

Modified Percolation Process in Dilute-Acid Hydrolysis of Biphasic Hemicellulose

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ABSTRACT

To improve the performance of a percolation reactor in dilute-acid pretreatment of biomass containing biphasic hemicellulose, a reactor simulation study was conducted focusing on the refinement of operating strategies and conditions. The optimum temperature difference in step-change operation was determined to be 30°C for a wide range of reaction temperature. Application of temperature step change along with flow-rate step change brought about a 0.6% improvement in product yield over the case with temperature step change alone. The most significant improvement, however, was seen with the application of the two-stage reverse-flow reactor arrangement with temperature change (a design concept originally developed at NREL). Use of this reactor has given an additional 5% improvement in product yield over that of the best-case percolation reactor employing temperature step change.

In addition, the effect of intraparticle diffusion on product yield was investigated. The critical chip size (above which the effect of diffusion becomes significant) was determined to be 0.40 cm for 140–170°C operation and 0.29 cm for 150–180°C operation.

Index Entries: Dilute-acid pretreatment; percolation reactor; optimization; diffusion; hemicellulose.

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NOMENCLATURE

* Unit of concentrations: % w/v

A	hemicellulose
B	xylose and soluble xylose oligomer
b	characteristic particle dimension, one-half of length in longitudinal direction, cm
C	decomposed product
$C_A, C_{AF}, C_{AS}, C_{A0}, C_{AF0}, C_{AS0}$	concentration of xylan as a xylose
C_B, C_{BF}, C_{BS}	concentration of xylose
C_{BA}	average concentration of B inside particles
C_{BL}	concentration of B inside particles
D_e	effective diffusivity, cm^2/s
H_F, H_S	the fraction of fast and slow hemicellulose
k_i	reaction rate constant, min^{-1}
L	reactor length, cm
P	packing factor
PDE	Partial differential equation
t	time, min
u	velocity inside reactor, cm/min
x	distance coordinate along reactor length, cm
Y_B, Y_{BF}, Y_{BS}	yields of B for uniform temperature operation: overall; fast reaction; slow fraction
$Y_{BSTEP}, Y_{BF1}, Y_{BF2}, Y_{BS1}, Y_{BS2}$	yields of B for step-change operation
y	distance coordinate inside particle
z	x / L

Greek

α_1	$k_3/k_i, i = 1, 2$
α'	$\alpha(1 + \eta p \Theta)$
β_F	$k_1 L / u$
β_S	$k_2 L / u$
ϵ	void fraction in reactor
η	overall effectiveness factor
Θ	porosity within solid
ϕ	thiele modulus
τ	tu/L
ω	the ratio of velocity in high-temperature phase to the velocity of low-temperature phase

Subscripts

A	denotes component A
B	component B
F	fast xylan
i	reaction no.

S	slow xylan
o	value at $t = 0$
1	indicates early phase in step-change process
2	latter phase in step-change process

INTRODUCTION

Dilute-acid pretreatment of biomass carries an additional benefit of hydrolyzing the hemicellulose fraction. In the layout of this process, it is important to consider the utilization of hemicellulose sugar as well as the effectiveness of the pretreatment. From the standpoint of sugar production, the treatment condition, type of reactor, and reactor operation mode are the major design factors. In our previous study along these lines (1-3), we established that the percolation reactor (packed-bed flow-through type) is one of the reactor types most appropriate for biomass pretreatment. In application of this reactor, the sugar product is discharged from the reactor as it is formed. This permits the process to attain high sugar yield by minimizing the sugar decomposition. Furthermore, the sugar product from a packed-bed-type reactor is obtained at a relatively high concentration level because of the high solid-to-liquid ratio that exists in a packed-bed reactor.

We have explored the use of this reactor specifically in pretreatment/hydrolysis of hemicellulose of hybrid poplar. At the present time, it is regarded as one of the most promising renewable cellulosic resources in the United States. The hemicellulose in hardwood species has been modeled to biphasic (4-9), i.e., it is composed of two different fragments (fast-hydrolyzing fraction and slow-hydrolyzing fraction). The biphasic nature of substrate brings about a number of interesting points concerning the reactor design and operation, especially with regard to the temperature policy and the flow configuration in the reactor system.

We have reported on the kinetics and the possible advantage of applying the nonuniform temperature (10). In this study, further improvement in the performance of this reactor was sought by way of optimization of process variables and application of unconventional flow arrangement. In addition, the adverse effect owing to nonideal behavior of the reactor, especially the effect of intraparticle diffusion, was investigated.

THEORETICAL MODEL OF A PERCOLATION REACTOR

A simplistic description of a percolation reactor is given in Fig. 1. The following assumptions are made in the modeling procedure: (1) The hemicellulose in hybrid poplar is composed of different fragments, fast- and

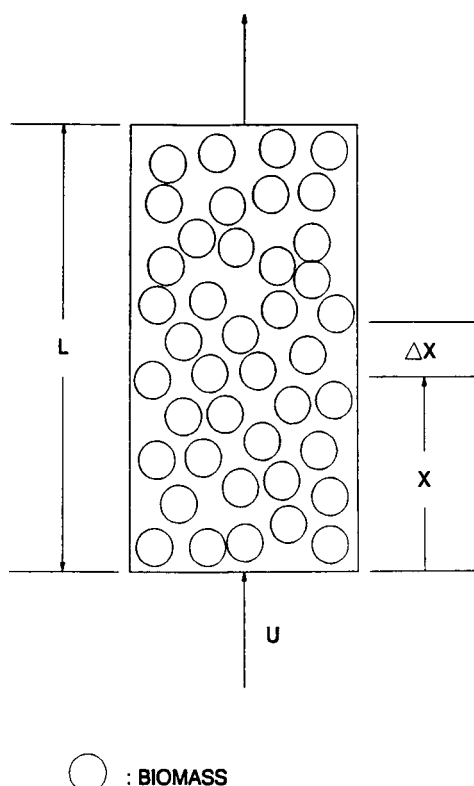
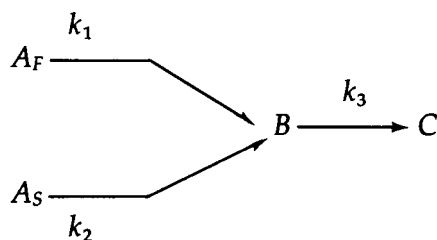


Fig. 1. Conceptual sketch of percolation reactor.

slow-hydrolyzing ones, and (2) its kinetics follows the parallel consecutive first-order reactions:



where A_F and A_S are fast-hydrolyzing fraction and slow-hydrolyzing fraction of hemicellulose, respectively, termed as fast and slow hemicellulose henceforth; B is xylose; and C is decomposed product.

Simple Model

Governing PDEs

A material balance over an incremental column height on component B leads to the following expression:

$$u \left[\left(\frac{\partial C_B}{\partial x} \right) \right] + k_3 C_B - k_1 C_{AF} - k_2 C_{AS} = - \left[\left(\frac{\partial C_B}{\partial t} \right) \right] \quad (1)$$

where

$$C_{AF} = C_{AF_0} e^{-k_1[(t - (x/u))], t > (x/u)}$$

and

$$C_{AS} = C_{AS_0} e^{-k_2[(t - (x/u))], t > (x/u)}$$

The pertinent initial and boundary conditions are:

$$x = 0, C_B = 0 \quad (2)$$

$$t = 0, C_B = 0 \quad (3)$$

Yield, Concentration, and Optimum Conditions for Single-Temperature Operation

From the solution for Eqs. (1-3), the yield for fast hemicellulose is obtained as (see ref. 1):

$$Y_{BF} = \int_1^{\tau+1} (S_{BF})_{z=1} d\tau = [(1 - e^{-\alpha_F \beta_F}) / \alpha_F \beta_F] (1 - e^{-\beta_F \tau}) \quad (4)$$

The yield for slow hemicellulose is similarly expressed:

$$Y_{BS} = \int_1^{\tau+1} (S_{BS})_{z=1} d\tau = [(1 - e^{-\alpha_S \beta_S}) / \alpha_S \beta_S] (1 - e^{-\beta_S \tau}) \quad (5)$$

The combined yield is:

$$Y_B = H_F Y_{BF} + H_S Y_{BS} \quad (6)$$

Yield for Temperature Step-Change Operation

The term τ_1 represents the dimensionless time up to the temperature shifting point. τ_2 represents the rest of the time period:

$$\tau = \tau_1 + \tau_2 \quad (7)$$

We further define ρ such that

$$\rho = (\tau_1 / \tau) \quad (8)$$

Total yield consists of four parts: namely, fast fraction reacting for duration of τ_1 , slow for τ_1 , fast for τ_2 , and slow for τ_2 . The total yield is then expressed as:

$$Y_{BSTEP} = H_F(Y_{BF1} + R_{AF}Y_{BF2}) + H_S(Y_{BS1} + R_{AS}Y_{BS2}) \quad (9)$$

where

$$Y_{BF1} = \int_1^{\tau_1+1} (S_{BF})_{z=1} d\tau = [(1 - e^{-\alpha_{F1} \beta_{F1}}) / \alpha_{F1} \beta_{F1}] (1 - e^{-\beta_{F1} \tau_1})$$

$$Y_{BS1} = \int_1^{\tau_1+1} (S_{BS})_{z=1} d\tau = [(1 - e^{-\alpha_{S1} \beta_{S1}}) / \alpha_{S1} \beta_{S1}] (1 - e^{-\beta_{S1} \tau_1})$$

$$Y_{BF2} = \int_1^{\tau_2+1} (S_{BF})_{z=1} d\tau = [(1 - e^{-\alpha_{F2} \beta_{F2}}) / \alpha_{F2} \beta_{F2}] (1 - e^{-\beta_{F2} \tau_2})$$

$$Y_{BS2} = \int_1^{\tau_2+1} (S_{BS})_{z=1} d\tau = [(1 - e^{-\alpha_{S2} \beta_{S2}}) / \alpha_{S2} \beta_{S2}] (1 - e^{-\beta_{S2} \tau_2})$$

$$R_{AF} = e^{-\beta_{F1} \tau_1}$$

$$R_{AS} = e^{-\beta_{S1} \tau_1}$$

MODEL ACCOUNTING FOR THE EFFECT OF DIFFUSION

Governing PDEs

To account for the effect of sugar diffusion, one needs to set up the PDEs separately for the solid part and liquid part.

PDE within Solid

The material balance on component B within the solid feed yields an equation in the form of:

$$D_e (\partial^2 C_B / \partial y^2) + k_1 C_{AF} + k_2 C_{AS} - k_3 C_B = (\partial C_B / \partial t) \quad (10)$$

$$C_{BA} = (1/b) \int_0^b C_B dy \quad (11)$$

PDE within Liquid

A material balance on component B, which considers the liquid that exists both inside and outside of solid particles, leads to the following expression:

$$\begin{aligned} -\epsilon u (\partial C_{BL} / \partial x) + (1 - \epsilon) \Theta k_1 C_{AF} + (1 - \epsilon) \Theta k_2 C_{AS} - k_3 [\epsilon C_{BL} + (1 - \epsilon) \Theta C_{BA}] \\ = \epsilon (\partial C_{BL} / \partial t) + (1 - \epsilon) \Theta (\partial C_{BA} / \partial t) \end{aligned} \quad (12)$$

By the principle of superposition, the above equations were divided into two sets of equations. They were solved analytically by Laplace transform method (11, pp. 16–18). The yield is expressed as:

$$Y_{BSTEP} = H_F(Y_{BF1} + R_{AF}Y_{BF2}) + H_S(Y_{BS1} + R_{AS}Y_{BS2}) \quad (13)$$

where

$$Y_{BF1} = \eta [(1 - e^{-\alpha'_{F1}\beta_{F1}}) / \alpha'_{F1}\beta_{F1}] (1 - e^{-\beta_{F1}\tau_1})$$

$$Y_{BS1} = \eta [(1 - e^{-\alpha'_{S1}\beta_{S1}}) / \alpha'_{S1}\beta_{S1}] (1 - e^{-\beta_{S1}\tau_1})$$

$$Y_{BF2} = \eta [(1 - e^{-\alpha'_{F2}\beta_{F2}}) / \alpha'_{F2}\beta_{F2}] (1 - e^{-\beta_{F2}\tau_2})$$

$$Y_{BS2} = \eta [(1 - e^{-\alpha'_{S2}\beta_{S2}}) / \alpha'_{S2}\beta_{S2}] (1 - e^{-\beta_{S2}\tau_2})$$

$$R_{AF} = e^{-\beta_{F1}\tau_1}$$

$$R_{AS} = e^{-\beta_{S1}\tau_1}$$

It is noteworthy that, when $\eta = 1$ and $p = 0$, the yield equation in diffusion model reduces to the corresponding one in the simple model.

RESULTS AND DISCUSSION

A computer program based on the theoretical basis described in the previous section was developed to identify the optimum operating conditions of a two-stage percolation-type pretreatment reactor. The objective of this computational study was to maximize the yield of sugar (xylose) during pretreatment. The program incorporates experimentally determined kinetic data with the solution of modeling equations. It is composed of one main program and 23 subroutine programs.

The program was constructed in such a way that it takes in high/low temperatures, acid concentration, residence time, flow rate, and ω (the ratio of velocity in high-temperature phase to the velocity in low-temperature phase) as input data and generates product yield, concentration, and the optimum set of operation conditions as the output. Sample input and output data are given in Table 1.

The computation procedure is as follows. From the input data, the reaction rate constants are calculated. This information is then put into the reactor modeling equation from which the yield and the concentration of product are evaluated. This computation is done with the provision of the additional input parameters of β , ρ , and ω . These parameter values were then optimized to maximize the yield for a given τ value (dimensionless reaction time). The optimization process was done by repeated calculation of the model equation applying multiple levels of each parameters, an exponential design. This computation was done for three different cases of temperature policy: uniformly low temperature, uniformly high temperature, and step-change (from low to high) temperature.

Optimal Temperature Difference

We have previously reported that the yields with step-change temperature policy in the three sample cases are higher than that with uniform high- or uniform low-temperature operation (10). In this work, the temperature policy was further refined. The first item investigated in this regard was to determine the optimum level of temperature difference in step-change operation. Figure 2 shows the sugar yield vs temperature difference when low temperature is 140, 150, and 160°C. Highest yield occurred when temperature difference is 28, 29, and 29°C, respectively. It appears that with a representative reactor operating conditions: acid concentration = 0.83% w/v (0.17N sulfuric acid) and $\tau = 3$, the optimal temperature difference is about 30°C. For example, when low temperature is set at 150°C, the optimum high temperature should be 180°C. The reactor is then first run at 150°C for a certain duration and then at 180°C for the rest of the operation.

Table 1
Sample Output of the Simulation Program

-----INPUT DATA-----								
LOW T(C)	HIGH T(C)	ACID CONC.(%/V)	LENGTH(CM)	w=VELOCITY RATIO				
140.0	170.0	0.83370	5.0800	1.7				
-----RESULTS-----								
#1 XYLOSE YIELD AND XYLOSE CONCENTRATION UNDER VARIOUS OPERATION MODES								
TAU	UNI LOW		UNI HIGH		STEP CHANGE			
	YIELD	CONC.	YIELD	CONC.	YIELD	CONC.		
1	71.26	2.47	75.19	2.61	77.29	2.68		
2	77.31	1.34	81.65	1.42	84.94	1.47		
3	81.07	0.94	85.22	0.99	88.51	1.02		
4	83.68	0.73	87.52	0.76	90.62	0.79		
5	85.58	0.59	89.13	0.62	92.03	0.64		
#2 XYLOSE DECOMPOSED AND HEMICELLULOSE UNREACTED								
TAU	UNI LOW		UNI HIGH		STEP CHANGE			
	DECOMP.	HC UNREAC.	DECOMP.	HC UNREAC.	DECOMP.	HC UNREAC.		
1	9.67	19.07	10.14	14.67	15.05	7.65		
2	9.86	12.82	9.94	8.41	11.24	3.82		
3	9.90	9.02	8.90	5.88	8.81	2.69		
4	9.55	6.78	8.01	4.47	7.42	1.96		
5	8.85	5.57	7.40	3.47	6.29	1.68		
#3 OPTIMAL REACTION TIME(MINS)& VOLUMETRIC FLOW RATE(CC/MINS)								
TAU	R.T.	UNI LOW		UNI HIGH		STEP CHANGE		
		VFR	R.T.	VFR	R.T.1	R.T.2	VFR1	VFR2
1	70.646	0.303	8.695	2.460	29.345	14.705	0.394	0.669
2	133.141	0.321	15.760	2.714	33.747	23.304	0.583	0.991
3	191.561	0.335	20.379	3.148	34.236	27.811	0.787	1.338
4	239.111	0.358	23.911	3.578	38.801	31.519	0.926	1.574
5	271.717	0.394	27.172	3.935	38.040	33.565	1.124	1.912
#4 FINAL PRODUCT CONC.(%) & PRODUCT YIELD(%) WITH REVERSE STREAM								
TAU	YIELD	CONC		ρ		OPTIMAL β		
1	4.784	74.422		0.540		4.000		
2	2.830	82.918		0.460		2.700		
3	1.948	87.062		0.420		2.000		
4	1.503	89.414		0.420		1.700		
5	1.214	91.058		0.420		1.400		

HC = Hemicellulose

R.T. = Reaction time, minutes

TAU = τ

VFR = Volumetric Flow Rate, cc/minutes

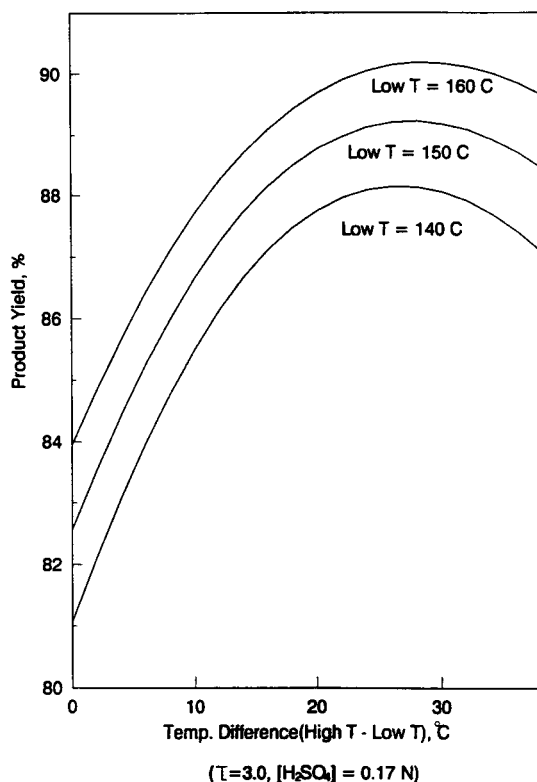


Fig. 2. Effect of temperature difference on product yield in step-change operation.

Step Change of Flow Rate (Along with Temperature)

The preceding simulation was conducted with the assumption that the liquid flow rate is kept uniform throughout the reactor operation for a given run, even though the temperature has gone through a step change. The simulation process was refined by eliminating this assumption. From the previous simulation results, it became obvious that the β value ($k_i L/u$) has a profound effect on the xylose yield (10). Since β is an operational parameter involving both the reaction temperature and the flow rate, it is probable that the β value shift owing to change of velocity (along with temperature) may also affect the xylose yield. In an effort to verify this thesis, the velocity ratio was included between the two phases of reactor operation as an additional adjustable parameter in the percolation reactor simulation program. The ratio of velocity in high-temperature phase to the velocity in low-temperature phase was defined as ω . The simulator program was run for $\omega = 0.5, 1.0, 1.5, 2.0$, and 2.5 , covering two different temperature ranges. The results are listed in Table 2. The column for $\omega = 1.0$

Table 2
Effect of Velocity Step Change on Xylose Yield

T set	Yield									
	140-170°C					150-180°C				
τ $\omega = 0.5,$	1.0	1.5	2.0	2.5	0.5	1.0	1.5	2.0	2.5	
1	74.26	76.40	77.17	77.36	77.27	75.95	78.09	78.74	78.81	78.65
2	82.01	84.32	84.89	84.92	84.73	83.61	85.69	86.12	86.05	85.80
3	86.01	88.05	88.48	88.46	88.26	87.42	89.18	89.49	89.39	89.15
4	88.50	90.27	90.61	90.57	90.37	89.74	91.23	91.46	91.36	91.13
5	90.31	91.75	92.03	91.97	91.79	91.30	92.59	92.77	92.67	92.46

($[\text{H}_2\text{SO}_4] = 0.17\text{N}$)

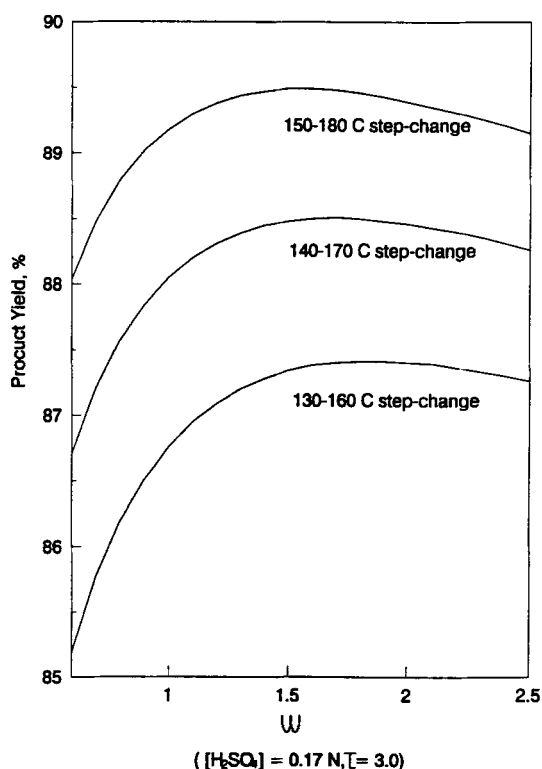


Fig. 3. Effect of flow-rate ratio on product yield.

in the table represents the base case (uniform velocity). Taking 140-170°C, and $\tau = 2.0$ as an example, the highest yield of 84.92% occurred at $\omega = 2.0$. The improvement ($\omega = 2.0$) over the base case (84.32%) is then 0.6%. The average value of yield improvement for various cases listed in Table 2 is estimated to be about 0.5%. The effect of ω on product yield is also shown in Fig. 3. In this figure, the maximum yield is seen to occur at ω value

slightly < 2 . In view of the fact that the velocity variation is a simple operation adjustment, it would be a worthy item to be considered in process design and operation.

Two-Stage Reverse-Flow Percolation Reactor

The yield increases with τ , whereas the product concentration is expected to decrease with it. An inverse relationship thus exists between the yield and the product concentration. A point to be emphasized is that the sugar concentration of the product is an important factor in the economics and energy efficiency of overall biomass processing. Obviously, the higher the concentration, the less processing cost and energy would be required in the final product separation phase, such as distillation of fermentation products. Certainly, there is a trade-off between the yield and product concentration. The true optimum point could only be determined from consideration of the overall process economics.

In this regard, an intriguing idea was developed by NREL investigators (including one of the authors, Torget) and made available for the authors to analyze from a theoretical standpoint. This concept also involves two-stage processing of biomass as was done in the preceding simulation study. However, there is an important modification in the process. The biomass is first treated at a low temperature in the percolation mode. Then it is treated again at a high temperature. Up to this point, the procedure is identical to the preceding two-stage process with a step-change in temperature. The throughput stream from the high-temperature treatment is again put through a percolation reactor packed with fresh biomass at low temperature. The reacted residue in this reactor is then treated with fresh acid at high temperature. This process is repeated. Figure 4 illustrates the difference between temperature step-change and two-stage reverse-flow configuration.

Depending on the acid throughput applied at each stage of the processing, the process stream for low-temperature processing is either supplemented with fresh acid or partially bypassed to the sugar product as shown in Fig. 5. The term ρ in Fig. 5 is defined as the amount of the liquid used at low-temperature processing over the total amount of liquid used for the entire process. Because the reverse flow is operated based on temperature step-change, the ρ value, which is predetermined in the temperature step change, is also used in reverse-flow arrangement. The ρ value of 0.5 thus indicates that the amount of liquid throughput in the reactor for high-temperature processing is the same as that for low-temperature processing. The overall contact pattern in this process resembles that of a countercurrent reactor, in that fresh biomass is met with the acid effluent containing the sugar product, and the fresh acid is met with the partially treated biomass. This process, thus, combines the concept of two-stage processing and a countercurrent processing. Countercurrent

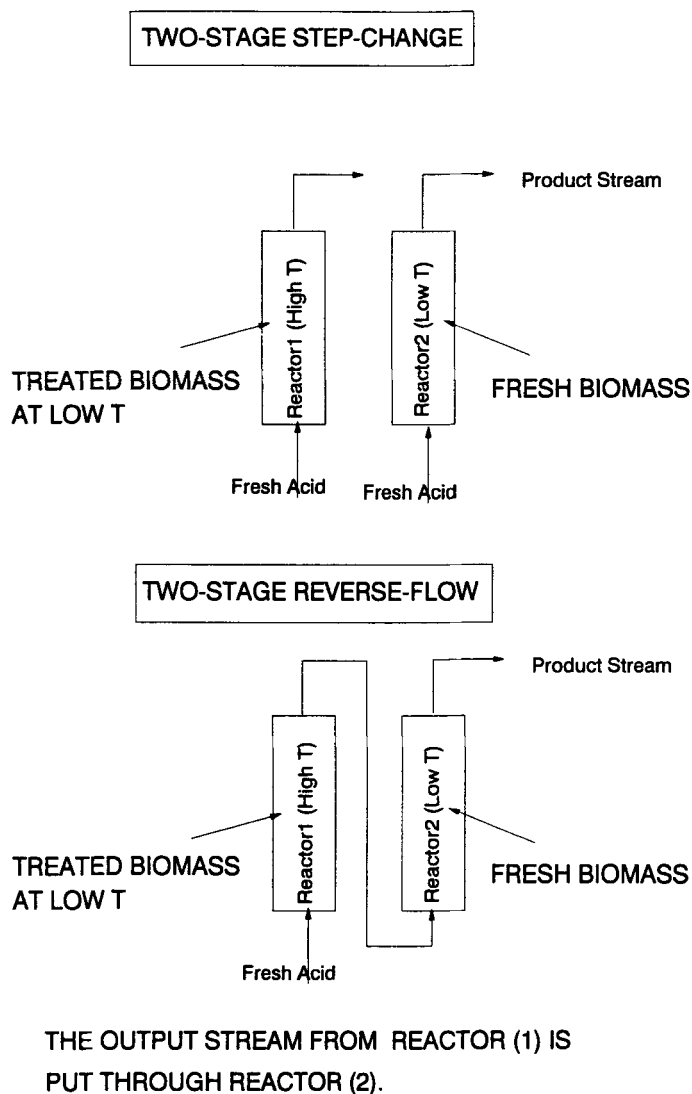


Fig. 4. Schematics of temperature step-change and two-stage reverse flow.

processing is effective in attaining a high product concentration as evidenced in the leaching processes. In the percolation process, the product yield is inversely related to product concentration. From this viewpoint, the reverse-flow reactor concept should apply well, especially for the percolation reactor system.

The results of the simulation with optimized process parameters are summarized in Table 3 and in Fig. 6. Since yield is inversely related to τ , and thus to product concentration (Fig. 6), the yield value alone is rather meaningless in the percolation process. To make a valid comparison, the yield value must be taken at a given level of product concentration. Taking

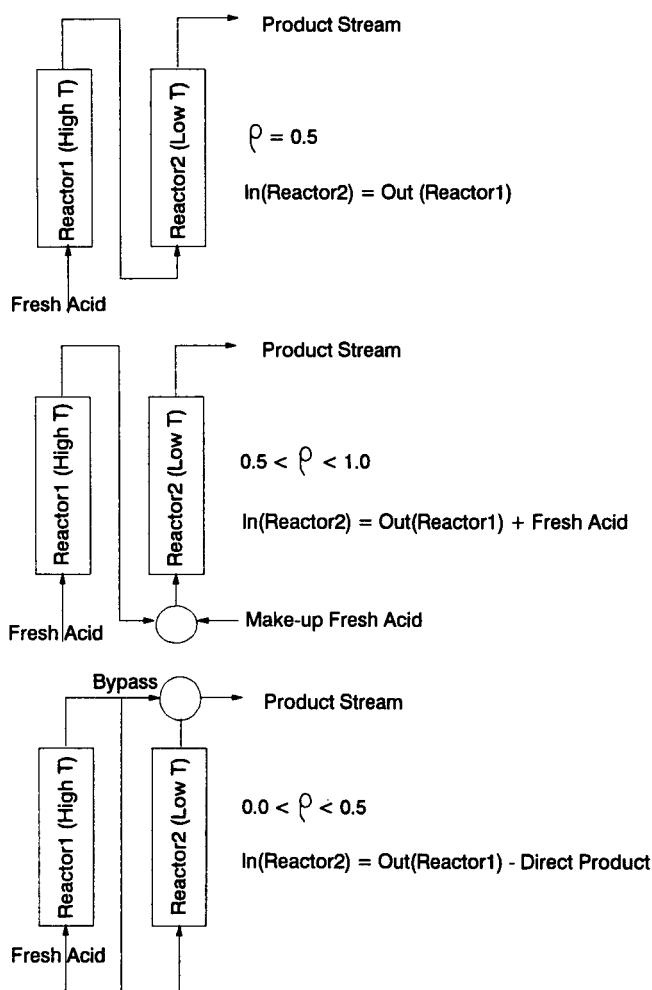


Fig. 5. Flow configuration in reverse-flow two-stage percolation reactor.

an example from Table 3, for the case of the 140–170°C step-change percolation reactor operation without reverse-flow arrangement, the yield and concentration of xylose at $\tau = 2$ are 84.94 and 1.47% w/v, respectively. Looking at the next column, under the same reaction conditions, but with a reverse-flow arrangement, at $\tau = 4$, the xylose yield is 89.41% and the xylose concentration is 1.50% w/v. Comparing the two cases (with and without reverse-flow arrangement), a significant improvement of yield was found from 84.94 to 89.41% at the same product concentration level (1.47–1.50%). The superior performance of the reverse-flow reactor is also shown in Fig. 6, where the yield vs concentration curve for this reactor is positioned above all other cases of percolation reactor operations. It is believed that the result of this simulation is a positive indication that the proposed reverse-flow reactor scheme is superior to any other known

Table 3
Xylose Yield and Concentration
in Two-Stage Reverse-Flow Percolation Reactor

τ	140–170°C ($\omega = 1.7$)				150–180°C ($\omega = 1.6$)			
	w/o R-flow		w/R-flow		w/o R-flow		w/R-flow	
	Yld.	Conc.	Yld.	Conc.	Yld.	Conc.	Yld.	Conc.
1	77.29	2.68	74.42	4.78	78.78	2.73	75.85	5.06
2	84.94	1.47	82.92	2.83	86.13	1.49	84.20	2.87
3	88.51	1.02	87.06	1.95	89.49	1.04	88.11	1.97
4	90.62	0.79	89.41	1.50	91.46	0.79	90.38	1.51
5	92.03	0.64	91.06	1.21	92.76	0.65	91.90	1.22

[H₂SO₄] = 0.17N
R-flow: reverse-flow.

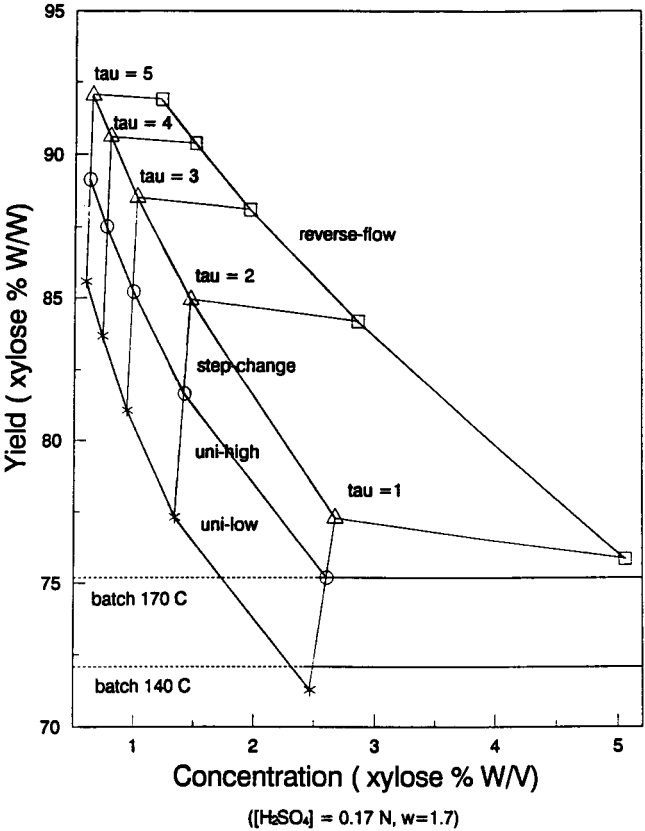


Fig. 6. Yield vs product concentration under various operation modes of percolation reactor.

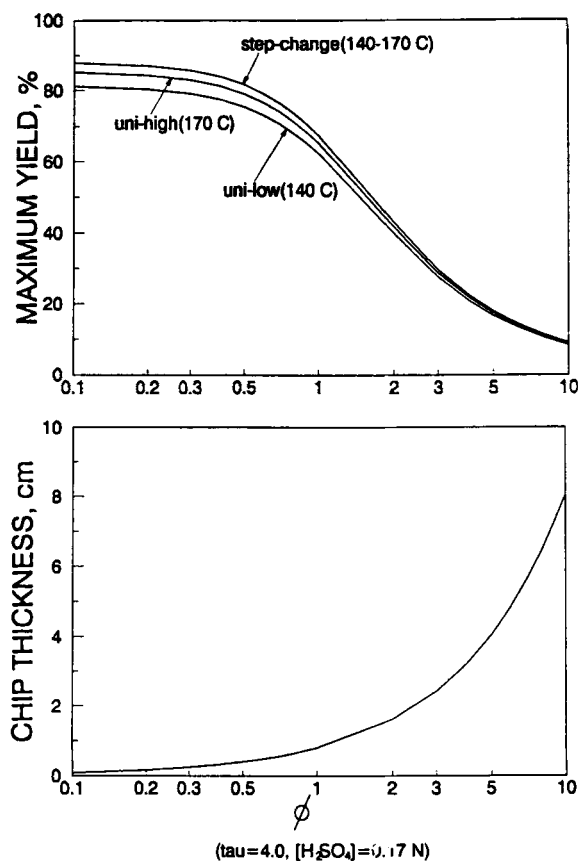


Fig. 7. Effect of intraparticle diffusion on product yield: yield vs chip-thickness.

reactor arrangement, especially in attaining high-yield and/or product concentration. The main reason for the existence of variational optimal temperature is the biphasic nature of the hemicellulose in the biomass.

Effect of Intraparticle Sugar Diffusion on Yield

Intraparticle diffusion of sugar component is a factor adversely affecting the performance of a percolation reactor. The effect of intraparticle sugar diffusion is related to product yield and size reduction of biomass feed. The analytical results in the diffusion model were used as a component in the reactor simulation program. Two cases of temperature policy (140–170°C and 150–180°C) were chosen and studied for the effect of the intraparticle diffusion of xylose on product yield. The computational results concerning the effect of intraparticle diffusion are summarized in Figs. 7 and 8. Each figure consists of two parts: Yield vs Thiele Modulus and Chip Thickness vs Thiele Modulus. These figures are constructed in

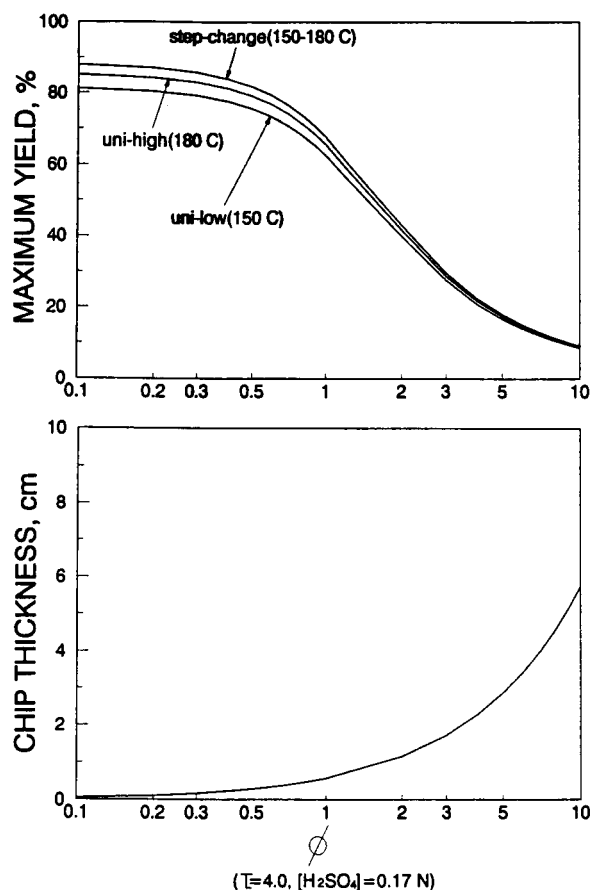


Fig. 8. Effect of intraparticle diffusion on product yield: yield vs chip-thickness.

such a way that one can determine the yield in relation to chip size and reaction condition. For example, in Fig. 8, when chip thickness = 0.29 cm, Thiele modulus is 0.5 (from lower figure) and the corresponding product yield is 79.2% (from upper figure).

The characteristic length (particle size) was determined as follows: Taking an example of 150–180°C step change, it is seen from Fig. 8 that for ϕ (Thiele Modulus) < 0.5 , the intraparticle diffusion becomes insignificant. To put this into practical terms, the following values of estimated parameters were used (10,12–14): D_e (effective diffusivity) = $D \times (\text{micro-porosity}) = 5.65 \times 10^{-5} \times 0.52 = 2.94 \times 10^{-5} \text{ cm}^2/\text{s}$, and k_3 (xylose decomposition rate at 165°C = average value of 150 and 180°C, 0.17N H_2SO_4) = $3.57 \times 10^{-4} \text{ s}^{-1}$.

$$\phi(\text{thiele modulus}) = b [(k_3 / D_e)]^{0.5} \quad (14)$$

Substituting these values into $\phi < 0.5$, we obtain b (characteristic length = half of thickness) $< 0.145 \text{ cm}$ (from Eq. [14]). For woody material, it is known that the diffusion occurs mostly in the longitudinal direction.

Therefore, the effect of intraparticle diffusion is insignificant if the size of feed material (in the longitudinal direction) is < 0.29 cm. Conversely, for the particle size greater than this, the intraparticle diffusion becomes progressively more important. Therefore, the critical chip thickness is 0.29 cm for 150–180°C step-change operation. Similarly, the critical chip thickness for 140–170°C was determined to be 0.4 cm.

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