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Effect of Transient Variation of Temperature on Acid Hydrolysis of Aspen Hemicellulose

Scientific Note

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ABSTRACT

Thermal diffusivities of Aspen wood were experimentally determined and subsequently incorporated into a theoretical model to establish the effect of transient temperature variation within a solid substrate during acid catalyzed hydrolysis of hemicellulose. The simulation results were analyzed to evaluate the impact of particle size on hemicellulose hydrolysis. Total xylose yield was found to decrease for increasing chip size and this effect was intensified by increasing reaction temperature. Quantitative criteria were established for assessment of transient temperature effect on xylose yield and reaction time at various reaction conditions.

Index Entries: Thermal diffusivity; hemicellulose hydrolysis; acid catalyzed; transient temperature variation.

NOMENCLATURE

A	"easy" hemicellulose
B	"difficult" hemicellulose
C	xylose
D	decomposition products
C_i	concentration
k_d	rate constant for decomposition

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k_{do}	frequency factor for decomposition
H	acid concentration (wt%)
n_d	acid concentration exponent
E_d	activation energy for decomposition
R	gas constant
T	absolute temperature
t	reaction time
x	position in slab as measured from center
z	x/L
T_s	steam temperature
T_o	initial temperature
p	density
k	thermal conductivity
h	heat transfer coefficient
L	half-thickness of slab
Nu	Nusselt number = hL/k
α	thermal diffusivity = $k/\rho C_p$
l_n	Eigen value as defined by Eq. (7)
Φ	dimensionless temperature = $(T - T_s)/(T_o - T_s)$
τ	dimensionless time = $\alpha t/L^2$
CHT	chip half thickness

INTRODUCTION

Selective removal of hemicellulose from cellulosic biomass is an integral part in the overall biomass conversion process. As such, much effort has been devoted to the investigation of the kinetics, reactor design, and diffusional problems associated with hemicellulose hydrolysis (*1–6*). A primary assumption for many of these studies has been that of isothermal reaction conditions. Such an assumption may lead to erroneous results based on the following rationale.

A typical acid hydrolysis process, for either cellulose or hemicellulose, presoaks the cellulosic substrate with sulfuric acid and then attains reaction temperature via steam heating. It is during this transient heating period that temperature within the biomass structure varies markedly from position to position. Initially, the entire substrate is at a low uniform temperature. On heating, high temperature regions occur at the surface and lower temperature regions near the center point. Eventually, a uniform high temperature is reached and isothermal conditions prevail. The temperature variation during preheating manifests itself in deviations to the predicted isothermal reaction progress. The impact of this transient temperature variation depends primarily on the rate of heat conduction relative to the rate of reaction. For example, if conduction is rapid in comparison to the reaction rate, isothermal temperature profiles are quickly developed within the substrate and reaction progress during the transient heat up period is minimal, thereby justifying an isothermal assumption. Conversely, if the reaction rate is more rapid than conduction, a significant portion of the hydrolysis reaction would occur during the transient heat up period, invalidating an isothermal assumption completely. The rate of reaction and rate of conduction are heavily dependent on the reaction conditions and the size of the solid feed, respectively. These two parameters are key to the understanding of hydrolysis reactions in which biomass size imposes a nonuniform temperature distribution. In addition, size reduction is a cost intensive unit operation and, therefore, subject to both economic and technical constraints (*7–8*).

This study was undertaken to ascertain the impact of biomass size on xylose yields and reaction times for specified reaction conditions and what role, if any, transient temperature variation plays in prehydrolysis of Aspen hemicellulose.

EXPERIMENTAL METHODS AND MODEL DEVELOPMENT

Determination of Thermal Diffusivity

Thermal diffusivity ($\alpha = k/pC_P$) of Aspen wood was determined experimentally via a dynamic method. For the procedure, a thermocouple was inserted into the center point of an Aspen sample. The sample was then heated and the variation of center point temperature was monitored and recorded through the use of a data acquisition program on an IBM PC/XT. The experimental setup consisted of a Sigma thermocouple/thermometer, a signal amplifier/offset unit, IBM data acquisition and control board, and an IBM PC/XT. Aspen samples were cut into a cylindrical form with a diameter to height ratio of 6:1. The curved surface of the samples was insulated with silicone rubber to force unidirectional heat flow. Samples were prepared to obtain heat conduction data for both the longitudinal (parallel to grain) and radial (perpendicular to grain) directions. Temperature vs time data was statistically analyzed utilizing a SAS nonlinear regression algorithm (IBM mainframe, Auburn University) to determine the thermal diffusivity value. This statistical estimation utilized the analytical solution for one-dimensional unsteady state heat conduction (Eq. (6)) as its model.

Kinetic Model

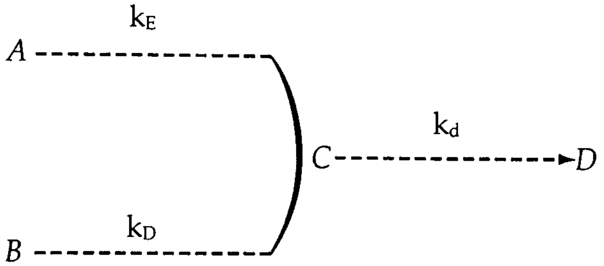
Literature pertaining to the kinetics of acid catalyzed hydrolysis of hemicellulose is abundant and diverse (*1–6*). Significant disagreement exists among the literature because of the dependence of reaction kinetics on substrate species, pretreatment method, and reaction conditions. For this study, the kinetic data specifically determined for Aspen wood by Grohmann et al. (*9*) has been chosen for the hydrolysis reaction. This

Table 1
Kinetic Parameters of Grohmann, Torget, and Himmel
Utilized in Computer Simulation of Aspen Hemicellulose Hydrolysis[a]

Temp., C	Fraction "easy" hemicellulose, percent of total	k_E, Rate constant for "easy" hemicellulose, 1/min	k_D, Rate constant for "difficult" hemicellulose, 1/min
95	20	0.0019	0.000038
120	29	0.047	0.0029
140	23	0.20	0.010

[a] Activation energy (kcal/mol): "easy" reaction=28; "difficult" reaction= 37.

kinetic data is summarized in Table 1. The hydrolysis reaction was modeled as two parallel first order reactions



where

A = "easy" hemicellulose
B = "difficult" hemicellulose
C = xylose
D = decomposition products

For the decomposition step, the parameters for Aspen wood of Brennan et al. (3) were employed and may be summarized as follows

$k_{do} = 2.33 \times 10^{12}$ 1/min
$n_d = .69$
$E_d = 27{,}130$ cal/mol

where

$k_d = k_{do} H^{n_d} \exp(-E_d/RT)$
H = acid concentration (wt%)

Acid concentration (.8237 wt%) and temperature values (T=95, 120, and 140 C) were duplicated from the study of Grohmann et al. (9) to insure consistency with the kinetic constants employed.

Heat Balance

A heat balance within a differential segment of the chip results in the unsteady state heat conduction equation

$$\delta T/\delta T = \alpha\, \delta^2 T/\delta x^2 \qquad (2)$$

with boundary and initial conditions

$$x = O,\ \delta T/\delta x = O \qquad (3)$$

$$x = L,\ -k\, \delta T/\delta x = h(T - T_s) \qquad (4)$$

$$t = O,\ T = T_o \qquad (5)$$

The analytical solution to Eqs. (2–5) in dimensionless form is as follows

$$\Phi = \sum_{n=0}^{\infty} 2Nu(Nu^2 + l_n^2)^{1/2}/l_n(Nu^2 + l_n^2 + Nu) \exp(-l_n^2 \tau) \cdot \cos(l_n z) \qquad (6)$$

where

$$\begin{aligned} \Phi &= (T - T_s)/(T_o - T_s) \\ \tau &= \alpha t/L^2 \\ z &= x/L \\ Nu &= hL/k \\ l_n \tan(l_n) &= Nu \qquad l_n > 0 \end{aligned} \qquad (7)$$

This classical solution may be found in various heat transfer textbooks and during mathematical computation it was found that Nu values were large enough to render the solution essentially the same as that for a boundary condition of $T = T_s$ at $x = L$.

Experimental Thermal Diffusivities

The thermal diffusivities of presoaked Aspen wood (as lumped into the dimensionless time, $\tau = \alpha t/L^2$) were determined by fitting experimental data to Eq. (6) via a statistical parameter estimation algorithm. Thermal diffusivities for the longitudinal and radial directions were $(2.33 \pm .052) \times 10^{-7}$ m²/s and $(1.72 \pm .048) \times 10^{-7}$ m²/s, respectively (for hemicellulose-free Aspen samples). Error intervals represent a 95% confidence level and both values are consistent with literature values for hardwood (*10*). In consideration of the fact that wood is generally chipped for hydrolysis in such a way as to produce random grain orientations, the two diffusivity values were averaged to yield 2.03×10^{-7} m²/s, and this value was used in subsequent calculations.

Material Balance

For the reaction scheme developed, rate constants are a function of temperature but based on the thermal situation described above, the rate constants are additionally functions of position and time such that

$$\begin{aligned} k_E &= k_E\,(T) = k_E\,(t,x) \\ k_D &= k_D\,(T) = k_D\,(t,x) \\ k_d &= k_d\,(T) = k_d\,(t,x) \end{aligned}$$

The reaction progress in the wood chip may be described by

$$-\,dC_A/dt = k_E\,C_A \tag{8}$$

$$-\,dC_B/dt = k_D\,C_B \tag{9}$$

$$dC_C/dt = (k_E\,C_A + k_D\,C_B) - k_d\,C_c \tag{10}$$

with initial conditions of

$$C_A = C_{AO}\quad C_B = C_{BO}\quad C_c = C_{co} \text{ at } t = 0 \tag{11}$$

The above equations were put into dimensionless forms and entered into the overall model development. The computer simulation was designed so that it first determines the temperature for values of τ and z. Next, the program evaluates the rate constants k_E, k_D, and k_d at that particular temperature. Finally, with known rate constants, a fourth-order Runge-Kutta method is employed to solve the initial value problems of Eqs. (8-11). Simpson's rule was then applied to determine total xylose concentration at any time by integrating over the length of the chip. In essence, the computer simulation provided local xylose and local hemicellulose (easy and difficult) concentration profiles in addition to the total xylose production for a nonuniform temperature distribution and compared these values to their isothermal counterparts.

RESULTS AND DISCUSSION

Figure 1 gives total xylose yield as a function of reaction time for a temperature of 140°C and is representative of other plots constructed for temperatures of 95 and 120°C. These figures gave yields for various chip sizes ranging from thicknesses of .20-4.0 cm (CHT=chip half thickness). For a temperature of 95°C, results were relatively uninteresting because of long reaction times and relatively low xylose yields (a direct consequence of the low reaction temperature). In addition, hydrolysis at 95°C showed minimal deviation in xylose yields for large variations in chip size. For a temperature of 120°C, chip size imposed a sizable impact on xylose yields. At a chip thickness of .20 cm, xylose yield was approximately 72%, whereas at a chip thickness of 2.0 cm xylose yield dropped to less than 60%. This trend is even more evident in Fig. 1 (T=140°C), where a

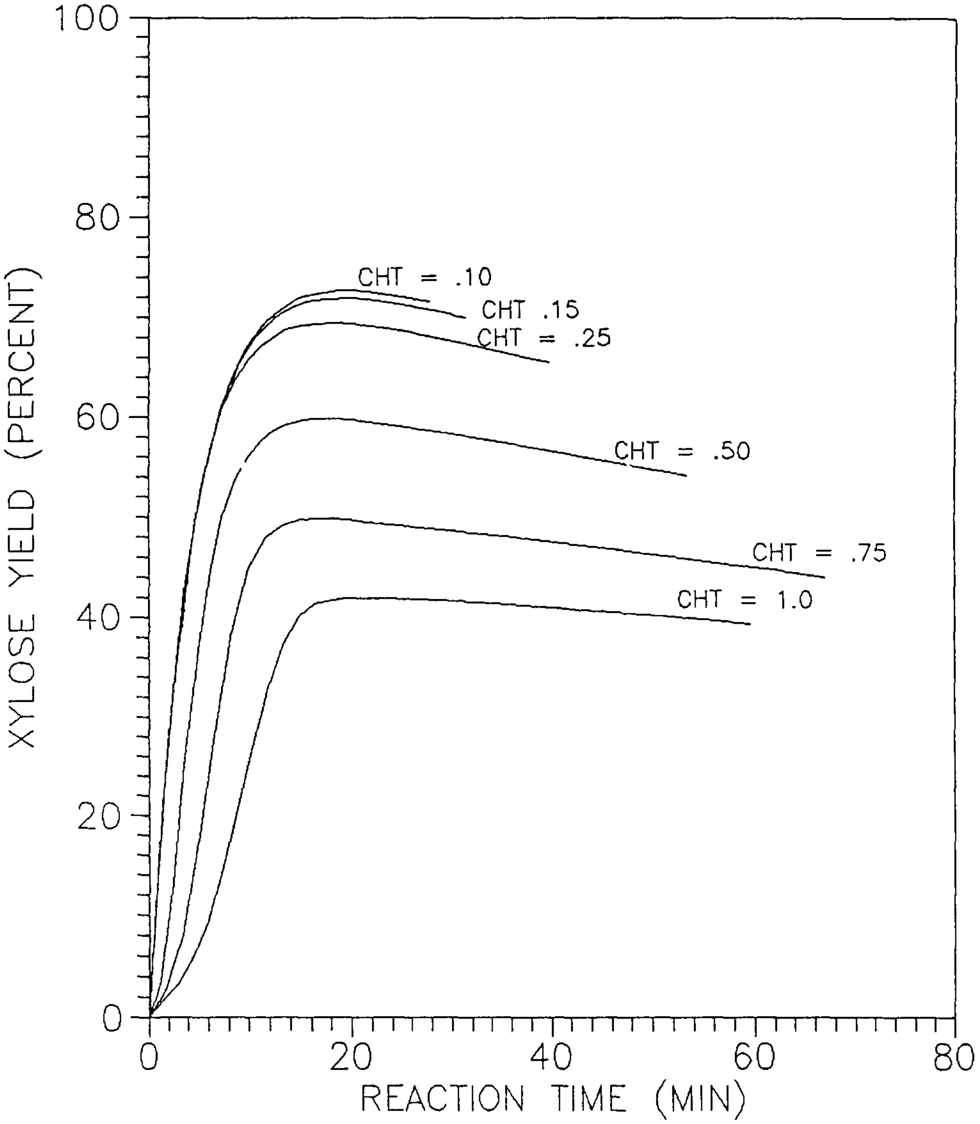


Fig. 1. Xylose yield as a function of reaction time for various chip sizes (hemicellulose hydrolysis at 140°C).

chip thickness of .20 cm gave a yield of about 73%, but at a thickness of 2.0 cm, xylose yield plummeted to approximately 42%. As evidenced by the above, increasing chip size decreased xylose yield, and this effect was intensified as temperature was increased.

The next family of plots (as represented by Fig. 2) contrasted xylose yield for isothermal conditions to that for nonuniform temperature conditions. Deviations from isothermal predictions appeared initially at the two higher reaction temperatures and at a chip thickness of .50 cm. Severe deviations from isothermal predictions were observed for chip thicknesses of 1.0 cm and larger. For instance, the reduction in xylose yield from iso-

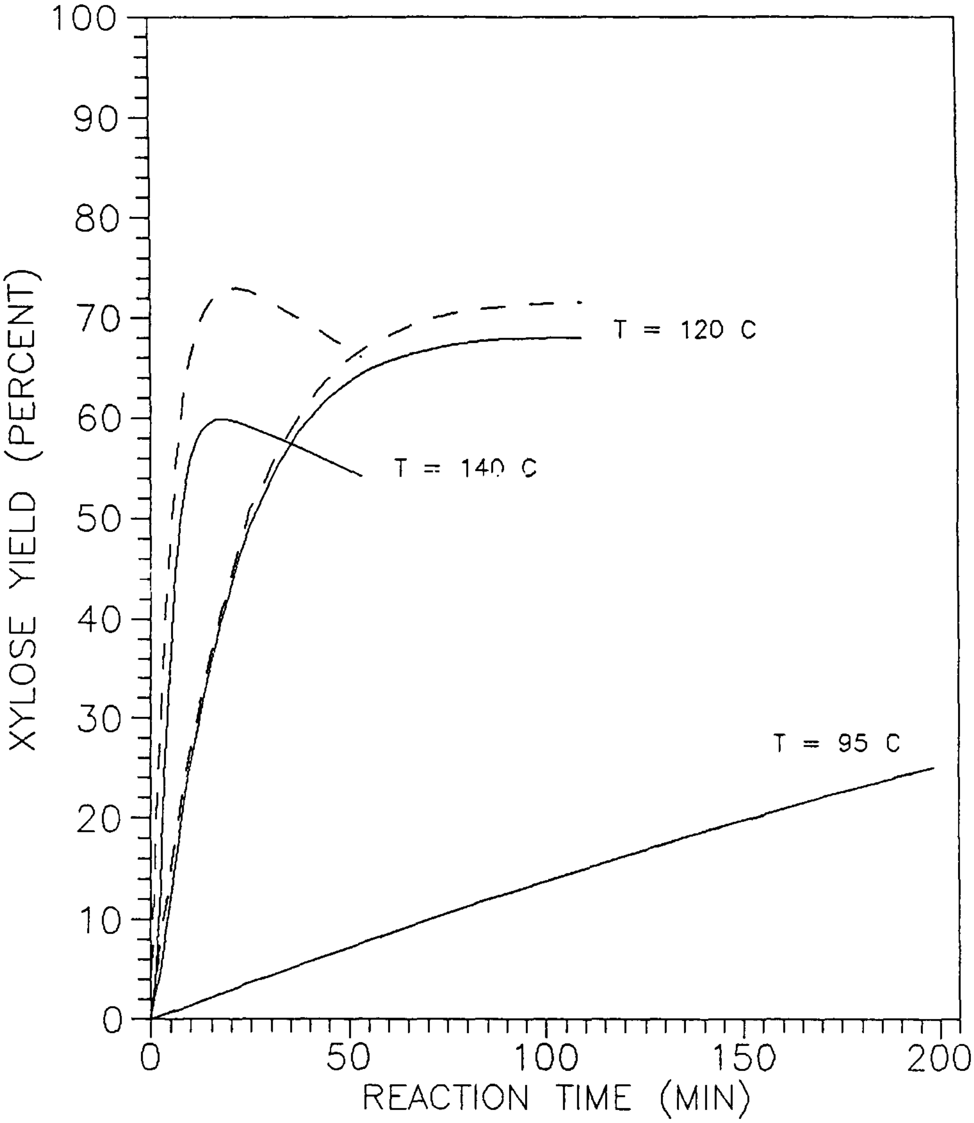


Fig. 2. Isothermal and nonisothermal xylose yields as a function of reaction time for three hydrolysis temperatures (hemicellulose hydrolysis with CHT = .50 cm).

thermal conditions at a thickness of 2.0 cm and temperature of 140°C was from 73 to 42%. At a temperature of 95°C, for the conditions investigated, isothermal conditions were closely maintained and transient temperature effects were not observed. In stark contrast, for chip thicknesses greater than .50 cm and temperatures of 120 and 140°C, xylose yields were much less than their isothermal counterparts. This effect was again accentuated as temperature and chip size were increased.

Figure 3 typifies the final set of figures that plotted local xylose yield as a function of position for various τ values. For isothermal conditions,

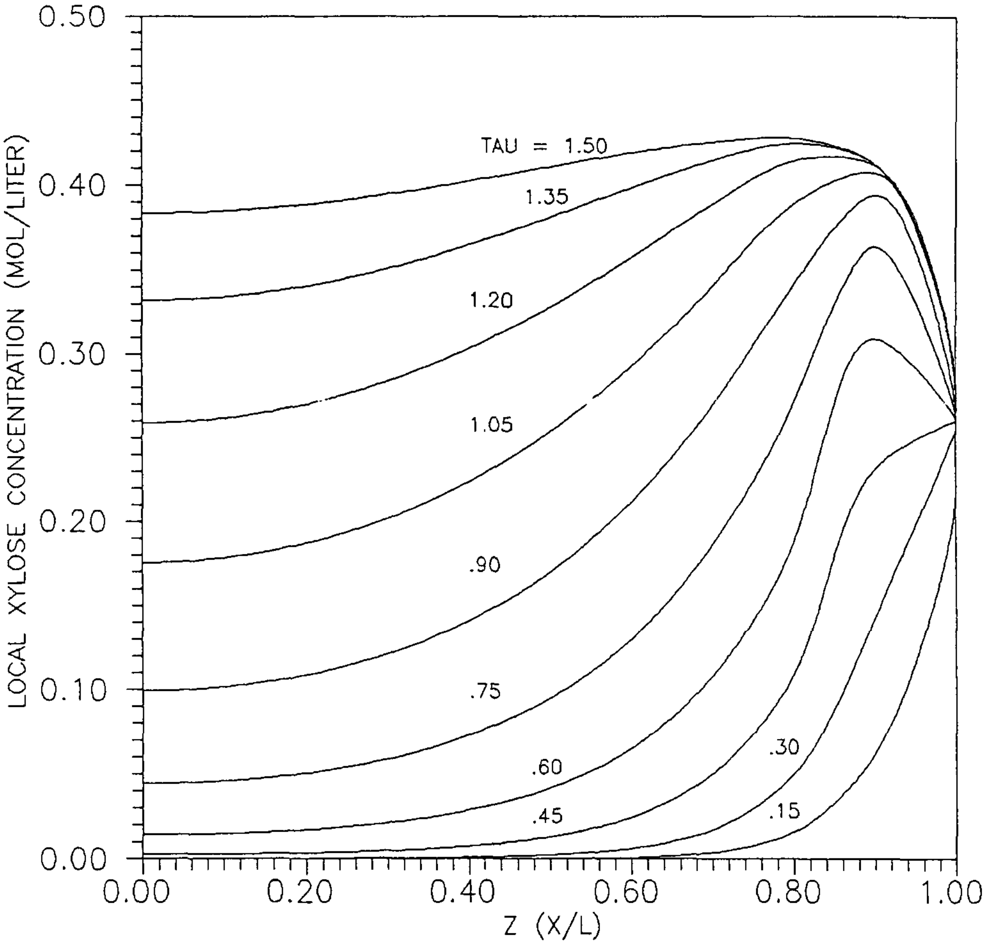


Fig. 3. Local xylose concentration as a function of position for various tau values (hemicellulose hydrolysis at 140°C with CHT= 1.0 cm).

each τ value should exhibit a flat profile. In Fig. 3, profiles flatten as τ increases but at early reaction times, the hydrolysis is surface oriented at higher z values. This surface intensive reaction zone increases its dominance as temperature and chip size increase. Figure 3 also illustrates how decomposition occurs at the surface regions (high z values) in direct competition with xylose production at the interior positions. This canceling effect serves to drive yield down from that predicted isothermally. All figures exhibited a lag in xylose yield at low z values until transient temperature effects diminished and isothermal conditions were established.

Table 2 summarizes much of the information presented in Figs. 1-3. Table 2 presents the ratios of maximum xylose yield and time at maximum xylose yield for uniform vs nonuniform temperature conditions. A numerical value of one in a column indicates that for the stated conditions no transient temperature effect was detected and, consequently, isothermal conditions prevail. For each experimental condition, the quantitative ef-

Table 2
Comparison of Maximum Yield and Reaction Time at Maximum Yield for Aspen Hemicellulose Hydrolysis

	T=95 C		120 C		140 C	
CHT, cm	a[a]	b[b]	a	b	a	b
0.10	1.00	1.00	1.00	0.95	1.00	0.94
0.15	1.00	1.00	1.00	1.02	0.99	1.10
0.25	1.00	1.00	0.99	1.06	0.95	1.21
0.50	1.00	1.00	0.95	1.02	0.82	1.21
0.75	0.99	1.00	0.89	1.02	0.68	1.20
1.00	0.97	1.00	0.83	0.96	0.58	1.07

[a] a = (maximum yield)$_{\text{nonisothermal}}$/(maximum yield)$_{\text{isothermal}}$
[b] b = (time @ maximum yield)$_{\text{isothermal}}$/(time @ maximum yield)$_{\text{nonisothermal}}$

fect of temperature variation may be discerned and utilized as a guide for feed preparation, reactor design, and optimal operation strategy.

CONCLUSIONS

The conclusions of this study as evidenced by the data presented and Table 2 may be summarized as follows

1. The thermal diffusivity of Aspen wood was measured by a dynamic method for both the longitudinal and radial directions;
2. A theoretical model was developed to investigate the effects of nonuniform temperature distribution inside an Aspen wood chip during hemicellulose hydrolysis;
3. Total xylose yield was found to decrease with increasing chip size;
4. The decrease in total xylose yield with increasing chip size was intensified by increasing reaction temperature;
5. Severe deviations in xylose yield relative to isothermal values occur for temperatures of 120 and 140°C and at chip thicknesses above .50 cm;
6. Such deviations from isothermal predictions increase in severity with increasing temperature and increasing chip thickness; and
7. A quantitative guideline was presented to assess transient temperature effects for specific reaction conditions.

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