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An Aspen Simulation of Fuel Production by Hydrolysis of Woody Biomass

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ABSTRACT

An integrated process, in which woody biomass was converted to fuel, was simulated using the ASPEN simulator. For purposes of simulation, the process was divided into four sections, biomass refining, hydrolysis, bioreaction, and fuel separation. Detailed attention was paid to the hydrolysis process and the bioreactor, while a general simulation of the front-end biomass refining process and fuel separation step at the end of the process is included. A simulation of the biomass and active microbial system required the definition of nonconventional streams. The emphasis in this study was upon the effect of varying acid recycle in the two-step hydrolysis process. As the recycle ratio increases the operating cost of the overall process passes through a minimum. Suggestions for the refinement and extension of this approach are discussed. Its advantages in establishing the cost of proposed technologies, assessing areas where research and development are required and evaluating schemes for enhancing energy efficiency were all evaluated.

Index Entries: Simulation; hydrolysis; woody biomass; bioreactors; fuels.

INTRODUCTION

A wide variety of processes have been studied and are currently under development that use waste- or low-valued carbonaceous materials as a feedstock to facilities for the production of fuel or other chemicals by hydrolysis to sugars and subsequent conversion to a variety of chemical species by fermentation. Many variations have been proposed on this basic theme but each has its merit and failings. Comparison of competitive

processes is often made difficult by complexities of the processes, differing levels of optimization to which the processes have been subjected, and problems that are hidden in the separation and disposal of wastes. These cannot be ignored in the overall evaluation of these processes.

Generally, experimental programs that seek to explore all of the important features and variables of a complex process must be more extensive than most funding will support. Therefore, judgment and compromises become important in arriving at an optimal process. However, computer simulation can also be used as a tool to aid in the decision process. Typically, biomass conversion includes four process areas: feedstock preparation, which includes such processes as size reduction, washing, screening, and dispersion; hydrolysis, which includes reaction, acid recovery, and sugar purification; bioreaction; and product purification. There is a great deal of interaction between the sections of typical plants, and therefore an optimization based on any reasonable criteria is a formidable task, even with computer assistance.

The choice of a computer simulator was a relatively simple process of elimination. Because we wanted to retain the possibility of simulating any process, a commercial simulator, which allowed the "assembly" of plant units as modules was absolutely necessary. The other major factor, which led to the elimination of all simulators but ASPEN, was the need to deal with materials that are not characterizable by normal molecular properties, such as molecular weight, and critical properties (*1*). ASPEN is the only major simulator which allows the processing of these "nonconventional" solid materials in a wide range of reaction and separation equipment. Therefore, it was selected for the current study.

The primary objective of this study was to demonstrate the use of the ASPEN simulator with the complex materials like wood and biomass, using a typical process example to illustrate the power of the method. Although most simulators deal exclusively with materials that are characterizable by molecular weight, critical parameters, and standard thermodynamics calculations, which describe standard chemical species, such as water, ethanol, and glucose, ASPEN adds nonconventional components. Streams are subdivided into conventional and nonconventional substreams, which coexist and are acted upon separately by the processing steps through which the streams pass. Thus, heat and material balances may be obtained for all of the standard processing devices with both types of material. This capability is a particular advantage in addressing simulation problems that involve microorganisms and biomass. Here we can define the nature of those materials that are particularly germane and still retain the material and energy information that is appropriate to materials characterized by molecular weight.

A significant number of approaches are available for economic evaluation of bioprocessing plants. (*2,3*). The ASPEN simulator has built-in costing and economic analysis capabilities that allow preliminary-estimate quality investment predictions to be made on any stream. Indeed, it

is possible to optimize a given flowsheet based on a maximum rate of return criterion. In this study we have chosen to confine our analyses to mass and energy balances, but economic analyses will be an important part of future work.

ASPEN MODELING OF STREAMS CONTAINING BIOMASS

Because the processes we are dealing with contain two materials (wood and biomass), which cannot be characterized by conventional means, it is important to discuss the description of these materials before the specifics of the flowsheet are analyzed. The feedstock to most proposed processes is some variety of plant material such as wood, paper, or vegetable matter, for example, corn stovers. All of these can be described within the framework of a single material type. For the sake of unity of approach, the mass of bacteria used in the subsequent bioreactors was modeled within the same framework, although some of the detailed structure of woody biomass was not required in this study and was omitted.

ASPEN allows the defining of primary and secondary attributes in characterizing nonconventional materials. As shown in Table 1, the composition of woody biomass is divided into four primary attributes that closely match typical characterizations that are used in the pulp and paper industry (*4*). The ***fiber*** is the cellulosic portion of the material. The fibers can be further characterized by an associated secondary attribute called the *Fiber Index*. This is, of course, the portion of the woody biomass that is generally of specific interest in biomass hydrolysis. The fiber fraction of a woody biomass varies considerably from material to material, but 55% is a typical value. ***Moisture***, which makes up about 21.4 wt% of the woody biomass, is the second primary attribute listed. Since it simply consists of water, no further characterization is required. On the other

Table 1
Attributes of Woody Biomass

Primary attribute	Secondary attribute
Fiber	Fiber index
Moisture	
Volatile material	Hydrogen
	Oxygen
	Nitrogen
	Void volume
Fixed solids	1
	2
	3
	4
	5

hand the third primary attribute, ***volatile material***, which consists of fixed gases and void space, requires a secondary attributes list to specifically quantify these constituents. ***Volatile material*** contributes ~8% to the woody biomass, half of which is *Void Volume*. Finally, ***fixed solids*** make up the remainder of the material. As secondary attributes, five solids have been allowed; we have specified only two (ash and lignin) in this simulation.

The specification of the attributes of the woody biomass allows us to perform all of the tasks associated with the mass- and energy-balance simulation. Specifically, we have used a linear summation of the mass contributions to the primary attributes to specify the enthalpy of the material. Thus, composition changes will be reflected in the enthalpy. A similar technique was used to estimate the density of the woody biomass, again taking account of both the temperature and composition variations. Since reactions and separations occur in any biomass process in which there is interest, the composition (say of ***fiber***) will serve as the driving force for the hydrolysis reaction, and as a result of the process, be depleted. Similarly, the microbial mass will be increased by the conversion of glucose to ethanol. Provision for such processes are included in ASPEN.

In the handling and separation of nonconventional solids, it is crucial to characterize the particle-size distribution of the material. Reaction rate is closely dependent on penetration into the material; and hence, the degree of subdivision of the material is a primary factor in the overall reaction rate. Second, many separation processes, such as filtration, centrifugation, and electrostatic precipitators, are dependent on differences in particle sizes to perform separations. Therefore, it is necessary to include a particle-size distribution along with the substream composition to accommodate such requirements.

MODELING OF A BIOMASS CONVERSION PLANT

The detailed simulation of a major biomass simulation plant is a relatively long-term task; however, it is possible within the ASPEN context to simulate at different levels of accuracy. Therefore, as an initial effort we sought to divide a generic processing plant into units that were not interdependent, and thus could be viewed as independent entities. The result, based on a review of some current processes (*4–6*) is shown in Fig. 1, which consists of a four-process plant. Coupling of the four processes into an overall processing plant is simply a matter of tying streams, a relatively straightforward operation, when all portions of the simulation are complete. In this study, the emphasis was on resolving some of the simulation questions surrounding the hydrolysis and biomass reactors, which are the central parts of the overall processing plant.

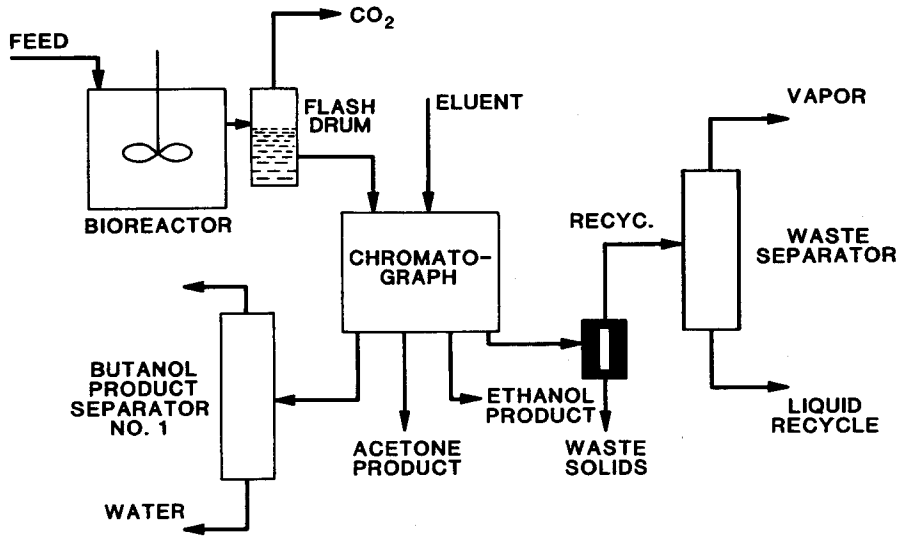

Fig. 1. Flowsheet for the simulation of a woody biomass conversion process.

Since a significant portion of the energy and materials used in processing woody biomass to produce fuels is often expended in the preparation of the material for the hydrolysis process, it is important that a feed preparation section be included in the proposed simulation. There are wide differences among starting materials, mitigating against providing a general simulation. The overall objectives of this portion of the plant are to remove unusable portions of the feedstock, such as bark, and to reduce the size of the feed material to a size that will allow it to be used as feed to hydrolysis reactors. The ultimate result of these operations should be clean particulates, ~10–50 μm in size, in a 10% aqueous suspension. Wood pulping for papermaking is a good example of such a process. An ASPEN simulation of a pulping process is available and has been accommodated to the current study. A flowsheet of the pulping process is given in Fig. 2. Although there would be significant change in a process that used corn stovers or waste paper, the flowsheet shown in Fig. 2 could be accommodated to such service. Furthermore, we can conclude that, aside from some recycle of process water and possibly some heat economies, there is little feedback from the downstream parts of the process. Therefore, as a first generation simulation this portion can stand alone.

The second and third major sections, shown in Fig. 1, are the hydrolysis and bioreaction parts of the plant. These were considered in detail in succeeding sections. Again, there is little feedback from the third to the second section in the preliminary flowsheet simulation that has been achieved in our study. Therefore, they can be separately considered without loss of generality, thus avoiding time-consuming internal itera-

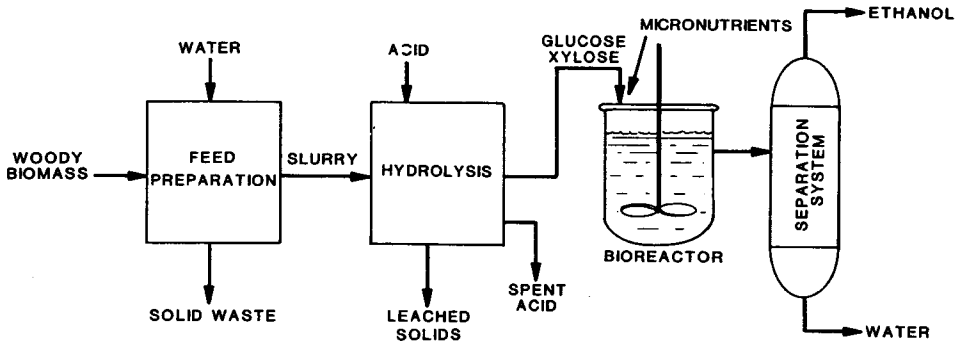

Fig. 2. A flowsheet for the simulation of the pulping woody biomass using ASPEN.

tions. In future work, a closer examination of the coupling of these two section will be required.

The separation section of the plant is the fourth process portion. It is typical of distillation units, extraction systems, and heat exchangers, which are routinely simulated throughout the processing industry. These simulations are considered to be established coding procedures. Therefore, these have been simulated using zero-order procedures, with the expectation of upgrading them when the hydrolysis and bioreaction sections attain a suitable level of precision. Feedback to the reactor section is unlikely to be important, at least at the current level of detail.

DETAILED MODELING OF THE HYDROLYSIS UNIT

The central portion of any proposed woody biomass facility is its hydrolysis process. Two fundamentally-different approaches have been proposed; enzyme hydrolysis (*7*) and acid hydrolysis (*8*). The latter was selected for this study because of the more extensive information base available on the process. A large number of studies are available on which a simulation could have been based. The work of Clausen and Gaddy (1984) on the acid hydrolysis of corn stovers was selected, because most of the information on which a simulation could be based was available from the results of their experiments.

A two-stage acid hydrolysis process, which is typical for woody biomass conversion, was selected. In the prehydrolysis, the hemicellulose fraction of particulate stover slurry is reacted under mild processing conditions, whereas the cellulose is removed by stronger acid in the hydrolysis step. In the prehydrolysis, acid concentration may be traded with temperature to achieve the conversion to xylose. The degradation of xylose to furfural occurs more rapidly at higher temperatures (~100°C) than at high sulfuric acid concentrations (10*N*). Because of the expense of high acid concentrations, the middle road of moderate acid

concentrations and moderate temperatures is normally taken. At 100°C, Clausen and Gaddy (1984) propose the following first-order rate-constant expression for the prehydrolysis reaction.

$$k_p = .020C_A^{.67} \quad (1)$$

where C_A is the acid concentration in units of normality.

The second hydrolysis step, conversion of cellulose to glucose, is highly acid-concentration and temperature dependent. Again, there is a tradeoff between the cost of acid when high concentrations are used and degradation and repolymerization when the reaction proceeds at high temperature. The first-order rate constant for the hydrolysis reaction is given as

$$k_h = .001C_A^{.51} \quad (2)$$

where the temperature is 100°C. Note that in both Eqs. [1] and [2] there is no dependence on the amount of hemicellulose or cellulose available for reaction. That assumption bears further investigation. Our simulation assumes there is no acid depletion during the reaction.

The overall process for the hydrolysis and the subsequent separation of the acid product is shown in Fig. 3. Two mixer reactors are the central units in the flowsheet. A routine was written to simulate the reaction kinetics in the two vessels and used in conjunction with the mixed reactor model resident in ASPEN. The temperature dependency of the reaction was given by an Arrhenius form, using typical activation energies for hydrolysis reactions [10 kcal·mol^{-1} (42 kJ·mol^{-1})]. The preexponential term

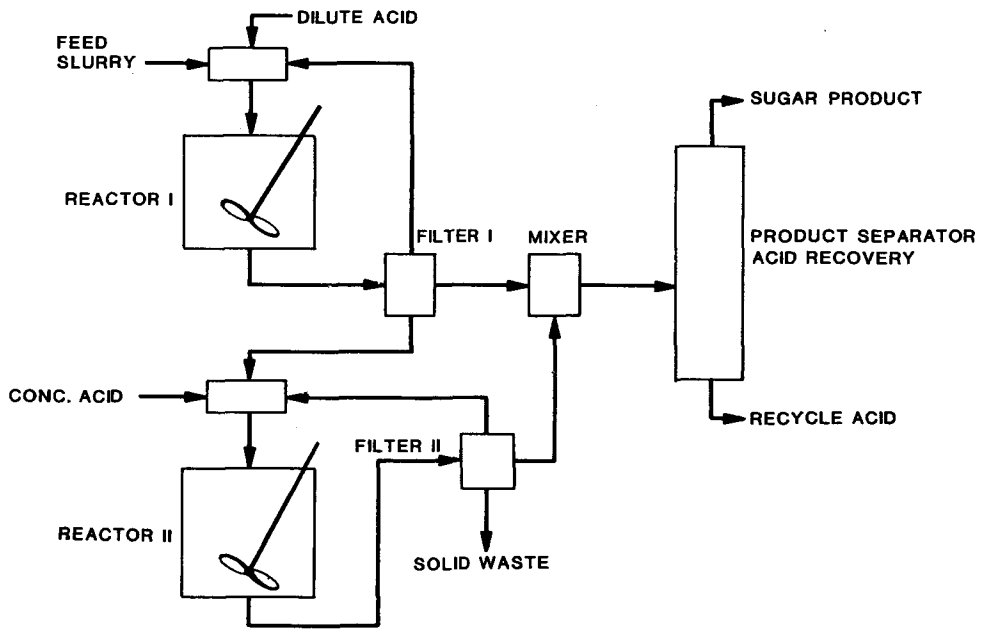

Fig. 3. ASPEN flowsheet for the acid hydrolysis of woody biomass.

was adjusted so that the value matched the constants in Eqs. [1] and [2]. The product distribution between glucose and xylose was adjusted to match that found by Clausen and Gaddy (1984).

It is possible to include the effect of particle size distribution upon the reaction, but no specific information was available on this variable. Therefore, the size distribution, although available to the reactor, was not directly used at this stage of the simulation process. An upcoming version of the simulation will allow the inclusion of the effect of particle size distribution on the hydrolysis reaction, based on first principles. The reactor selected was a mixed reactor in which the conversion was selected and the reactor volume was adjusted within the algorithm to satisfy the kinetics and the material balance. This procedure allowed the computation of the enthalpy input to the reactor.

Recycle is an extremely important aspect of the proposed process. Figure 3 shows recycle loops associated with each of the reactors. The filter module consisted of two parts, a rotary vacuum filter in which the size was computed to satisfy a cake-dryness criterion, and a separator, in which the acid is partially separated from the product. The physical machinery with which the latter task might be accomplished is a matter of considerable effort in the field. In the prehydrolysis loop, the solids were used as the feed to the hydrolysis reactor, whereas in the hydrolysis loop, the solids were the spent waste from the process. There was no solid recycle. In both loops the liquid from the filters was separated in a primary stream divider, which provided the recycle stream to the reactor and the product from the reactor. The acid concentration in the reactor was maintained by a design specification that controlled the makeup acid that entered in the "dilute acid" and "conc. acid" streams. Recycle increases the reactor volume and sugar concentrations, the latter being significantly advantageous to downstream operation. The dilution effect on the solids in the reactor was not explored here. Higher sugar concentrations tend toward furfural production.

A series of studies was performed in which the recycle ratios varied from 0 to an average of .75. The recycle ratio is defined as the ratio of recycled acid to makeup acid in the reactor. The relative economics of reflux reduces to a tradeoff between operating a larger system using less acid and benefiting from a higher product concentration. In our study, base conditions with zero recycle were set to be as close as possible to the Clausen and Gaddy (1984) study, in which the production cost was found to be $1.85/gal ethanol. An economic balance was drawn as a function of recycle ratio. The results are shown in detail in Table 2 and summarized in Fig. 4. There is ample indication shown on this graph that there is room for improvement in the operation of hydrolysis systems. Only a single variable was changed; but with ASPEN, we can explore all of the variables, singly or in conjunction with each other. Since there is considerable uncertainty in several variables, particularly those associated with acid recovery, Fig. 4 should be considered an illustration until a

Table 2
Relative Product Cost as a Function of the Recycle Ratio of Acid Flow

Reflux—Prehyd	Base Case	—	.2	.4	.5	.6	.6	.6
Reflux—Hydro	Base Case	—	.2	.4	.5	.6	.8	.9
Capital: In M$ - - - Base Case = 20 million gal ethanol/yr								
Feed Preparation	2.10	2.10	2.10	2.10	2.10	2.10	2.10	2.10
Hydrolysis	8.00	8.00	7.18	6.35	5.94	5.53	5.10	4.87
Acid Recovery	12.40	12.40	10.47	8.53	7.56	6.59	5.59	5.05
Fermentation	8.10	8.10	6.97	5.84	5.27	4.70	4.12	3.80
Utility/Offsites	11.60	11.60	10.13	8.65	7.91	7.17	6.41	6.00
Total Capital (M$)	$42.20	$42.20	$36.84	$31.47	$28.78	$26.08	$23.32	$21.82
Operating Cost:								
Biomass ($20/ton)	6.70	6.70	6.78	6.91	7.02	7.20	8.21	11.44
Utilities	4.30	4.30	3.86	3.41	3.19	2.97	2.74	2.62
Chemicals	5.60	5.60	5.63	5.69	5.73	5.81	6.23	7.58
Labor	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Fixed Charges								
Maintenance (5%)	2.10	2.11	1.84	1.57	1.44	1.30	1.17	1.09
Deprec- (10%)	4.20	4.22	3.68	3.15	2.88	2.61	2.33	2.18
Tax/Ins. (2%)	.80	.84	.74	.63	.58	.52	.47	.44
Profit, 25%	10.30	10.55	9.21	7.87	7.20	6.52	5.83	5.46
Annual Cost, M$	$37.00	$37.32	$34.74	$32.23	$31.04	$29.93	$29.98	$33.80
Cost/Gal	$1.85	$1.87	$1.74	$1.61	$1.55	$1.50	$1.50	$1.69
Average Reflux	.00	.00	.20	.40	.50	.60	.70	.75
			Supporting Calculations and Factors					
Glucose Rate		15.55	15.37	15.08	14.84	14.48	12.69	9.11
Feed Ratio, Base/Actual		1.000	1.012	1.031	1.048	1.074	1.225	1.707
Volume of Reactor 1		1725	7.29	2.81	1.89	1.28	1.28	1.28
Reactor 2		1186	43.4	17.66	12.3	8.7	4.35	2.78
Water Flow, GPM*1000		4800	3813	2824	2329	1832	1324	1047
Water/Water Base		1.000	.794	.588	.485	.382	.276	.218
Enthalpy Reac 1		6.89E + 07	6.70E + 07	6.54E + 07	6.54E + 07	6.36E + 07	6.36E + 07	6.36E + 07
Enthalpy Reac 2		1.39E + 08	1.38E + 08	1.36E + 08	1.35E + 08	1.34E + 08	1.32E + 08	1.31E + 08
Total Entalpy		2.08E + 08	2.05E + 08	2.01E + 08	2.00E + 08	1.98E + 08	1.96E + 08	1.95E + 08
Enthalpy/Base		1.00	.99	.97	.96	.95	.94	.94

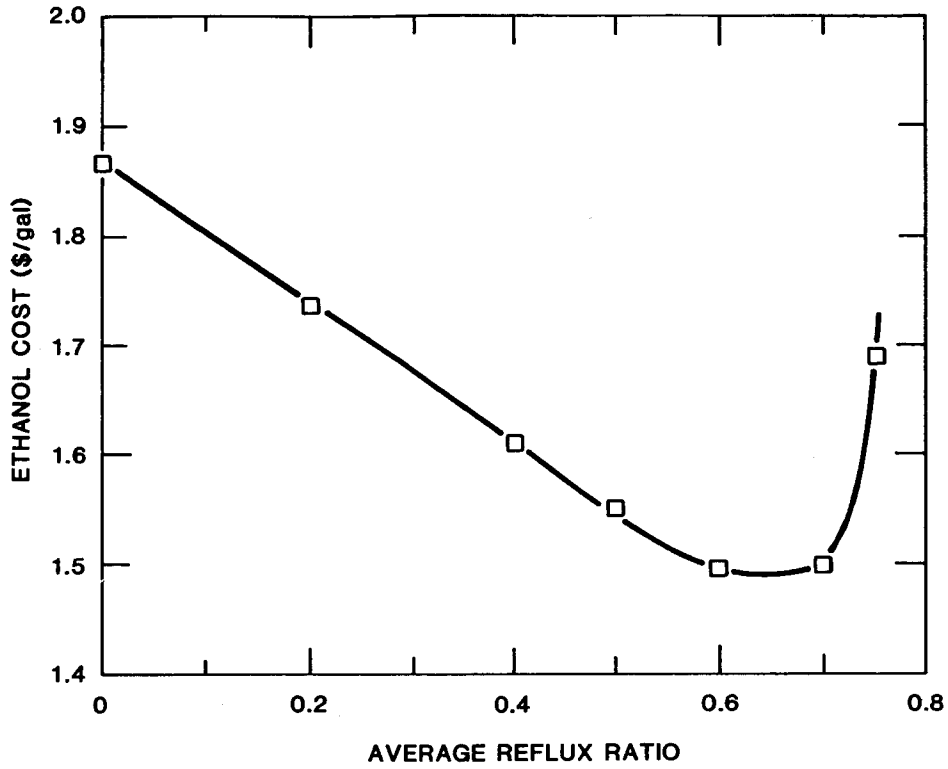

Fig. 4. Relative ethanol cost as a function of acid recycle ratio.

firmer factual foundation can be established. However, we have established the power of ASPEN to simulate processes and to point to potential areas where optimization is possible.

In product recovery there are a number of issues. The objective must be to remove the product, free of acid, while recycling the acid to the process at an appropriate concentration. In our flowsheet, the product streams are mixed before product recovery. Our objective was simplification. It is probable that the concentration levels in both acid and products are sufficiently different that two parallel recovery trains would be used. Another important issue is the method of separation on which there continues to be a considerable challenge. Generally, a complex train of conventional processes is envisioned. To complete this section of the conversion process, a simple zero-order separator module was selected. No acid recycle from the end of this section was specified in the current version, although this will be an important consideration in improving the simulation.

MODELING OF THE BIOREACTOR SECTION

The modeling of bioreactors has been an active topic for many years. The ASPEN approach offers the advantage that the microbial mass can

be effectively modeled as an integral part of the process. As stated earlier, the structure of the bacteria has been approached similarly to the woody biomass. At first glance, this appears an awkward way of approaching the simulation; but with only minor changes in the definitions of the attributes, biomass is very well described.

The bioreactor shown in Fig. 5 was modeled as a single reactor, although there is a mixture of xylose and glucose in the feedstock; and hence it is likely that a more complex reaction train would be required to assure utilization of the sugar. A butanol fermentation using *Clostridium acetobutylicum* is shown as the fuel conversion process (*9,10*). Table 3 shows the pertinent information generated by ASPEN for a typical simulation. A "user subroutine" was written to perform the bioreaction in a mixed-tank reactor. A more sophisticated model is required to account for the variations in the microbial activity that will be found in such reactors. The conversion was quite low because of the low temperature of the run in question.

The remainder of the flowsheet (Fig. 5) shows some of the downstream separations that could possibly be used. A continuous chromatograph was used in this operation as an example of a module that might be used in this type of operation (*11*). A more rigorous simulation of the downstream separations would be needed to provide a detailed economic evaluation.

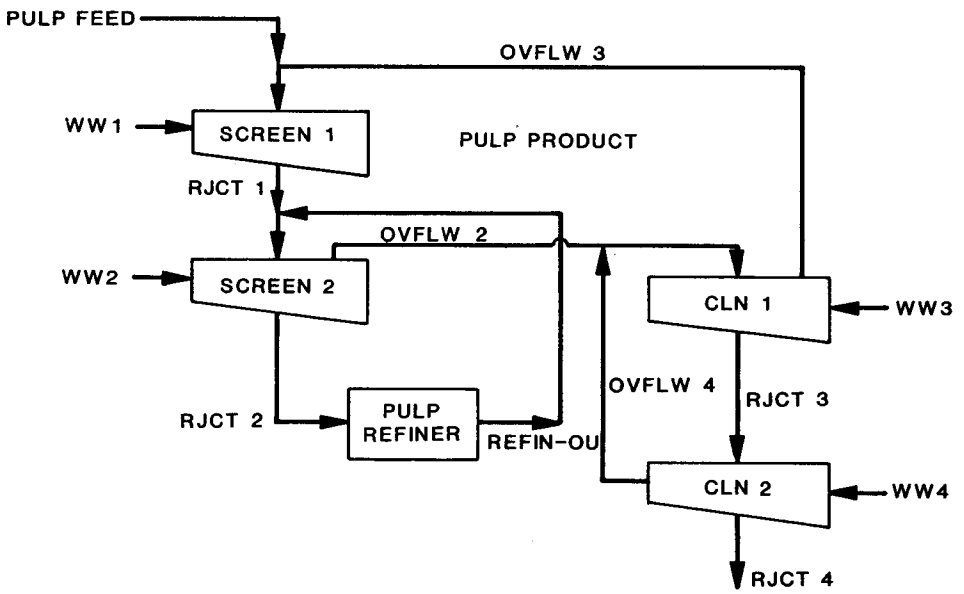

Fig. 5. Butanol fermentation/separation—ASPEN simulation flowsheet.

Table 3
Butanol Bioreactor—Chromatographic Separation Flowsheet

	Mass and Energy Balance[a]			
	In	Out	Generation	Relative Diff.
Total balance				
Mol, kmol/s	.450E − 04	.459E − 04	.9110E − 06	.230E − 17
Mass, kg/s	.179E − 02	.179E − 02		−.338E − 06
Enthalpy, watt	−1.406E + 04	−1.430E + 04		.170E − 01
	Results			
	V–L Phase Equilibrium of Product Stream			
Component	F(I)	X(I)	Y(I)	K(I)
Butanol	.47257E − 02	.37168E − 02	.71508E − 01	19.241
Acetone	.18903E − 02	.18692E − 03	.11464	613.36
ETOH	.94515E − 03	.94872E − 03	.70867E − 03	.74702
CO_2	.13232E − 01	.12188E − 02	.80841	663.28
Glucose	.12570	.12760	.78151E − 05	.61248E − 04
H_2O	.85350	.86633	.47279E − 02	.54574E − 02

Stream Data		
Stream ID	Feed	Rxout
From	—	Biorx
To	Biorx	CO_2out
Phase	Liquid	Mixed
Components, kmol/s		
Butanol	—	2.16E − 07
Acetone	—	9.63E − 10
ETOH	—	4.33E − 08
CO_2	—	6.07E − 07
Glucose	6.07E − 06	5.77E − 06
H_2O	3.89E − 05	3.91E − 05
Total Flow, kmol/s	4.50E − 05	4.59E − 05
State Variables		
Temp K	293.00	298.00
Pres Atm	10.00	5.00
LFRAC	1.00	.985
Enthalpy, J/kmol	−3.12E + 08	−3.11E + 08
Entropy, J/kmol − K	−2.07E + 05	−2.02E + 05
Density, kmol/m^3	33.76	10.15
Avg. MW	39.82	39.03

[a]Inlet stream, feed; outlet stream, rxout.
[b]Outlet temperature, 298.00K, outlet pressure, 5.0000 atm, 0.5 mPa heat duty −243.23 watt, vapor fraction 0.149.

CONCLUSIONS

Based on this preliminary study of portions of a woody biomass conversion process using the ASPEN simulator, the following can be concluded.

1. The facilities based into ASPEN, which include nonconventional solids-handling, user-defined reaction kinetics, and the capability to include costing and economic analysis within the context of the flowsheet, make it a powerful tool for use in bioprocess simulation and economic evaluation.
2. A method is proposed to describe the composition, enthalpy, and density of woody biomass that allows detailed simulation of the behavior of a broad class of materials that are used as feedstocks for conversion processes.
3. The reaction behavior of woody biomass was simulated for a two-stage continuous acid hydrolysis. The recycle rate was found to strongly affect the process economics.
4. Acid recovery remains an important problem in this process.
5. Preliminary efforts in modeling the bioreactor section of the plant indicate that ASPEN is a good means to that end.

NOMENCLATURE

C_A	Acid concentration in reaction, Normality
c	Concentration of product (such as glucose, xylose) g/cm^3
d_p	Particle diameter
k_p	Prehydrolysis rate constant, h^{-1}
k_h	Hydrolysis rate constant, h^{-1}
M	Molecular weight
T	Temperature (K)
t	Time, h

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