

Initial Evaluation of Simple Mass Transfer Models to Describe Hemicellulose Hydrolysis in Corn Stover

MICHAEL A. BRENNAN AND CHARLES E. WYMAN*

*Thayer School of Engineering, Dartmouth College,
8000 Cummings Hall, Hanover, NH 03755,
E-mail: Charles.Wyman@Dartmouth.edu*

Abstract

The uncatalyzed hydrolysis and removal of xylan from corn stover is markedly enhanced when operation is changed from batch to continuous flowthrough conditions, and the increase in hemicellulose removal with flow rate is inconsistent with predictions by widely used first-order kinetic models. Mass transfer or other physical effects could influence the hydrolysis rate, and two models reported in the literature for other applications were adapted to investigate whether incorporation of mass transfer into the kinetics could explain xylan removal in both batch and continuous flowthrough reactors on a more consistent basis. It was found that a simple leaching model and a pore diffusion/leaching model could describe batch and flowthrough data with accuracy similar to that of conventional batch models and could provide a more rational explanation for changes in performance with flow rate.

Index Entries: Pretreatment; flowthrough; batch; mass transfer; hemicellulose hydrolysis.

Introduction

Cellulosic biomass can be pretreated by removing the hemicellulose fraction to expose cellulose to enzymes and recover sugars in high yields for fermentation to fuels and chemicals with unique and powerful economic, environmental, and strategic benefits (1). Accurate, predictive tools would be valuable in scaling up pretreatment by hemicellulose hydrolysis and in defining opportunities to advance pretreatment, but current hemicellulose hydrolysis kinetic models, which have changed little since the mid-1940s, display some inconsistencies that call into question their mechanistic valid-

*Author to whom all correspondence and reprint requests should be addressed.

ity (2). For example, significant differences are observed in predicting whether or not sugar yields increase or decrease with increasing acid concentration or temperature. In addition, hemicellulose removal has been observed to change with solids concentration and flow through the solids, contrary to conventional first-order kinetic model predictions (3–5). Furthermore, one would not expect homogeneous first-order reaction kinetics to necessarily describe solid-liquid reactions in which mass transfer, solubility limitations, and nonhomogeneous reactions at the solid-liquid interface could be important (2,3,6). Oligomers could also play an important role in governing the performance of hemicellulose hydrolysis, and understanding their behavior could help explain some of the deviations from first-order kinetics (7). Jacobsen and Wyman (2) postulated that limitations in the solubility of hemicellulose oligomers in hydrolysate liquid coupled with mass transfer could account for the differences among batch, cocurrent, and flowthrough/countercurrent systems.

In the present study, two mass transfer models were adapted from other applications, and preliminary comparisons were made to conventional reaction-only models to assess their abilities to describe hemicellulose hydrolysis in batch and flowthrough reactors. Particular attention was paid to including production and diffusion of oligomers in these models with the intent of exploring whether this approach holds promise for explaining the performance of batch and flowthrough systems in a more consistent manner.

Conventional Kinetic Models

In 1945, Saeman (8) described acid hydrolysis of cellulose as a homogeneous two-step first-order reaction, in which acid catalyzes the breakdown of cellulose to glucose followed by the breakdown of the glucose released to form hydroxymethylfurfural and other degradation products. This modeling approach has since been applied to hemicellulose hydrolysis with the hemicellulose portion hydrolyzed to xylose, which breaks down to form furfural and other degradation products (9). These reactions are assumed to follow a first-order dependence on reactant concentration with an Arrhenius temperature relationship for the rate constant. Additional refinements were made to improve such models in describing hemicellulose hydrolysis (2). For example, Kobayashi and Sakai (10) incorporated two fractions of hemicellulose with independent kinetic constants into a biphasic model, with one fraction hydrolyzing faster than the other.

While the previous models assume that oligomers break down to monomers so quickly that they can be neglected, Mehlberg and Tsao (11) suggested a reaction mechanism for hemicellulose hydrolysis in which oligomers formed during reaction have varying degrees of polymerization (DPs) and their reaction rates vary with their respective DP value (lower DP corresponds to a faster reaction). Another reaction model incorporated two types of oligomers, some with high DPs and the rest with lower DPs, and assumed that xylan is hydrolyzed to the high-DP oligomers that further react to lower-DP oligomers (12). This model showed that the oligomers

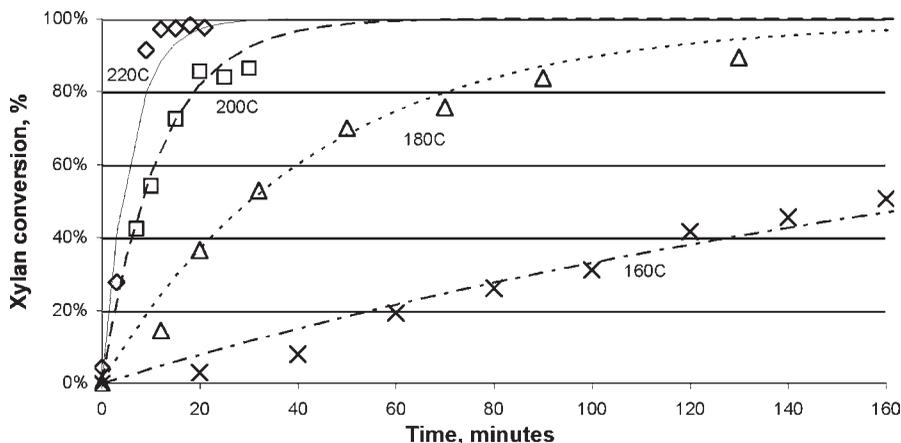


Fig. 1. Data and biphasic chemical reaction model predictions of xylan conversion vs time for batch pretreatment of corn stover with only water at 160, 180, 200, and 220°C and 5% solids concentration.

could either directly form degradation products or be converted to monomers that can then degrade.

On the basis of these approaches, the following biphasic equation can be applied to describe the amount of xylan left in the solid phase for hemicellulose hydrolysis:

$$M_A(t) = F_{fast} \times \exp(-k_1 t) + (1 - F_{fast}) \times \exp(-k_2 t) \quad (1)$$

in which $M_A(t)$ is the mass fraction of the initial xylan left in the solids; F_{fast} is the fraction of the total xylan that hydrolyzes more rapidly for a biphasic reaction; k_1 and k_2 are the first-order rate constants for hydrolysis of the fast and slow fractions of xylan, respectively; and t is the time. We applied this expression throughout this analysis to describe hydrolysis of xylan for batch and flowthrough pretreatment of corn stover for varying temperatures, solids concentrations, acid levels, and flow rates. The fast fraction F_{fast} was determined to minimize the sum of the squares of the differences between experimental and predicted yields for application of Eq. 1 to batch data collected at different reaction conditions for dilute-acid (T. Lloyd and C. Liu, personal communication, March 2002) and water-only pretreatment of corn stover (13). Then, the kinetic constants k_1 and k_2 were fit to the data using the Solver Routine in Excel to minimize the sum of the squares of the differences between the experimental data and predicted values for batch and flowthrough data.

Figures 1 and 2 present some representative results for the application of Eq. 1 to describe data for hydrolysis of hemicellulose in corn stover in only water by batch and flowthrough systems, respectively. In Figs. 1 and 2, xylan conversion is calculated as the initial mass of xylan minus the mass of xylan at a time t all divided by the initial mass of xylan. Although the data are not presented, acid-catalyzed systems behaved similarly.

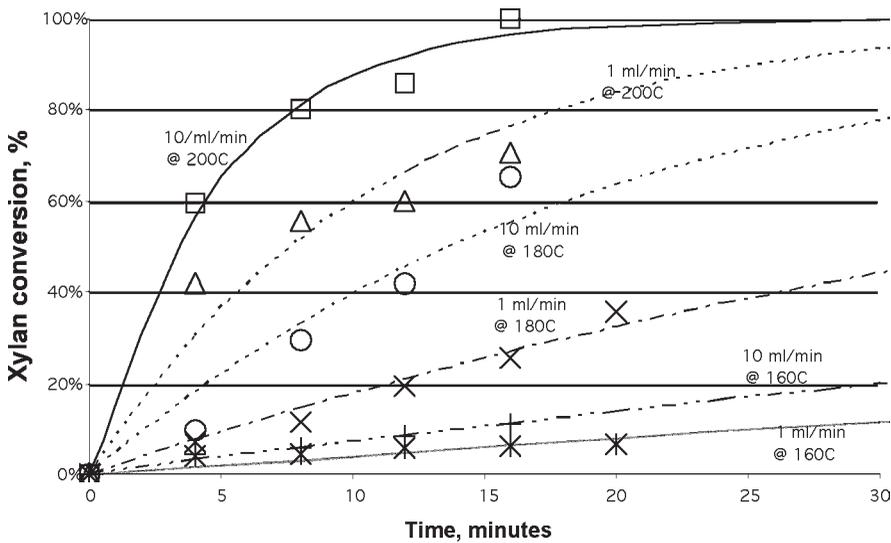


Fig. 2. Data and biphasic chemical reaction model predictions of xylan conversion vs time for flowthrough pretreatment of corn stover with only water at 160, 180, and 200°C and flow rates of 1 and 10 mL/min.

Table 1
Rate Constants for Biphasic Chemical Reaction
and Leaching Kinetic Models at 180°C

Reactor	Condition	Reaction only		Leaching-only model	
		k_1	k_2	k_1	k_2
Batch					
No acid	5% Solids	0.81396	0.2268	0.03336	0.0
	10% Solids	0.21252	0.1884	0.02193	0.00011
	20% Solids	0.11568	0.0060	0.02417	0.06310
0.5% Acid	25% Solids	81.389	78.984	89.418	0.01580
1.0% Acid	25% Solids	120	—	120	224
Flowthrough					
No acid	10 mL/min	0.51320	0.008366	0.04946	0.000120
	1 mL/min	0.19820	0.003252	0.01397	0.001584

Table 1 summarizes the rate constants for this model, and Table 2 presents the sum of squares of the differences (SS_E) between the experimental data and the results predicted from application of Eq. 1. Interestingly, the plots of $\ln(k)$ vs $(1/T)$ (not shown) yield straight lines, suggesting that an Arrhenius relationship is appropriate.

Table 2
Sum of Square of Differences Between Experimental Data
and Predicted Results (SS_E) for Flowthrough
and Batch Reactors Without Acid Addition at 180°C

Reactor	Condition	Reaction only (SS_E)	Leaching (SS_E)	Branched pore (SS_E)
Batch	5% Solids	840	2491	3408
	10% Solids	479	210	1477
Flowthrough	10 mL/min	2638	1104	8522

Mass Transfer Considerations

Although the rate constants in Eq. 1 can be fit to describe hemicellulose hydrolysis in both batch and flowthrough systems, the change in rate constants with flow is not consistent with chemical reaction control. Thus, one would expect that mass transfer or other physical effects could be important. For example, Table 3 summarizes the effect of some key process variables on kinetics and their implications for control by chemical reactions vs mass transfer (6). Although many hemicellulose hydrolysis studies have pointed out the significance of solids concentrations, relative densities, viscosities, particle size, and reactor design on the overall removal of hemicellulose sugars from biomass (3,7), Table 3 illustrates that such factors should not affect purely chemical reactions but should be indicative of a role of mass transfer in governing hemicellulose hydrolysis. Yet mass transfer considerations have not been incorporated into hemicellulose hydrolysis models (2). Thus, while current models may be useful for data regression, their inability to describe rationally the effect of flow and other inconsistencies could undermine their accuracy in predicting the effects of scale-up or technology improvements.

Biphasic Mass Transfer Leaching Model

Mass transfer models have been used to describe the leaching of soluble substances from porous particles into solution. Such models include a concentration difference that drives the concentration of soluble components in the solids and solution to equilibrate (14). Application of one such model (14) to track release from a solid into solution results in the following equations when applied to xylan conversion in a batch system:

$$\text{Solid} \quad \frac{dc_A}{dt} = -\frac{k_c A_s}{V_c} (c_A - c_{A\infty}) \quad (2)$$

$$\text{Solution} \quad \frac{dc_{A\infty}}{dt} = -\frac{k_c A_s}{V_t} (c_A - c_{A\infty}) \quad (3)$$

Table 3
Qualitative Relationships Among Performance and Process Parameters
for Control by Mass Transfer and Chemical Reaction (6)

Controlling step	Variables affecting observed reaction rate		
	Major influence	Minor influence	Insignificant influence
Liquid-solid mass transport (liquid reactant)	<ul style="list-style-type: none"> • Amount of catalyst • Catalyst particle size • Concentration of reactant in liquid phase 	<ul style="list-style-type: none"> • Temperature • Agitation rate • Reactor design • Viscosity • Relative densities 	<ul style="list-style-type: none"> • Concentration of gas-phase reactant • Concentration of active components on catalyst
Chemical reaction (with insignificant pore diffusion resistance)	<ul style="list-style-type: none"> • Temperature • Amount of catalyst • Reactant concentrations • Concentration of active components on catalyst 		<ul style="list-style-type: none"> • Stirring rate • Reactor design • Catalyst particle size

Table 4
Rate Constants for Branched Pore Model at 180°C

Reactor	Conditions	k_1	k_2	k_3	
Batch	No acid	5% Solids	0.7200	0.00120	—
		10% Solids	0.057768	0.23514	—
		20% Solids	0.024168	0.63096	—
Batch	1.0% Acid	25% Solids	60.00	—	—
	0.5% Acid	25% Solids	53.77	84.00	—
Flowthrough	No acid	10 mL/min	0.63284	0.011880	—
		1 mL/min	0.23521	0.055030	—
	0.05% Acid	10 mL/min	3.6498	0.150324	$8.06e^{-4}$
		1 mL/min	0.8474	0.393264	$8.86e^{-6}$
		0 mL/min	1.8338	1.696000	—
	0.10% Acid	10 mL/min	9.6000	2.2530	—
		5 mL/min	5.9110	0.9721	—
		1 mL/min	3.6240	9.8269	1.8166
		0 mL/min	0.7632	0.2446	0.08748

in which c_A is the concentration of the xylan in the solid, $c_{A\infty}$ is the concentration of xylan in solution, k_c is a mass transfer coefficient, A_s is the surface area of the particles, V_c is the volume of the solid, and V_t is the total volume of solution. The concentrations in both phases change with time, and these two mass balance equations are coupled. c_A and $c_{A\infty}$ can be related by dividing Eq. 2 by Eq. 3 and integrating with the initial concentrations c_{Ai} and $c_{A\infty i}$ to give

$$c_{A\infty} - c_{A\infty i} = -V_r (c_A - c_{Ai}) \tag{4}$$

Substituting this relationship into the solid mass balance, Eq. 2, one obtains a single equation for c_A :

$$\frac{dc_A}{dt} + \left(\frac{k_c A_s}{V_c}\right) (1 + V_r) c_A - \left(\frac{k_c A_s}{V_c}\right) (c_{A\infty i} + V_r c_{Ai}) \tag{5}$$

in which $V_r = \frac{V_c}{V_t}$.

Based on the solution developed by Plawsky (14), the concentration of xylan in the solid is described by

$$c_A(t) = c_{Ao} \exp \left[-\left(\frac{k_c A_s}{V_c}\right) (1 + V_r) t \right] + \left(\frac{c_{A\infty o} + V_r c_{Ao}}{1 + V_r}\right) \times \left\{ 1 - \exp \left[-\left(\frac{k_c A_s}{V_c}\right) (1 + V_r) t \right] \right\} \tag{6}$$

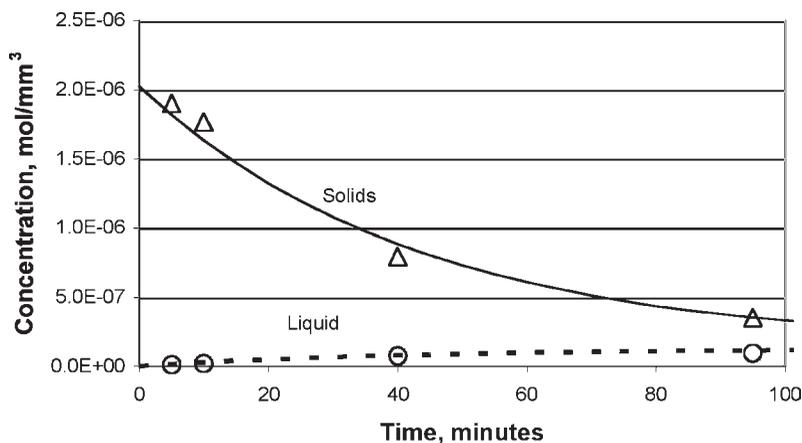


Fig. 3. Data and biphasic mass transfer leaching model predictions of xylan concentrations in solids and solution vs time for water-only batch tube hydrolysis of corn stover at 180°C and 10% solids.

while the concentration in solution is predicted to be:

$$c_{A\infty}(t) = c_{A\infty} - V_r \left\{ \left(\frac{c_{A\infty} + V_r c_{Ao}}{1 + V_r} - c_{Ao} \right) \left(1 - \exp \left[- \left(\frac{k_c A_s}{V_c} \right) (1 + V_r) t \right] \right) \right\} \quad (7)$$

It was found that applying the biphasic concept of Eq. 1 to Eq. 6 improved the results, and the constants k_1 and k_2 and the fraction of faster reacting material were calculated using the Solver Routine in Excel to minimize SS_E for batch tube (13) and flowthrough systems (T. Lloyd and C. Liu, personal communication, March 2002).

Figure 3 shows that the leaching model predicts that xylan will dissolve until it equilibrates with its concentration in solution for batch systems. However, as seen in Fig. 4, although there is an initial spike in solution concentration for the flowthrough system, the solution concentration drops quickly owing to continual replacement of solution with fresh water, and as a result, a concentration gradient is maintained throughout the period as c_A is maintained larger than $c_{A\infty}$. Thus, equilibrium between the xylan concentration in the solute and solution cannot be met for the flowthrough reactor until all of the xylan is exhausted from the solids. Table 1 presents mass transfer coefficients for the leaching model, and Table 2 summarizes SS_E for this model. Overall, the predicted and measured values agree reasonably well for both batch and flowthrough reaction systems with only water.

Branched Pore Leaching Model

Cao et al. (15) developed a branched pore leaching model in order to simulate the leaching of water-soluble organic carbon from soil in a column

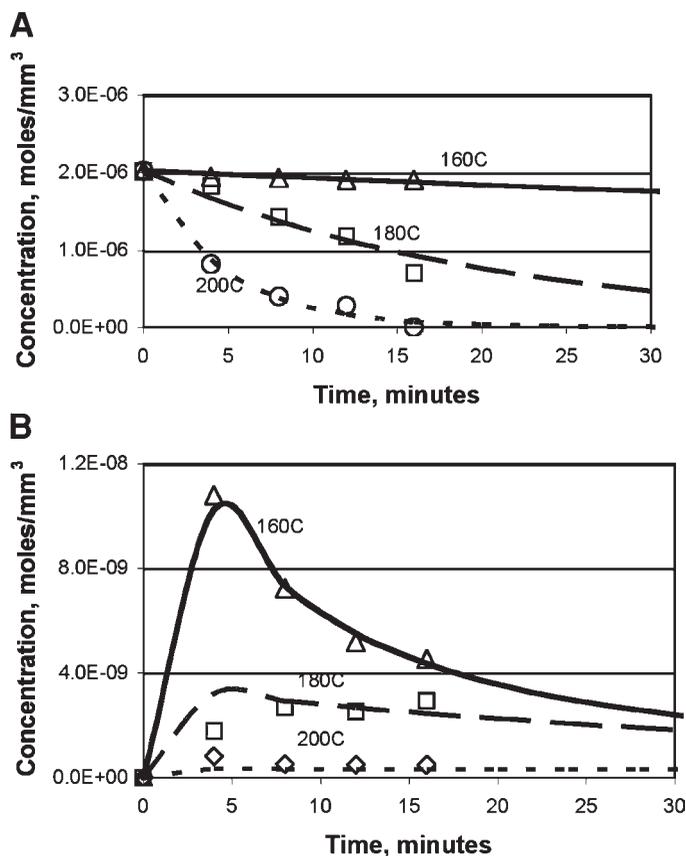


Fig. 4. (A) Data and biphasic mass transfer leaching model predictions of xylan concentration in solids vs time for flowthrough pretreatment of corn stover with only water at 160, 180, and 200°C and flow rate of 10 mL/min; (B) xylan concentrations in solution vs time for same conditions.

leaching system. The model and its extension to xylan hydrolysis can be depicted as the release of material (xylan) inside the solid matrix (biomass) to internal capillary and gravitational pores in four sequential steps: (1) degradation of insolubles (xylan) to form solubles (xylose oligomers), (2) desorption of the solubles into capillary pore water, (3) diffusion of solubles from capillary pores into the gravitation pore water, and (4) leaching of the solubles from gravitation pore water into the bulk solution by convection. Furthermore, the overall kinetics are described by three additive terms for degradation, desorption/diffusion, and convection. Because there is no turbulence in capillary pore water, the solute migrates through the pores by molecular diffusion alone, and the rate of molecular diffusion can be much slower than the rate of desorption, through which the solubles that are sorbed on the surface of the particles enter the capillary pore water.

Therefore, steps 2 and 3 can be combined into a single step, and the overall kinetics can then be described in three compositional fractions: the permanent (formed from insolubles), the resistant (in capillary pores and sorbed within aggregates), and the labile (in gravitational pores). The contribution of the permanent fraction (the insoluble portion) to the soluble portion in the leachate is proportional to its concentration. The release of the resistant fraction is represented by mass transfer, and the translocation of the labile fraction relates to convection flow and dispersion.

The overall release of water soluble organic carbon from soil, on which this model for xylan hydrolysis is based, was expressed as three additive terms (15):

$$C_t = C_1 e^{-k_1 t^2} + C_2 e^{-k_2 t} + C_3 (1 - e^{-k_3 t}) \quad (8)$$

in which C_t is the concentration of leachate at time t ; k_1 , k_2 , and k_3 are the transfer rate constants for the labile, the resistant, and the permanent fractions, respectively; C_1 and C_2 are concentration components of the solute for the first two fractions in the matrix at time zero; and C_3 is the equilibrium concentration of the solute from degradation as time becomes infinite. The k values (kinetic coefficients) are plotted for each velocity, and it is postulated that they should be related to a power function of the form

$$k_1 = AV^n \quad (9)$$

in which A is a constant, V is the velocity, and n is some power close to unity.

This model was applied to the same data for batch and flowthrough systems with and without acid addition as for the previous two models, and some of the xylan conversion predictions calculated from the data and concentration predictions via Eq. 8 are summarized in Figs. 5 and 6 for batch and flowthrough systems, respectively. Tables 4 and 2 present the parameters and the SS_E values for the branched pore model, respectively. Overall, although some data are better matched than others, hemicellulose hydrolysis models based on mass transfer alone can predict performance in batch and flow systems as well as, if not better than, reaction-only models. In addition, the changes in mass transfer coefficient with flow are consistent with expectations for a mass transfer model but not for strictly a chemical reaction.

Conclusion

This preliminary study suggests that mass transfer models could describe many features of xylan hydrolysis with accuracy similar to that of conventional first-order reaction-only models that have been long used to describe such systems. For example, a simple leaching model can describe release of xylan into solution as the product of a concentration gradient times a mass transfer coefficient. This model predicts that flowthrough operation could improve xylan release compared to a batch system by reducing the concentration in solution and thereby increasing the concen-

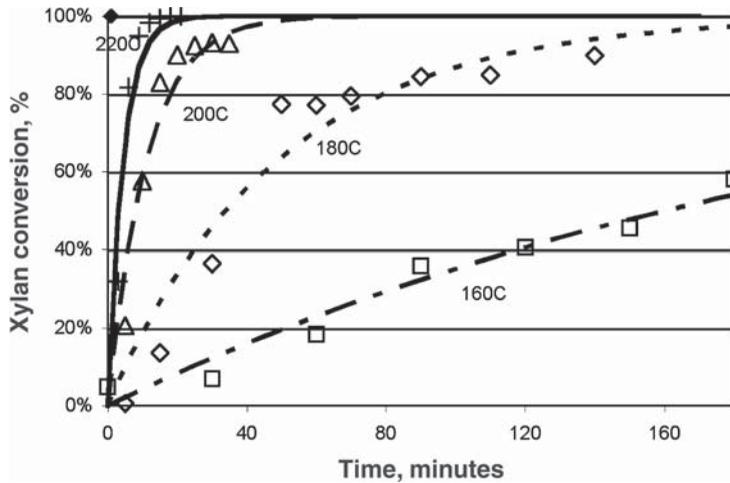


Fig. 5. Data and branched pore leaching model predictions of xylan conversion vs time for batch pretreatment of corn stover with only water at 160, 180, 200, and 220°C and 20% solids concentration.

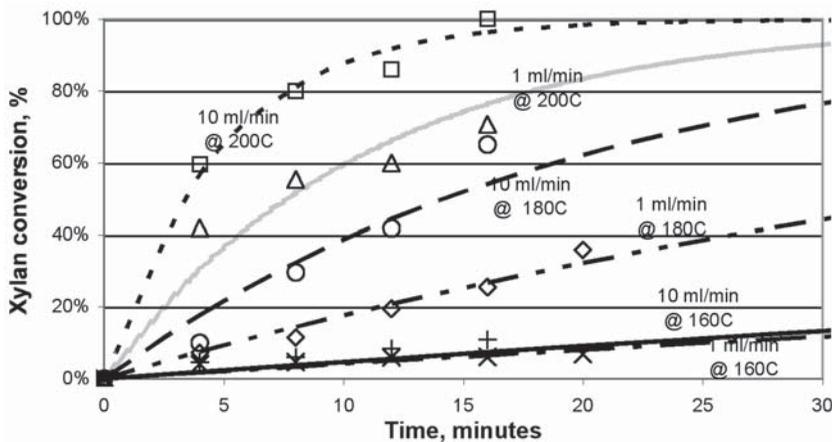


Fig. 6. Data and branched pore leaching model predictions of xylan conversion vs time for flowthrough pretreatment of corn stover with only water at 160, 180, and 200°C and flow rates of 1 and 10 mL/min.

tration difference that drives solubilization. In addition, the film thickness of a diffusive film around particles would be expected to decrease with introduction of flow, increasing the mass transfer coefficient and enhancing release of xylan. Although similar accuracy can be obtained for a conventional chemical reaction-only model, only temperature and acid concentration should impact performance in this case, and no rational explanation can be offered as to why flow rate would enhance xylan removal.

A branched pore leaching model as applied to release of water-soluble carbon from soil incorporates reaction to soluble compounds coupled with pore diffusion within the solids and leaching into the bulk solution. Application of such a model appears to describe hemicellulose hydrolysis reasonably well but not significantly better than chemical reaction only or simple leaching models.

These results could suggest that what has been traditionally been described as "biphasic" behavior may reflect a combination of chemical reaction and mass transfer effects, with each limiting xylan reaction and removal at different stages or modes of operation. This effect might be better described by a model that incorporates reaction of solids to form soluble species as a function of temperature and acid concentration coupled with a second mass transfer step that is affected by flow. On this basis, we plan to investigate whether the pore leaching model could be simplified and adapted in this way to better describe hemicellulose hydrolysis.

Acknowledgments

This work was made possible through the funding of the Office of the Biomass Program of the United States Department of Energy through contract nos. DE-FC36-00GO010589 and DE-FC36-01GO11075. We also appreciate the support of the Thayer School of Engineering at Dartmouth College for making this research possible.

References

1. Wyman, C. E. (1999), *Annu. Rev. Energy Environ.* **24**, 189–226.
2. Jacobsen, S. E. and Wyman, C. E. (2000), *Appl. Biochem. Biotechnol.* **84–86**, 81–96.
3. Jacobsen, S. E. and Wyman, C. E. (2002), *Ind. Eng. Chem. Res.* **41(6)**, 1454–1461.
4. Brennan, M. A., Liu, C., Wyman, C. E., and Yang, B. (2002), in *24th Symposium on Biotechnology for Fuels and Chemicals*, Oral presentation 3-02, Gatlinburg, TN.
5. Bobleter, O. (1994), *Prog. Polym. Sci.* **19**, 797–841.
6. Fogler, H. S. (1999) *Elements of Chemical Reaction Engineering*, 3rd Ed., Prentice Hall, Upper Saddle River, NJ.
7. Abatzoglou, N., Chornet, E., Belkacemi, K., and Overend, R. (1992), *Chem. Eng. Sci.* **47(5)**, 1109–1122.
8. Saeman, J. F. (1945), *Ind. Eng. Chem.* **37**, 42–52.
9. Lee, Y. Y., Iyer, P., and Torget, R. W. (1999), *Adv. Biochem. Eng. Biotechnol.* **65**, 93–115.
10. Kobayashi, T. and Sakai, Y. (1956), *Bull. Agric. Chem. Soc. Jpn.* **20**, 1–7.
11. Mehlberg, R. and Tsao, G. T. (1979), in *Abstracts of Papers of 178th ACS National Meeting*, American Chemical Society, Washington, DC, p. 36.
12. Garrote, G., Domínguez, H., and Parajó, J. C. (1999) *Holz als Roh- und Werkstoff* **57**, 191–202.
13. Stuhler, S. L. (2002), MS thesis, Thayer School of Engineering, Dartmouth College, Hanover, NH.
14. Plawsky, J. L. (2001), *Transport Phenomena Fundamentals*, Marcel Dekker, New York, NY.
15. Cao, J., Tao, S., and Li, B. G. (1999), *Chemosphere* **39(11)**, 1771–780.