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Simulation of Ethanol Production Processes Based on Enzymatic Hydrolysis of Lignocellulosic Materials Using ASPEN PLUS

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ABSTRACT

The process simulator ASPEN PLUS was used for simulation of an ethanol production process based on enzymatic hydrolysis of lignocellulosic materials. The effect of water recycling, necessary to reduce the amount of waste water and to increase the ethanol concentration in the feed to the distillation, was investigated. For a process based on 20 t/h raw material, the amount of waste water can be reduced from 70.7 t/h, without recycling, to 7.1 t/h. Furthermore, the ethanol concentration in the distillation feed increased from 2.5 to 10%. The concentration of byproducts and possible inhibitors increased by a factor of 20–40 in the hydrolysis and fermentation steps. This gives new conditions for future hydrolysis and fermentation experiments.

Index Entries: Process simulation; ASPEN PLUS; flowsheeting; recycling streams; ethanol.

INTRODUCTION

Processes for the production of ethanol from cellulosic materials by bioconversion have been studied (*1–3*) and are currently under development in many countries. The processes consist of a large number of process steps of which the major ones are: the pretreatment of the raw material, enzyme production, enzymatic hydrolysis, enzyme recovery, pentose fermentation, hexose fermentation, ethanol recovery and purification, steam

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generation, and waste treatment. These process steps are all strongly interrelated. It is impossible to explore all of the important features and variables of such a process by experimental investigations alone. Computer simulation is an invaluable tool for the analysis, design, and economic evaluation of the individual process steps, and for comparing and optimizing various process alternatives. It can also be used for assessing areas where future research and development are required. Computer simulations naturally cannot replace experimental studies, but are more of a tool used in the planning and evaluation of the experiments.

To simulate a process, it is necessary to model each unit operation in the process, to assemble the units into a flowsheet, and to solve the material and energy balances. This is facilitated if some kind of flowsheeting program is used. We are working with the development of a process simulator based on the commercially available flowsheeting program, ASPEN PLUS from Aspen Tech. Inc. Cambridge, MA. This program was primarily chosen because of the following features:

A modular approach, which facilitates the use of user-developed unit operation models;
Processing of nonconventional solid materials (such as wood and yeast);
Built-in flowsheeting and equation-solving tools; and
Built-in models for standard unit operations (such as heat exchangers, flashers, pumps, and distillation columns).

This study addresses how process development can be improved by the use of a process simulator, such as ASPEN PLUS. The simulator is used to investigate the problems encountered with water recycling streams, which are required to reduce the amount of waste water produced in the process and to increase the ethanol concentration in the feed to the distillation. So far, most experiments reported in the literature on enzymatic hydrolysis and fermentation have been performed using pure buffer or water solutions (*4–6*). The use of recycling streams will increase the concentration of inhibitors, such as acetic acid, furfural, and nonvolatiles, which will influence the performance of these reactions steps. Simulations based on mass and energy balances are performed for different process configurations to determine the buildup of inhibitors. This will provide new conditions for the hydrolysis and fermentation experiments.

ASPEN PLUS Modeling

Simulation with ASPEN PLUS, and most other flowsheeting programs, consists of three principal parts:

Component property data, which consist of the thermodynamic properties of the chemical substances used in the simulation;

Stream data for all input streams to the process, defining the flow rate, composition, and physical state; and
Unit operation models for all the unit operations considered in the process being simulated.

The simulation of ethanol production from cellulosic materials differs from the simulation of conventional chemical processes, since complex solid materials are used (wood and biomass). Most process simulators are not capable of handling these kinds of components, which cannot be characterized by conventional means (standard thermodynamic properties). In ASPEN PLUS, the user may define components that take part in normal vapor–liquid phase equilibria, solid components that are inert with respect to phase equilibria, and solid components that are heterogenous, such as wood and coal (*7*). These components coexist in the streams and are acted upon separately in the unit operation modules. Furthermore, the process involves a solid-phase transition that requires unit operation modules that can handle solid materials participating in the reactions. This is also provided for in ASPEN PLUS. These features make ASPEN PLUS suitable for the simulation of ethanol production processes. A more detailed description of these features is given by Byers (*8*), who used the program for simulation of a process for fuel (Butanol/Acetone) by acid hydrolysis of woody biomass.

The actual simulation is made by arranging different unit operation modules, such as mixers, splitters, reactors, distillation units, and so on, in such a way that a complete flowsheet is produced. The user may also write his or her own FORTRAN subroutines to be incorporated into the program. This is necessary for this kind of process, since there are no built-in models for process steps, such as wood pretreatment and washing. The convergence routines are fast, which is important when recirculation and optimization problems are being studied.

PROCESS CONFIGURATION

In this work, wood is assumed to consist of cellulose, hemicellulose, lignin, and soluble material. The composition of the raw material is 36% cellulose, 24% hemicellulose, 21% lignin, and 19% solubles. Cellulose may be converted to hexoses and hemicellulose to soluble pentosans, which are further converted to pentoses. The lignin part is treated as an inert component, although some formation of pseudo-lignin may occur in real processes. The soluble part is also regarded as an inert material, consisting of proteins, extractives, and so forth. The present work is confined to mass and energy balances of the whole process to analyze the effect of recirculating streams on the buildup of possible inhibitors. We have therefore chosen to work with rather simple models for the various unit operations.

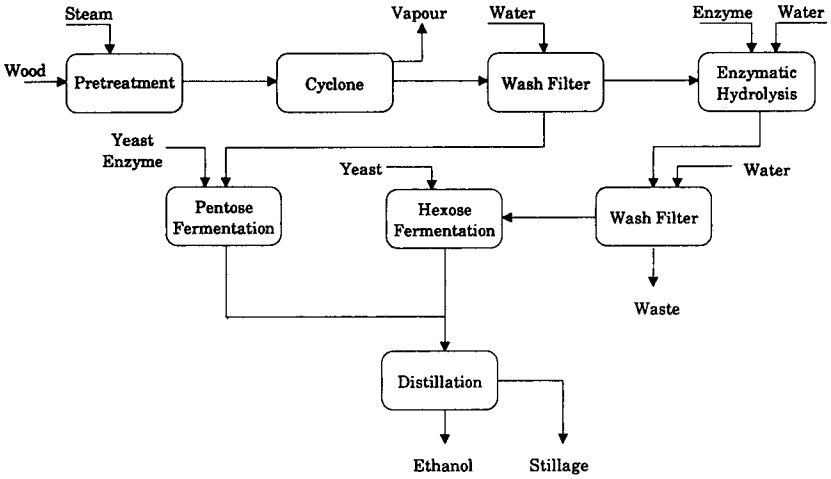

Fig. 1. Simplified flowsheet for base case without recycling streams.

The reactions have been modeled as yield reactions, that is, no models have been used in which inhibition of various reactions is present. A simplified flowsheet of the base-case is shown in Fig. 1. The process consists of the following process units.

Pretreatment

Pretreatment is performed by steam-treating the wood at 220°C. The feed is 20,000 kg/h raw material with a moisture content of 50%. Seventy percent of the hemicellulose is converted to fermentable pentoses (*9*). During the pretreatment, furfural and acetic acid are also formed. A small part of the cellulose is converted to hexoses.

The pretreated material is then washed to recover 85% of the solubilized pentoses, which are passed to a pentose fermentation step. The washing step is simulated in a user-written module, in which a washing efficiency, depending on the amount of washing liquid, is defined. The model is based on washing models developed for the recovery of sodium from pulp residues (*10*). If the ratio of washing liquid to bed volume is 1.5, the washing efficiency will be 0.85.

Pentose Fermentation

The pentoses are first isomerized by the enzyme xylose isomerase and then fermented by baker's yeast (*11*). It is assumed that, for every 100 kg of fermentable pentoses, 30.5 kg ethanol, 30.5 kg carbon dioxide, and 13 kg xylitol will be the result.

Table 1
Relative Volatilities of Byproducts

Component	Relative volatility
Ethanol	9.8
Furfural	11.2
Water	1.0
Acetic acid	0.6
Glycerol	0.0
Solubles	0.0

Enzymatic Hydrolysis

The solid material is introduced to an enzymatic hydrolysis (*12*), using 10 FPU/g solid substrate, where 90% of the cellulose is converted to hexoses. It is also assumed that 95% of the nonsolubilized hemicellulose is saccharified to pentoses. After the hydrolysis, the material is washed to remove the hydrolysis residue. Once again, it is assumed that a washing efficiency of 85% is reached. The solid residue leaves the system after the washing step, having a water content of 75%.

Hexose Fermentation

The liquid stream from the washing step, which is rich in hexoses, is fed to a fermenter. The hexoses are fermented by baker's yeast to ethanol, carbon dioxide, acetic acid, and glycerol. Every 100 kg of hexoses yield 48.5 kg ethanol, 47.4 kg carbon dioxide, 1.4 kg acetic acid, and 2.7 kg glycerol (*13*). The cell mass of the yeast is set to 2% (w/w) of the liquid in the fermenter.

Distillation

The fermentation products are passed to a distillation unit in which 99% of the incoming ethanol is recovered and concentrated to 95%. Glycerol leaves with the bottom stream, whereas furfural and acetic acid are distributed between the product and the stillage streams. The furfural concentration is about 3 times higher in the bottom product than in the distillate, whereas the acetic acid concentration is almost equal in both of the outgoing streams. The soluble products leave with the stillage stream.

One of the reasons for having chosen furfural, acetic acid, and glycerol as byproducts is their different relative volatilities (Table 1). Through this choice, it is possible to predict where other byproducts with a certain relative volatility will be found if the process is closed with respect to water.

RESULTS

In the base case (Fig. 1), fresh water is added in the washing steps and in the hydrolysis unit. The pretreated material is washed to separate the pentoses from the fibrous material, while the hydrolysis residue is washed to recover the hexoses from the liquid entrapped in the residue. Water is also added in the hydrolysis unit to adjust the dry matter content. Substrate levels above 10% ODM (oven dry material) will cause severe stirring and mass transfer problems, although the total amount of solids could be increased by a fed-batch procedure.

This process configuration is not very realistic for a commercial process. Large volumes of fresh water are used, which will result in a very diluted ethanol feed to the distillation and a considerable waste water treatment problem. It does however reflect the procedure and conditions used in most of the lab experiments on hydrolysis and fermentation.

The simulation of the base case shows that 6300 kg/h of steam are required in the pretreatment step. This step will be unaltered in all the process configuration alternatives. The total amount of water that enters the system is 90.3 t/h (t/h) divided between the following streams:

Raw material (50% ODM):	10.0 t/h
Steam (excluding flash-vapor):	6.3 t/h
Enzymes and yeast:	3.3 t/h
Water to adjust dry matter in the hydrolysis:	43.7 t/h
Wash water after pretreatment:	16.8 t/h
Wash water after hydrolysis:	10.2 t/h

The feed to the distillation is very diluted, containing 2.5% ethanol, which is in the cost-sensitive region for nearly all distillation technologies (*14*). It has also been shown by Zacchi and Axelsson (*14*) that preconcentration of sugar solutions, using reverse osmosis or multiple-effect evaporation, is not economically feasible for sugar solutions above 50 g/L.

Five process configurations, cases 1–5, with recycling streams were simulated. The flowsheets are shown in Figs. 2–5. The configurations for cases 1 and 2 mainly aim to diminish the amount of liquid waste, whereas the configuration of cases 3–5 increases the ethanol concentration in the feed to the distillation unit. Some of the results from the simulations are summarized in Tables 2–4. Table 2 shows the amount of fresh water used, and the concentration of hexoses, pentoses, and ethanol in the feed stream to the hexose fermentation, pentose fermentation, and distillation units, respectively. Tables 3 and 4 show the final concentration of the ethanol and byproducts in the hydrolysis and fermentation steps, and in the stillage stream. These values should not be interpreted as absolute values, but rather as relative values compared to the base case. For alternative pretreatment conditions with different byproduct concentrations, the relative values should still be the same. Other soluble byproducts, not

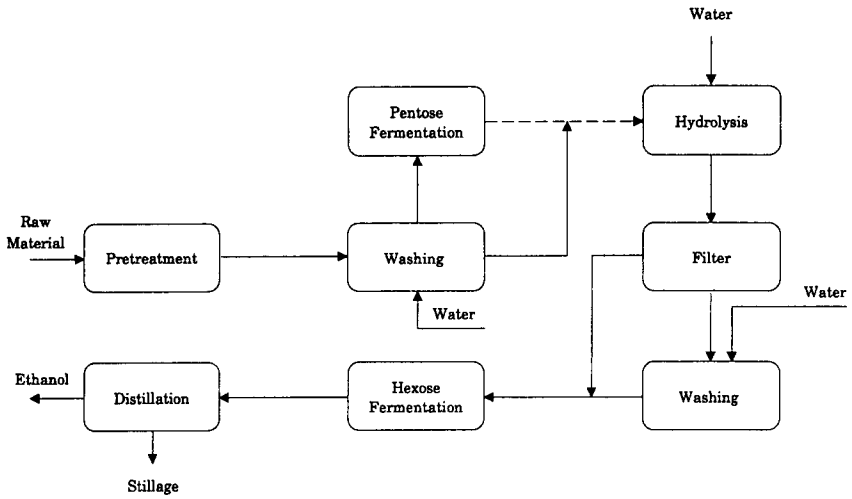

Fig. 2. Simplified flowsheet showing main liquid streams for case 1. Recirculation of liquid from pentose fermentation.

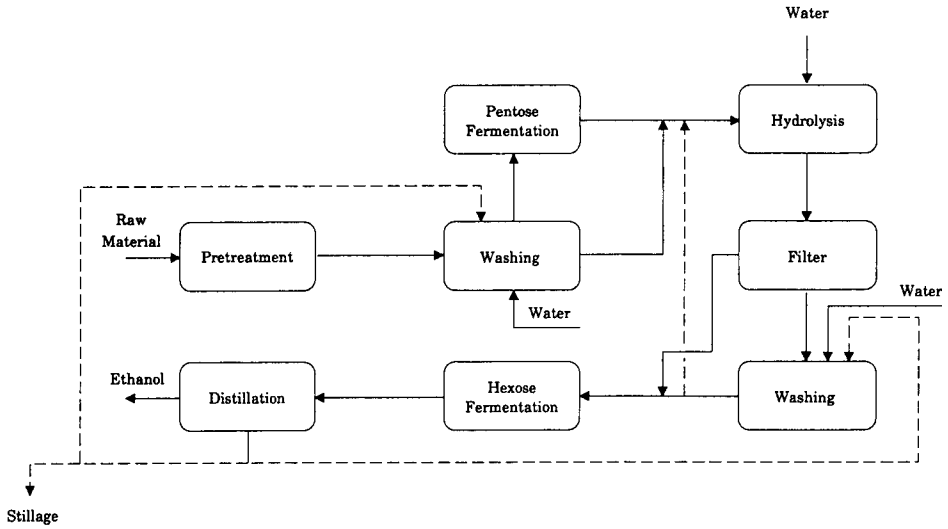

Fig. 3. Simplified flowsheet showing main liquid streams for case 2. Recirculation of stillage stream and liquid from the hydrolysis residue wash step.

included in this study, can be accounted for by comparison with the concentration distribution of components with similar relative volatilities.

Decrease of Liquid Waste Streams

Figure 1 shows a simplified flowsheet with the main streams. From this it can be seen that the feed to the distillation consists of two diluted streams, one from the pentose fermentation (2.1% ethanol) and the other from the hexose fermentation (2.6% ethanol). An obvious way to decrease

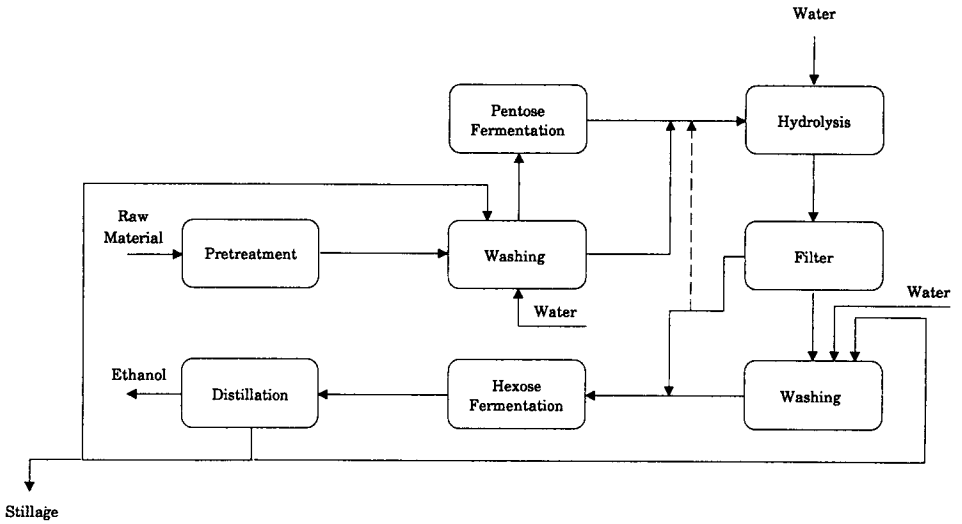

Fig. 4. Simplified flowsheet showing main liquid streams for case 3. Recirculation of liquid from hydrolysis.

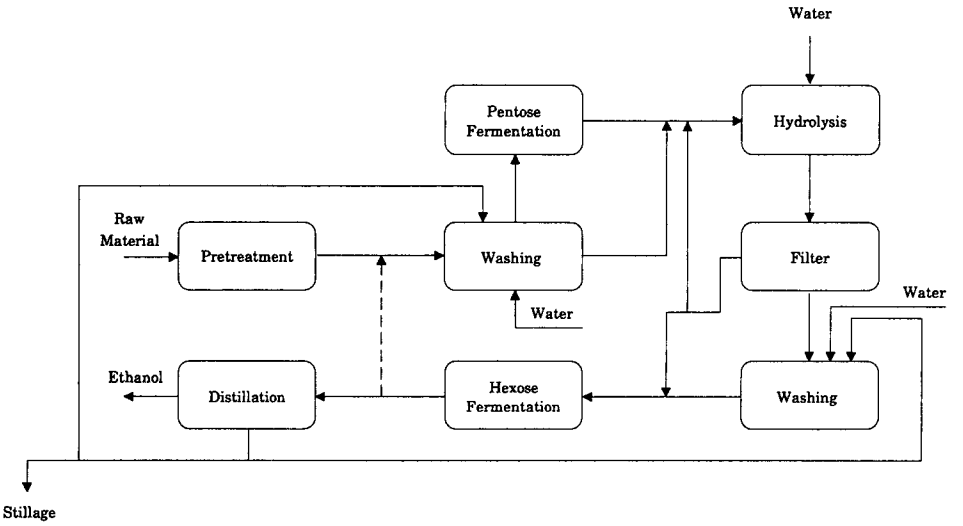

Fig. 5. Simplified flowsheet showing main liquid streams for cases 4 and 5. Recirculation of liquid from hexose fermentation.

the amount of fresh water and to increase the ethanol concentration is to use the same liquid in the two fermentation steps. This can be done by taking the outlet stream from the pentose fermentation to the hydrolysis (case 1), as shown in Fig. 2. This reduces the amount of fresh water required in the hydrolysis by 20.1 t/h (Table 2). The ethanol concentration in the feed to the distillation is increased to 3.3%, which is still rather low. From

Table 2
Fresh Water Supply and Concentration
of Hexoses, Pentoses, and Ethanol to the Hexose Fermentation,
the Pentose Fermentation, and the Distillation Unit, Respectively

	Base case	Case 1	Case 2	Case 3	Case 4	Case 5
Fresh water, t/h	70.7	50.6	—	—	—	—
Hexoses to fermentation, %	5.5	5.6	6.7	9.6	5.8	9.2
Pentoses to fermentation, %	6.9	6.9	9.5	9.5	9.6	10.0
Ethanol to fermentation, %	2.5	3.3	4.2	5.9	6.7	10.0

Table 3
Final Concentration of Ethanol and Byproducts
in the Hydrolysis and Fermentation Steps

	Base case	Case 1	Case 2	Case 3	Case 4	Case 5
Hydrolysis						
Ethanol, %	-	0.75	1.00	1.50	4.40	6.80
Furfural, %	0.02	0.12	0.38	0.38	0.37	0.39
Acetic acid, %	0.01	0.07	0.36	0.33	0.38	0.36
Glycerol, %	-	-	0.15	0.15	0.20	0.16
Solubles, %	0.60	3.50	11.30	11.30	11.00	11.40
Liquid HC, %	-	0.05	0.05	0.05	0.05	0.08
Hexose fermentation						
Ethanol, %	2.60	3.30	4.20	5.90	6.70	10.00
Furfural, %	0.02	0.11	0.35	0.35	0.34	0.35
Acetic acid, %	0.09	0.14	0.43	0.44	0.43	0.45
Glycerol, %	0.08	0.08	0.28	0.27	0.27	0.27
Solubles, %	0.53	3.00	10.50	10.30	10.00	10.10
Liquid HC, %	0.03	0.04	0.04	0.04	0.04	0.07
Pentose fermentation						
Ethanol, %	2.10	2.10	3.00	3.00	3.90	4.90
Furfural, %	0.29	0.29	0.40	0.40	0.41	0.43
Acetic acid, %	0.16	0.16	0.26	0.26	0.27	0.29
Glycerol, %	-	-	0.05	0.05	0.05	0.05
Solubles, %	8.30	8.30	11.70	11.70	11.90	12.30
Liquid HC, %	1.40	1.40	1.90	1.90	1.90	2.00

Table 4
Concentration of Byproducts in the Waste Stream, Stillage

	Base case	Case 1	Case 2	Case 3	Case 4	Case 5
Hydrolysis						
Ethanol, %	0.03	0.03	0.04	0.05	0.07	0.11
Furfural, %	0.08	0.11	0.36	0.36	0.36	0.37
Acetic acid, %	0.10	0.14	0.43	0.43	0.43	0.44
Glycerol, %	0.06	0.08	0.29	0.29	0.29	0.30
Solubles, %	2.4	3.13	11.00	11.00	10.80	11.30
Liquid HC, %	0.37	0.04	0.04	0.05	0.05	0.08

Table 3, it can also be seen that the concentration of the byproducts, formed in the pretreatment step, is increased by a factor of 6 in the hydrolysis. The pentose and hexose fermentations cannot be combined to a single fermentation step, since the pentoses would not be fermented as long as hexoses are present.

The amount of stillage is still very high, 60.6 t/h. This could be further reduced by replacing the fresh water in the washing steps and in the hydrolysis with a part of the stillage stream. This process alternative (case 2) is shown in Fig. 3. The minimum amount of water is the amount entering via the raw material, plus the steam in the pretreatment, and the enzyme and yeast streams. As shown in Table 2, the amount of fresh water in the washing steps and in the hydrolysis has been reduced to zero. The stillage stream is reduced to 7.1 t/h, although naturally with a much higher concentration of byproducts (*see* Table 4). The concentration of ethanol in the distillation feed has increased to 4.2% (Table 2). The concentration of byproducts is further increased in the hydrolysis. New components, formed in the hexose fermentation (glycerol for instance), are now also present in the hydrolysis.

Increase of Ethanol Concentration in the Distillation Feed

As stated above, the amount of liquid waste cannot be reduced further, unless the production of enzymes and yeast is performed with recycled liquid. This is not considered in this study. Alternative configurations that would lead to an increase of the ethanol concentration in the feed to the distillation may, however, be of interest. In case 3, shown in Fig. 4, part of the hydrolysate stream is recycled back to the hydrolysis unit. In case 4, shown in Fig. 5, part of the feed to the distillation is recycled to the pentose fermentation and hydrolysis units. As can be seen in Table 3, these alternatives have little effect on the concentration of byproducts compared with case 2. Case 3 involves the recirculation of sugars, which could have a negative effect, increasing the risk of infections. Case 4 is

more attractive, since it involves a recirculation of ethanol instead. The ethanol concentration in the feed to the distillation is increased to 6.7% (Table 2), which is comparable to the concentration when ethanol is produced from corn (*15*). It should, however, be noted that the ethanol concentration in the hydrolysis is increased to 4.4%. This requires further experimental investigation of the effect of ethanol on the hydrolysis kinetics.

In case 5, the same process configuration as in case 4 was used, except that the substrate concentration in the hydrolysis was increased from 10 to 15% ODM, assuming a fed-batch procedure. The main difference compared with case 4 is the increased hexose concentration in the hydrolysis (*see* Table 2), and the higher ethanol concentration in the hydrolysis and the fermentation units. The feed to the distillation has, for this alternative, an ethanol concentration of about 10%.

In all the investigated alternatives, a large amount of the hemicellulose is lost in the process. Pentoses formed during the hydrolysis cannot be recirculated to the pentose fermentation because of the high hexose concentration. More efficient pretreatment and washing steps can reduce the loss of pentoses. Other process configurations that increase the utilization of the pentose fraction are possible (*16*).

CONCLUSIONS

The ASPEN PLUS simulator is a powerful tool for the simulation of processes for the production of ethanol from lignocellulosics. The program was used to analyze the effects of water recycling, necessary to reduce the amount of waste water and to find a way of increasing the ethanol concentration in the feed to the distillation, for various process configurations. The liquid waste stream from the process can be reduced from 70.7 to 7.1 t/h by water recycling. The recycling results in a considerable buildup of byproducts, such as furfural, acetic acid, glycerol, and other soluble components, in both the hydrolysis and in the fermentation steps, as shown in Table 3. This necessitates new experimental investigations of these steps to study the influence of the byproducts on the kinetics. A process configuration with recirculation of an ethanol containing stream (Fig. 5) is also proposed where the ethanol concentration in the feed to the distillation is increased to 6.7 wt% from 2.5% in the base case. The effect of ethanol on the hydrolysis kinetics has to be investigated.

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REFERENCES

1. Mednick, R. L., Weiss, L. H., and Xippolitos, E. G. (1982), *Chem. Eng. Prog.* **78(8),** 68.
2. Purchase, B. S., Walford, S. N., and Waugh, E. J. (1986), *Proc. Annu. Congr—S. Afr. Sugar Technol. Assoc.* **60th,** 33.
3. Wright, J. D., Wyman, C. E., and Grohmann, K. (1987), US DOE, Report, Contract no. DE-AC02-83CH10093.
4. Sattler, W., Esterbauer, H., Glatter, O., and Steiner, W. (1989), *Biotech. Bioeng.* **33,** 1221.
5. Hogan, C. M., Mes-Hartree, M., Saddler, J. N., and Kushner, D. J. (1990), *Appl. Microb. Biotech.* **32(5),** 614.
6. Eklund, R., Galbe, M., and Zacchi, G. (1990), *Enzyme. Microb. Technol.* **12,** 225–228.
7. Evans, B. L. (1988), CHEMDATA 88, XIX Conference on the Use of Computers in Chemical Engineering EFCE, 20–25.
8. Byers, C. H. (1988), *Appl. Biotechnol. Biochem.* **18,** 143–157.
9. Eklund, R., Galbe, M., and Zacchi, G. (1988), *J. Wood Chem. Technol.* **8(3),** 379–392.
10. Grähs, L. E. (1976), *Swedish Paper J.* **79(4),** 123–128.
11. Linden, T., Peetre, J., and Hahn-Hägerdal, B. Isolation of yeasts from spent sulphite liquor (to be published).
12. Eklund, R., Galbe, M., and Zacchi, G. (1990), *Enzyme Microb. Technol.* **12,** 225–228.
13. Bu'lock, J. and Kristiansen, B. (1987), *Basic Biotechnology,* Academic, London, p. 320.
14. Zacchi, G. and Axelsson, A. (1989), *Biotechnol. Bioeng.* **34,** 223–233.
15. Busche, R. M. (1984), *Biotechnol. Bioeng. Symp. Ser.* **13,** 597.
16. Galbe, M. and Zacchi, G. Simulation of biotechnical processes for the production of ethanol (to be published).