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An Optimal Temperature Policy of Percolation Process as Applied to Dilute-Acid Hydrolysis of Biphasic Hemicellulose

Scientific Note

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NOMENCLATURE

A:	hemicellulose
A_i:	frequency factor for rate constant k_i, min^{-1}
B:	xylose and soluble xylose oligomer
C:	decomposed product
C_A, C_{AF}, C_{AS}, C_{Ao}, C_{AFo}, C_{ASo}	concentration of xylan as a xylose
C_B, C_{BF}, C_{BS}:	concentration of xylose
C_{Ho}:	(total xylan as a xylose)/(total liquid volume)
C_P:	average product concentration, w/v%
d_{cw}:	the density of crystalline wood, 1.54 g/mL
E_i:	activation energy for rate constant k_i
f:	τ_1/τ
H_F, H_s:	the fraction of fast and slow hemicellulose
k_i:	reaction rate constant, min^{-1}
L:	reactor length, cm
N_i:	acid concentration exponent
R:	universal gas constant
S_B, S_{BF}, S_{BS}:	C_B/C_{Ao}, C_{BF}/C_{AFo}, C_{BS}/C_{ASo}
t:	time, min

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T:	absolute temperature, °K
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
z:	x/L

Greek

α:	k_3/k_i, $i = 1, 2$
β_{opt}:	optimum β (corresponding to maximum yield)
β_F:	k_1L/u
β_S:	k_2L/u
ϵ:	void fraction in bed
Θ:	porosity within solid
τ:	tu/L

Subscript

A:	denoted component A
B:	component B
F:	fast xylan
i:	reaction no.
opt:	optimum
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 accompanies an additional benefit of hydrolyzing the hemicellulose fraction. In the design of this process, it is essential to consider the production of hemicellulose sugar as well as the effectiveness of the pretreatment. From the viewpoint of sugar production, the treatment condition, type of reactor, and mode reactor operation are important factors in the overall process. In previous studies (*1–3*), it has been established that the percolation reactor (packed-bed flow-through type) is one of the most suitable reactor types for biomass pretreatment.

In operation of this reactor, the sugar product is removed from the reactor as it is formed. This enables 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 high concentration level owing to high solid-to-liquid ratio that prevails in such a reactor.

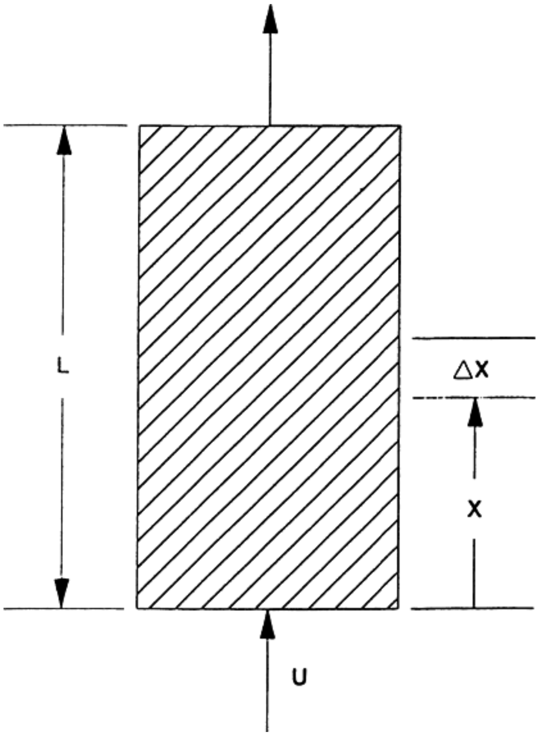


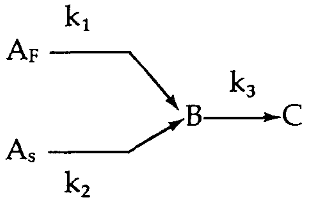
Fig. 1. Conceptual sketch of percolation reactor.

The authors are currently involved in research exploring the use of this reactor in pretreatment/hydrolysis of hemicellulose of hybrid poplar, a fast-growing (short-rotation) hardwood. At the present time, it is considered one of the most promising biomass resources in the United States. The hemicellulose in hardwood species is known to be biphasic (*4–8*), i.e., it is composed of two different fragments (fast-hydrolyzing fraction and the 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. This study was undertaken to see if there is a theoretical ground for a nonuniform optimum temperature policy and, if so, to verify its impact on the performance of this reactor.

MODEL DEVELOPMENT

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 slow-hyrolyzing ones.
2. Its kinetics follows the parallel consecutive first-order reactions:



Where A_F and A_s are fast and slow hemicellulose, respectively, B is xylose, and C is decomposed product.

3. The axial heat transfer after temperature step change is negligible.
4. Internal and external diffusion effects are negligible.

Material Balance

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

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

where $C_{AFo} = C_{AF} \exp\{-k_1 [t - (x / u)]\}$, $t > (x / u)$, and $C_{AS} = C_{ASo} \exp\{-k_2 [t - (x / u)]\}$, $t > (x / u)$.

The pertinent initial and boundary conditions are:

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

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

In order to apply the principle of superposition, we let $C_B = C_{BF} = C_{BS}$, where C_{BF} represents sugar released from fast fraction, and C_{BS} likewise. The above equations can be divided into two sets of equations with appropriate initial conditions and boundary conditions.

Both sets of equations have the same form, but different coefficients. The equation regarding fast hemicellulose is:

$$u[(\partial C_{BF} / \partial x)] + k_3 C_{BF} - k_1 C_{AF} = -[(\partial C_{BF} / \partial t)] \quad (4)$$

where $C_{AF} = C_{AFo} \exp\{-k_1 [t - (x / u)]\}$, $t > (x / u)$.

The equation for slow hemicellulose is:

$$u[(\partial C_{BS} / \partial x)] + k_3 C_{BS} - k_2 C_{AS} = -[(\partial C_{BS} / \partial t)] \quad (5)$$

where $C_{AS} = C_{ASo} \exp\{-k_2 [t - (x / u)]\}$, $> (x / u)$.
The boundary and initial conditions are same as Eqs. (2) and (3).

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

By Laplace transform method, we obtain the solution for Eqs. (4) and (5) as follows:

$$S_{BF} = (1 / \alpha_F) \exp \beta_F (z - \tau) \{1 - \exp[(-\alpha_F \beta_F) z]\} \quad (6)$$

$$S_{BS} = (1 / \alpha_S) \exp \beta_S (z - \tau) \{1 - \exp[(-\alpha_S \beta_S) z]\} \quad (7)$$

Addition of Eqs. (6) and (7) (superposition) yields the solution for the original Partial Differential Equation of Eqs. (1)-(3).

$$S_B = H_F S_{BF} + H_S S_{BS} \tag{8}$$

With regard to the reactor performance, there are two items of vital interest, namely, the yield and the product concentration. These are obtained from the solution as follows. The yield for fast hemicellulose is:

$$Y_{BF} = \int_1^{\tau+1} (S_{BF})_{z-1}\, d\tau = \{[1-\exp(-\alpha_F\beta_F)] / \alpha_F\beta_F\}\,[1-\exp(-\beta_F\tau)] \tag{9}$$

The yield for slow hemicellulose is:

$$Y_{BS} = \int_1^{\tau+1} (S_{BS})_{z-1}\, d\tau = \{[1-\exp(-\alpha_S F_S)] / \alpha_S\beta_S\}\,[1-\exp(-\beta_S\tau)] \tag{10}$$

The combined yield is:

$$Y_B = H_F Y_{BF} + H_S Y_{BS} \tag{11}$$

Average product concentration (C_P) can be expressed as follows:

$$C_P = C_{AO}\,(\text{Yield} / \tau) \tag{12}$$

where C_{AO} = (total xylan as a xylose inside the percolation reactor / total liquid volume inside the percolation reactor).

$$= \{(1-\epsilon)(1-\theta)\, d_{cw}\,(\%\text{xylan of hybrid poplar}) / [\epsilon + (1-\epsilon)\,\theta]\, 0.88\}$$
$$\cong 3.471\%\ (\text{w/v}) \tag{13}$$

The yield is now expressed as a function of reaction time and a number of dimensionless parameters, including β_F ($k_1 L/u$).

Since β_F is an important adjustable parameter, it would be of interest to

$$[(\partial Y_B / \partial\beta_F)]\,\alpha, \tau = [(\partial Y_B / \partial\beta_F)]\,\alpha, \tau, \beta_S +$$
$$[(\partial Y_B / \partial\beta_S)]\,\alpha, \tau, \beta_F\,[(\partial\beta_S / \partial\beta_F)]\,\alpha, \tau = 0 \tag{14}$$

maximize the yield with respect to β_F. In so doing, we set Eq. (14) provides an implicit equation from which the optimum β_F and, consequently, the corresponding maximum yield can be determined.

Yield for Temperature Step Change Operation

τ_1 represents the dimensionless time up to the temperature shifting point, and τ_2, the rest of the time period.

$$\tau = \tau_1 + \tau_2 \tag{15}$$

Thus, we further define f such that:

$$f = (\tau_1 / \tau) \tag{16}$$

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:

$$Y_{BSTEP} = H_F\,(Y_{BF1} + R_{AF} Y_{BF2}) + H_S\,(Y_{BS1} + R_{AS} Y_{BS2}) \tag{17}$$

where

$$Y_{BF1} = \int_{1}^{\tau_1 + 1} (S_{BF})_{z = 1}\, d\tau = \{[1 - \exp(-\alpha_{F_1}\beta_{F_1})] / \alpha_{F_1}\beta_{F_1}\} [1 - \exp(-\beta_{F_1}\tau_1)] \quad (18)$$

$$Y_{BS1} = \int_{1}^{\tau_1 + 1} (S_{BS})_{z-1}\, d\tau = \{[1 - \exp(-\alpha_{S_1}\beta_{S_1})] / \alpha_{S_1}\beta_{S_1}\} [1 - \exp(-\beta_{S_1}\tau_1)] \quad (19)$$

$$Y_{BF2} = \int_{1}^{\tau_2 + 1} (S_{BF})_{z-1}\, d\tau = {}_2[1 - \exp(-\alpha_{S_2}\beta_{S_2})] / \alpha_{S_2}\beta_{S_2}\} [1 - \exp(-\beta_{F_2}\tau_2)] \quad (20)$$

$$Y_{BS2} = \int_{1}^{\tau_2 + 1} (S_{BS})_{z-1}\, d\tau = \{[1 - \exp(-\alpha_{S_2}\beta_{S_2})] / \alpha_{S_2}\beta_{S_2}\} [1 - \exp(-\beta_{S_2}\tau_2)] \quad (21)$$

$$R_{AF} = \exp(-\beta_{F_1}\tau_1) \quad (22)$$

$$R_{AS} = \exp(-\beta_{S_1}\tau_1) \quad (23)$$

The concentration and the optimum condition (β_F, β_S) can be determined in the same manner as in uniform temperature operation. This completes the mathematical modeling.

RESULTS AND DISCUSSION

The kinetics of dilute acid catalyzed hydrolysis of hybrid poplar hemicellulose was investigated. The reaction pattern was modelled as consecutive reactions of hydrolysis of hemicelluloses followed by decomposition of xylose. From observation of our batch experimental data, it appeared that the hemicellulose in this substrate was biphasic, i.e., the hemicellulose in hybrid poplar is composed of two different fragments (fast-hydrolyzing fraction, denoted by A_F, and the slow-hydrolyzing fraction, A_S). This finding was in agreement with the kinetic pattern of hemicellulose hydrolysis in other species of woods, including Aspen and Southern red oak (*9,10*). The kinetic model was therefore set to follow the pattern of parallel-serial reactions. The kinetic parameters (Arrhenius factors and the acid exponents) were experimentally determined by nonlinear regression analysis. The results are shown in Table 1. The validity of this kinetic model is seen by close agreement of the experimental data with the model prediction as shown in Fig. 2.

This information was then used in the simulation of percolation reactor performing dilute acid pretreatment/hemicellulose hydrolysis. In so doing, the partial differential equation depicting percolation reactor operation was analytically solved to determine the product yield and concentration under various conditions. The simulation was designed to deal with these two factors as affected by reaction temperature, duration of operation (cumulative recovery of product effluent), and optimum flow rate under various reaction conditions. The main interest of this study, however, was placed on the temperature policy. The conventional temperature strategy in percolation reactor operation has been to apply a uniform temperature throughout. This subject has been previously reported on for simplified kinetics (serial reactions of hemicellulose-xylose-decomposition products [3]). On recognition of the fact that the

Table 1
Kinetic Parameters[a]

Reaction No. i	Preexponential factor A_i	 N_i	Activation energy, E_i
1	6.17×10^{13}	1.40	28,000
2	1.88×10^{14}	1.20	31,000
3	1.01×10^{11}	0.48	25,330

[a] Fraction of fast hemicellulose = $H_F = 0.71$; $H_S = 0.29$.
$k_i = A_i[C]^{N_i}\exp[-E_i/(RT)]$.
[C] = w/v% of sulfuric acid.

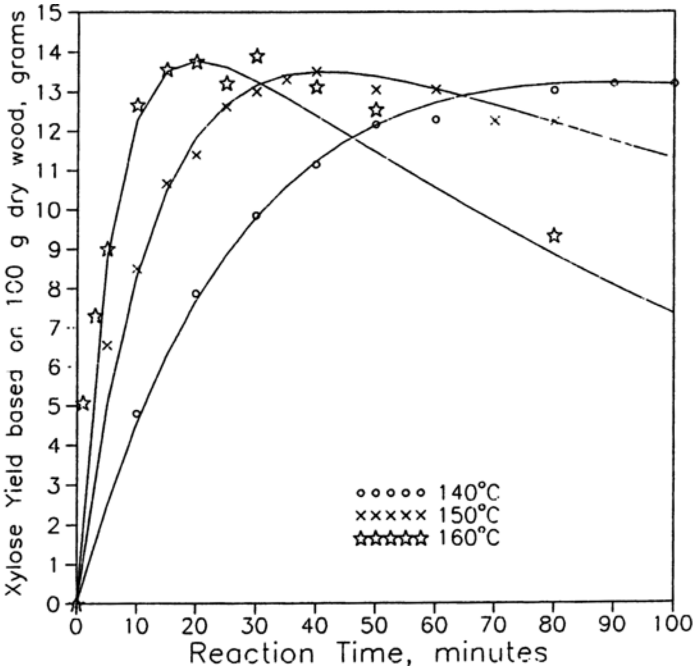


Fig. 2. Reaction progression in hydrolysis of hardwood hemicellulose at 0.49 w/v% H_2SO_4. (–: Model Prediction). ooooo 140°C, ××××× 150°C, ☆☆☆☆☆ 160°C.

hemicellulose of our interest is biphasic, it was thought that the uniform temperature policy may not be the best solution. For a simple serial reaction, high temperature is preferred because of the activation energy difference between the hydrolysis and decomposition. The upper limit of the temperature is determined by practical considerations. For biphasic substrate, however, applying uniformly high temperature may cause excessive decomposition of the sugar released from H_F fraction, which

Table 2
Optimal Yield vs τ[a]

	τ							
Temperature, °C	2	3	4	5	6	7	8	9
150	75.3	79.0	81.7	83.7	85.3	86.5	87.5	88.4
180	79.4	83.1	85.6	87.4	88.7	89.8	90.6	91.3
Step change	81.2	85.5	88.0	89.8	91.0	92.0	92.8	93.4
140	73.8	77.5	80.2	82.2	83.9	85.2	86.3	87.2
170	78.0	81.8	84.4	86.3	87.7	88.8	89.7	90.5
Step change	79.5	84.1	86.8	88.7	90.1	91.1	92.0	92.6
165	77.3	81.1	83.8	85.7	87.1	88.3	89.2	90.0
185	80.0	83.7	86.2	87.9	89.2	90.2	91.0	91.7
Step change	82.7	86.4	88.6	90.2	91.4	92.2	93.0	93.5

[a] Temperature: uniform low, uniform high, and step change.

builds up at the early phase of the reaction. Whether there exists an optimum uniform temperature for parallel-serial reaction in percolation reactor is unknown at this time. Consequently, it became of interest to see if variation of temperature during the process, especially a step change from uniform low to uniform high, can give better results than either limit case.

The simulation results addressing this point are summarized in Table 2. Three sets of temperature ranges were studied: 150–180, 140–170, and 165–185°C. These temperatures were chosen randomly below 185°C. It is well known that at temperatures above 185°C, an appreciable degree of cellulose hydrolysis occurs, which is highly undesirable in pretreatment practice. Temperature shift (from low to high) were made at about 60% of total reactor operation time. All yields and concentrations were calculated on the basis of a substrate loading of 10% weight hemicellulose/volume of liquid. The β value (a quantity inversely proportional to flow rate) was optimized at each reaction temperature and at a given τ value, so that it could give maximum xylose yield. We have limited the tau (τ) (dimensionless operation time) to 9 in order to maintain the average product concentration about 1% w/v. In all of the three cases, the xylose yield with step change in temperature was indeed higher than either of uniform temperature cases. The increase in yield was discernible: about 6.5% over that of low uniform temperature case and about 2.5% over uniform high temperature case. In the dilute acid pretreatment process, it is important to minimize hydrolysis of the cellulosic component in the biomass. The step change temperature policy provides an additional advantage in this regard. In this method, the high temperature is applied at the latter phase of the process. Since cellulose hydrolysis occurs only under high temperature condition, the loss of cellulose under this scheme is expected to be lower.

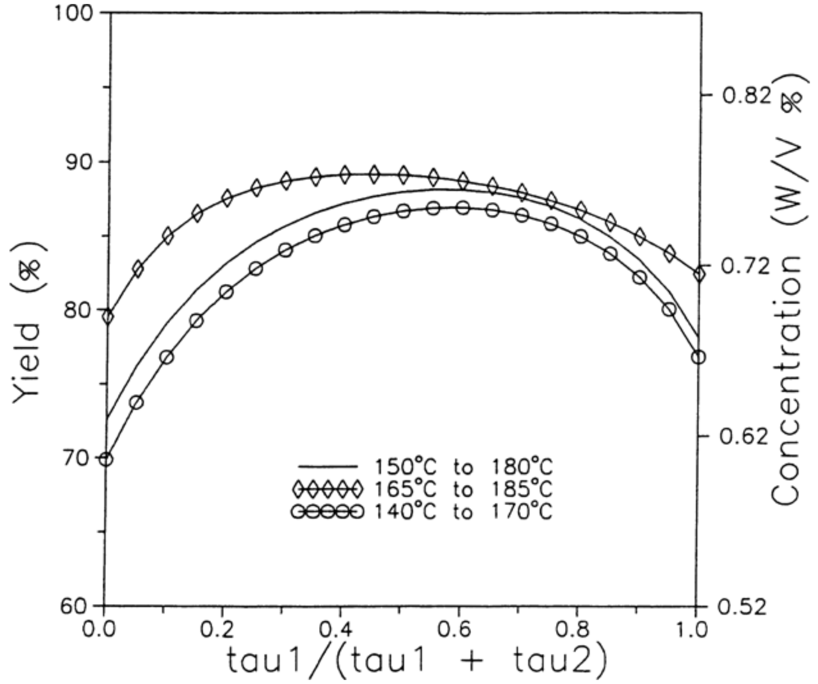


Fig. 3. Yield (concentration) vs $\tau_1/(\tau_1+\tau_2)$ ($\tau_1+\tau_2=4.0$). ——— 150–180°C, ⊟⊟⊟⊟⊟ 165–185°C, ⊖⊖⊖⊖⊖ 140–170°C.

A few other noteworthy points have been found from the simulation results. One of such has to do with the optimum shifting point in the step change (at what point do we shift the temperature). In numerical exercise, we fixed τ at 4, a representative value. The computed yield vs shifting is shown in Fig. 3. For the three cases, the maximum yield occurred with the shifting at 0.55, 0.45, and 0.6 of total τ for the respective runs.

The authors also sought a plausible explanation as to why the yield with step change is higher than those attainable at low- and high-end temperatures. It appears that β value holds the key to this answer. First of all, it was found that there is a vast difference in optimal β value (a quantity inversely proportional to flow rate) between fast hemicellulose and slow hemicellulose. Table 3 lists the β_{opt} values for each hemicellulose fragment. Taking 140°C as an example, β_{opt} for fast hemicelluose is about one-sixth of that for slow hemicellulose. Similar trends are seen at other temperatures. In reference to Table 3, in order to hydrolyze the fast hemicellulose (again at 140°C) in an optimal fashion, one must apply an operating condition, such that $\beta_{opt}=1.15$. On the other hand, to do the same for slow hemicellulose, one must adjust the β_{opt} to 6.50. Since the slow and fast hemicellulose cannot be processed separately, one must seek a compromised β_{opt}. We found such β_{opt} to be 2.95 (Table 3). Under uniform temperature condition, the overall β_{opt} lies between the two β_{opt}

Table 3
β_{opt} values for A_F, A_S, and for Combined Hemicellulose

Temperature, °C	β_{opt} for A_F	A_S	$A_F + A_S$
140	1.15	6.50	2.95
150	1.17	6.32	3.07
165	1.19	6.04	3.19
170	1.20	5.95	3.21
180	1.22	5.77	3.24
185	1.23	5.69	3.25

Table 4
β_{opt} for Step Change of Temperature

1st Temp., °C	2nd Temp., °C	Before step change, value of A_F	After step change, value of A_S
150	180	1.21 (1.71)	10.97 (5.77)
140	170	1.15 (1.15)	11.57 (5.95)
165	185	1.92 (1.19)	7.82 (5.69)

for each fragment. A similar computation was carried out for the case of step change. Table 4 lists the β_{opt} before and after the temperature shift. For the step change operation where temperature shifts from 165 to 185°C, the β_{opt} shifts accordingly from 1.92 to 7.82. The shift of β in this case can be practiced in reactor operation simply by adjusting the inlet fluid temperature and the flow rate. It is to be noted that the initial β_{opt} of 1.92 is close to 1.19, the optimal value for fast hemicellulose at 165°C. The final β_{opt} of 7.82 is somewhat close to 5.69, the β_{opt} for slow hemicellulose computed at 185°C. With the step change in effect, at low temperature phase (early phase), the reaction and operating condition is set to work primarily on the fast-hemicellulose fraction. At the shifting point, the substrate contains mostly the slow hemicelluose. At high-temperature phase (latter phase) then, reaction and operating condition is readjusted to work primarily on the slow hemicellulose. The authors believe this is the reason for the projected improvement in yield associated with the step change of temperature during percolation reactor operation.

In conclusion, a theoretical basis for the need of optimal temperature policy is diluted acid pretreatment of biomass has been provided. As one such case, the authors have proven that step change of reaction temperature during percolation process is advantageous especially in improving the sugar yield. The main reason for the existence of variational optimal temperature is the biphasic nature of the hemicellulose in biomass. A strong possibility exists that further variation of temperature policy (continual variation rather than step change of temperature, for example) may further improve the reactor performance. In this regard, our work on the subject matter is at an early phase. Nonetheless, the authors believe it is a significant finding that temperature policy in percolation reactor operation is an important factor that can impact on the process economics of biomass pretreatment.

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REFERENCES

1. Lee, Y. Y. et al., (1978), *Biotechnology & Bioengineering Symposium,* No. 8, 75.
2. Limbaugh, M. L. (1980), M.S. Thesis, Auburn University, AL.
3. Cahela, D. R. and Lee, Y. Y. (1983), *Biotechnol. Bioeng.* **25,** 3.
4. Veeraraghaven, S. et al. (1982). "Kinetic Modeling and Reactor Development for Hemicellulose Hydrolysis," presented at AIChE National Meeting, Orlando, FL, February.
5. Kobayashi, T. and Sakai, Y. (1956), *Bull. Agr. Chem. Soc. Japan* **20, No. 1,** 1.
6. Oshima, M. (1965), "Wood Chemistry, Processing Engineering Aspect," Noyes Development Corporation, New York.
7. Conner, A. H. (1984), *Wood and Fiber Sci.* **16(2),** 268.
8. Maloney, M. T. et al. (1985), *Biotechnol. Bioeng.* **27,** 355.
9. Grohmann, K., Torget, R., and Himmel, M. (1985), *Biotech. Bioeng. Symposium,* **15,** 59.
10. Kim, S. B. (1986), Ph.D. Dissertation, Auburn University, AL.