound of cellulosic materials) (7)*.

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*Based on newsprint. Excludes raw material cost.

Table 8.2. Effect of Corn Stover Price on Raw Material Cost of Hexose from Corn Stover *

Cost of Corn Stover $/dry ton	$15	$20	$25	$30	$35	$40
Raw Material Cost, $/lb. of hexose, Based on yield of 0.45 lb. hexose per pound of cellulosic materials	.04	.056	.070	.084	.098	.112
Raw Material Cost, $/lb. of hexose, Based on yield of 0.6 lb. hexose per pound of cellulosic materials	.032	.042	.052	.062	.072	.084
Raw Material Cost, $/lb. of hexose, Based on yield of 0.75 lb. hexose per pound of cellulosic materials	.026	.034	.040	.050	.058	.066

* GT calculations based on Reference (1).

Table 8.3. The Effect of Wheat Straw Prices on Raw Material Cost of Hexose from Wheat Straw *

Cost of Wheat Straw $/ton	$10	$15	$20	$25	$30	$35
Raw Material Cost, $/lb Hexose, Based on yield of 0.45 lb. Hexose per lb. of cellulosic material	.033	.050	.066	.081	.098	.114
Raw Material Cost, $/lb Hexose, Based on yield of 0.6 lb. Hexose per lb. of cellulosic material	.024	.038	.050	.062	.074	.086
Raw Material Cost, $/lb Hexose, Based on yield of 0.75 lb. Hexose per lb. of cellulosic material	.02	.030	.039	.050	.059	.069

* GT calculations based on Reference (3).

Table 8.4. The Effect of Wood Chip Price on Raw Material Costs of Hexose from Wood Chips

Cost of Wood Chips $/dry ton	$20	$25	$30	$35	$40	$45
Raw Material Cost, $/lb. of Hexose Based on yield of 0.45 lb. Hexose/ lb. cellulosic	.040	.051	.060	0.071	.080	.091
Raw Material Cost, $/lb. of Hexose Based on yield of .6 lb. Hexose/lb. cellulosic	.033	.041	.050	.058	.066	.074
Raw Material Cost, $/lb. of Hexose Based on yield of 0.75 lb. Hexose/lb. cellulosic	.025	.031	.037	.043	.048	.054

* GT calculations based on Table 8.3.

Arthur G. McKee & Company (1978) estimated a conversion cost of $0.035 per lb. of hexose for a facility to treat approximately 1800 tons of corn stover per day using a solvent acid hydrolysis process (yield of 1.07 lb. of hexose per pound of cellulosic material) (9). Battelle (1978) for a similar solvent acid hydrolysis process estimated a conversion cost of $0.047 per pound hexose for a facility to convert 1400 tons per day of corn stover (1.07 pounds of hexose per pound of cellulosic materials) (10).

Reported cellulosic conversion costs then range from $0.018 to $0.19 per pound of hexose. Since the cost estimating used to calculate the conversion costs varied dramatically, it is not possible to directly compare each process only on the basis of conversion costs. It appears safe to assume, however, that the conversion costs for the cellulosic materials will be at least twice that of starch (a nominal $0.01 per pound of hexose). From the relative raw material costs, it is apparent that high conversions of the cellulosic materials into hexose will be necessary for it to be competitive with corn. In all of the aforementioned conversion cost estimates, no credit was taken for by-products such as pentoses, unreacted cellulose, and single cell protein. Credits for such by-products can dramatically affect the unit costs of the hexose produced.

The current price of corn is approximately $2.50/bushel. For the production of hexose, the raw material cost due to the corn would be $0.061/pound (see Table 8.1).With a conversion cost of $0.01/pound hexose, the estimated sugar cost would be $0.071/pound for a corn process. The by-product from the corn process, distillers grain feed, could contribute a credit of $0.026/ pound of hexose (3). Thus hexose from corn would be from $.035 and $.071 per pound of hexose. In order to be cost effective, sugar from cellulosic materials must be competitive. This can be accomplished only by optimizing hexose from cellulose costs including raw material costs.

Ethanol at $1.20/gal. of 95% ($15/MMBTU) is the equivalent of $0.077/ pound of hexose. The cost of converting hexose to 95% ethanol is approximately $0.02 per pound of hexose. Thus the cost of ethanol (95%) can be held to below $1.20/gal. if hexose can be produced from cellulosic materials for $0.057/pound hexose.

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APPENDIX A

BIOMASS SURVEY DATA

INFORMATION FROM TELEPHONE CALLS MADE 1/11 - 1/15

STRAW RESIDUES

I. Cost estimates: $60 per ton appears to be a realistic estimate - assumes that Tech purchases when harvested. (wheat straw)

Estimates of cost supplied by individuals

McWhorter (Ga. Dept. of Transportation): Should be able to get it for $40-60 per ton.

<u>County Agents</u>

Bigham: $1 per bale (35-40 lbs. in bale) delivered to Atlanta.

Daniel: around $70-75 delivered; not over $80.

<u>Farmers</u>:

Waters: $1.25 per bale at barn; $1.50 per bale delivered in Atlanta; 70-75 bales in a ton

McClure: $70 per ton delivered

Anderson: 3 1/2¢ - 4¢ per pound delivered.

II. Factors affecting cost.

1. Weather: Amount of rain and variations in temperature
2. Price of wheat this season influences the amount planted the next season. Anderson (farmer) said he knew that 4,000 additional acres were planted in Newton County this year because of higher wheat prices.
3. Time of purchase: Virtually everyone remarked that the price would be less if the farmer didn't have to store the straw. Brannen (county agent) commented that storage changes/lessens the nutritive content of the straw.

4. Combining and delivery. "It costs as much to combine, etc. the

poorest straw as it does the best hay." The farmers don't want to sell in ton lots - they like handling bales. One of the farmers told me that the straw had to be baled to get it off the field - this I don't believe.

In discussing costs, one of the county agents referred to the impact of whether a farmer has to load and unload the truck. This could mean that if Tech supplied the manpower to unload the straw, the price might be less.

III. Straws Available:

Wheat straw appears to be the most likely feedstock - that is, it is available in sufficient quantities.

Only one farmer (Anderson) indicated that he had straws other than wheat available. The farmer who is closing shop has oat straw currently. There was general agreement among all the comments that wheat was the best prospect of those named, followed by oats and rye in that order. The comments about the availability of sorghum were all negative. One person said Georgia mountain area might have some but getting it would be too costly.

Several people asked if soybean and peanut vines were being considered and Bigham (county agent) stressed the values (from the farmers's point of view) using a "trash" crop as a feedstock for the project - "trash crop" being in effect the results of the cleaning of an idle, uncared for field.

IV. Sources/locations of supply:

Information provided indicates that wheat straws can be obtained from Newton, Henry, Fayette, Butts, and Jackson counties.

All 7 of the county agents indicated willingness to help identify farmers who could supply straw. Not surprisingly, agents in DeKalb, Fulton, and Cobb were not optimistic about straw being available in any significant amount in those counties. The agent in Cobb said you might get some if there were a central collection point in the county to which farmers could bring small amounts. Straw is available in Rockdale county the agent said, but all of it is sold to nurseries in Atlanta for mulch - going rate is $1.00 per bale delivered.

The agents from both Fayette and Butts counties said they were confident that straws could be obtained from those counties but they did not want to estimate how much. At the farmer's meeting in Henry County, Pipkin (county agent) said 15 farmers indicated interest in supplying straw and he has their names.

Each of the farmers I talked with volunteered the information that there were other farmers in his county who would have straw for sale. Anderson said he had approximately 150 tons this year. McClure said he usually had wheat straw available all year - about 10,000 bales this year (200 tons?). Waters couldn't estimate what he had. He did tell me that 70-75 bales = a ton; to offer delivery in 300 bale lots, as he did in his ad, suggests he must have a large quantity available.

V. Harvest time for wheat straw

Newton County: May 15 - June 15, no later than June 20

Butts County: June

Jackson County: Mid-June

Telephone Calls Jan. 11 - Jan. 15

Calls made to:

County Agents

DeKalb County	371-2821	Newton Hogg

Fulton County	572-3261	Robert Brannen
Cobb County	422-2320	Bill Durden
Rockdale County	922-7750	LeRoy Bigham
Butts County	404-775-2601	Millard Daniel
Henry County	957-9131	John Pipkin
Fayette County	404-461-4580	Aubrey Varner
Georgia Dept. of Transportation	293-8911	Barry McWhorter

Farmers advertising in Market Bulletin

Covington	404-786-0182	J.O. Anderson
Commerce	404-335-3867	Dan Waters
Jefferson	404-367-8695	B.E. McClure
Jackson	404-775-2550	Lester Barnes (Going out of business - won't have anymore)
Jack Mathis	894-3863	
Sandy Morehouse	581-7228	

call from

Bud Greer Dairy man in Henry County 946-3130

Telephone Conversation with Alexander Morehouse 1/16:

He is a farmer and apparently some kind of broker/agent. Jack Mathis referred me to him. Am not even certain I have spelled his name correctly. He is going to write me a letter, however.

He said he would like to supply the straw - all that Tech would need - that he would not have all of it on his farm - it would come different places.

He said straw is currently an "elusive" commodity. MARTA is responsible in part. It might be necessary to pay for it in advance to "definitely lock it in.

As to costs, he did quick figuring on the phone: $1.50 per bale delivered to Atlanta; 35 lbs. to bale; 57 to ton; $85 per ton. That he said was high; he thought he could do better.

Summary of Telephone Conversation with Barry McWhorter, Ga. Dept. of Transportation (292-8911) - MEA:

The Department uses the Market Bulletin to locate sources of supply. Once sources are identified, the Dept. has to get 3 bids and take the lowest bid.

The Dept. can't use mixed straw. Don't like it to include weeds. Uses a lot of week straw.

Dept. buys in ton lots. Prices vary. Time of year and weather/crop affect price. Last year during the winter were paying $80-90 per ton delivered to the site where it was to be used. In the summer right after it was harvested, price was $50-60 per ton but crop wasn't good because of dry weather. His estimate of normal price range is $40-60 per ton delivered to site.

He agreed that the farmers want to sell it by bale rather than ton but said that Tech should insist on tons. That the farmers can load it on the truck and then weigh it although they don't like to weigh.

He offered the name of a farmer from whom the Dept. had always been able to secure straw. Turned out to be McClure to whom I had already talked.

Call from Bud Greer (Dairyman in Henry County) 1/12:

Greer had attended the meeting (Henry County) at which Mr. Pipkin had asked about potential interest of farmers in supplying straws. Greer's call was an awkward one for me because I had someone in the office who had to wait while I talked with Mr. Greer and I had trouble bringing his call to a conclusion.

Among other items, Mr. Greer explained at some length that:

1. He believed you would get a better return from using manure or grain as feedstocks.
2. He felt the demonstration should be conducted outside of Atlanta - where wheat and the other grains are grown in quantity.
3. He had carried out lengthy but unproductive negotiations with a brewery in the Atlanta area in regards to selling it wheat and buying residues from the brewery.
4. He would be interested in selling straws to Tech and buying residues/waste from the project.
5. Dairies would be a source of supply.

Corn Stubble/Stover Telephone Summary

I. Costs: Maybe $45 per ton plus delivery

Most of the men seemed to feel that the cost of the stubble would be about the same as for the straws. Considering that 4 of the 5 estimates did, not incude delivery, their reaction seems consistent that is, the estimates they gave correspond to the estimates for the straws when delivery charges are included.

Unlike the straws, however, none of the cost estimates have come from farmers who are actually selling stubble. There have been no ads in the issues of the Market Bulletin that I have checked and I haven't asked the county agents for the names of specific farmers. Specific estimates provided by the various individuals were:

$40-45 per ton plus delivery (Brown, Laurens)
$30-50 per ton plus delivery (Andrews, Washington)
$50 per ton plus delivery (Brach, Carroll)
$40-50 per ton plus delivery (Hamilton, Coweta)
$50-75 per ton delivered (Sheffield, GFB)

II. Factors related to availability and costs:

Until big baling equipment came into use, the normal procedure was either to turn livestock into the fields to eat the stubble or to plow it back into the fields as a soil supplement. With the advent of big baling equipment, big bales (round bales) are harvested and used as a supplemental feed for livestock. The stubble has low nutritional value but farmers use it in connection with some of the new high protein feeds.

In harvesting, the machines take the ears of corn off the stalk and rub the grains off the cob. The cobs and shucks are ground to bits in the process. Stubble is, therefore, essentially the corn stalks.

The big bales (round bales) present no real storage problem because they do not have to be sheltered. Rain may penetrate as much as an inch but it's almost as if a protective coating or sealant developes that moisture cannot penetrate. Small bales (square bales) have to be sheltered so there is a storage problem with them.

The obvious factors of weather, amount of corn planted, etc. will influence both cost and availability of stubble.

III. Location and availability of supply: Laurens, Washington, Carrol Counties:

Mr. Brown said there was plenty of corn stubble available in Laurens County right now and unless there was an unusually poor crop, Tech should be able to secure large quantities (probably all that was needed) from that county. He recommended that 8 months prior to the anticipated time of need that Tech negotiate a contract with farmers to supply the stubble. He indicated that the contract should be written during the planting season. He can supply the names of farmers. He also said he knew one man who had big baling equipment with whom Tech could contract. And then this man could gather stubble from a number of farmers. We discussed Tech placing an ad in the Market Bulletin and he pointed out the disadvantages (possibility of getting hundreds of replies and having to check them) but felt it was worth doing.

Mr. Andrews said stubble is and will be available in Washington County. He can provide the names of farmers who have it.

Mr. Brach said that much of the corn in Carroll County is cut for silage but that some stubble is available. He can provide the names of farmers who have it.

Mr. Hamilton said the availability of stubble in Coweta County depends on the price of corn -- that the farmers there will not plant much corn unless the price of corn is higher than it is now. He is retiring during 1979 but said he was confident that his successor would help to identify farmers who would have stubble. Doesn't appear to be a good county to depend upon in spite of its proximity to Tech.

Mr. Emberson indicated that although corn is grown in Morgan County, it is either cut for silage or the stubble is used by the farmers as feed or as a soil supplement. He does not feel any of the stubble would be for sale.

IV. Harvest season: August - November

In the south Georgia counties (Washington and Laurens) harvesting begins in August; in the counties closer to Atlanta, in September.

Calls made to:

Dr. James J. Jackson	Agronomist, Univ. of Ga.	404/241-2978
Joe Kelley, Exec. Secretary	Ga. Corn Millers Assoc.	404/678-7971

The Association has been disbanded.

Mr. Sheffield	Grain Marketing Specialist	912/474-8411
	Ga. Farm Bureau Markeing Assoc.	
	County Agents	
John Emberson	Madison (Morgan County)	404/342-2214
Gerald Andrews	Sandersville (Washington)	912/552-2011
J.D. Brown	Dublin (Laurens)	912/272-2277
Bruce Hamilton	Newnan (Coweta)	404/253-2450
Carl Brach	Carrollton (Carroll)	404/834-2019

APPENDIX B

COST DATA

LISTED MARKET PULP PRICES AND ESTIMATED PRODUCTION COSTS

(January 25, 1979)

KIND	U.S.A. LISTED PRICE	U.S.A. ESTIMATED PROD. COST	CANADA LISTED PRICE	CANADA ESTIMATED PROD. COST
Sulphite Pulp				
Bleached	$345/S.T.	$242/S.T.	$370/M.T.	$259/M.T.
Unbleached	-	-	317/M.T.	222/M.T.
Kraft (Sulphate)				
Bleached:				
Softwood	$340/S.T.	$238/S.T.	$395/M.T.	$276/M.T.
Hardwood	320/S.T.	224/S.T.	365/M.T.	255/M.T.
Unbleached:				
Softwood	-	-	350/M.T.	245/M.T.
Hardwood	-	-	350/M.T.	245/M.T.
Semi-bleached	$345/S.T.	$242/S.T.	385/M.T.	270/M.T.
Groundwood Pulp				
Bleached	-	-	250/S.T.*	$200/S.T.
Unbleached	-	-	270/S.T.*	216/S.T.

* f.o.b.   S.T. = Short Ton   M.T. = Metric Ton

Notes: (1) Listed price for wood pulp is generally given on delivered basis except groundwood pulp which is given on f.o.b. basis.

(2) Actual sale prices are generally below of listed prices pending upon individual negotiation.

(3) Estimated production costs are based on 70% to 80% of given listed prices. Estimated production ocsts include depreciation and debt service.

APPENDIX C

PERSONAL CONTACTS

Personal Visits and Meetings

U.S. Army Laboratories, Natick

Dartmouth College, Thayer School of Engineering

Massachusetts Institute of Technology, Biochemical Engineering

Dynatech R/D Co.

University of California, Berkeley, LBL

U.S. Department of Energy, Fuels-from-Biomass Branch

Vogelbusch (Austria: Houston, U.S.A.)

Alfa-Laval (Sweden)

Arizona Chemical Co.

Glidden-Durkee, Div. of SCM

Champion Paper Co.

Brusnwick Pulp and Paper

Hercules (Brunswick, GA)

Telephone Communications

University of Alabama (G.C. April)

University of Pennsylvania (E. Kendall Pye)

Battelle (E. Lipinsky)

Bechtel National, Inc. (J. Yu)

Iotech (E.A. DeLong)

Rutgers (B. Montenecourt)

General Electric R & D, Schenectady (R.E. Brooks)

Vulcan Cincinnati, Inc. (D.R. Miller)

Purdue University (G. Tsao)

Stake Technology (M.S. Ozechowsky)

Gulf Oil Chemicals Co.

U.S. Forest Products Lab, Madison (J.F. Saeman)

Reed Canada (J. Benko)

Rensselaer Polytechnic Institute (H. Bungay)

U.S. Army Laboratories, Natick (L. Spano et al)

Columbia University (H. Gregor)

Hydrocarbon Research, Inc. (M.W. Jones)

Dept. of Energy, Mines & Resources, Canada (R. Overend)

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