KINETIC MODELING OF HARDWOOD PREHYDROLYSIS. PART III. WATER AND DILUTE ACETIC ACID PREHYDROLYSIS OF SOUTHERN RED OAK

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ABSTRACT

The hemicelluloses in wood are more readily hydrolyzed than is cellulose. Because it is advantageous to process the hemicellulose sugars separately from the glucose obtained from the cellulose, most processes for utilizing wood as a source of chemicals and liquid fuels include a prehydrolysis step to remove the hemicelltdose prior to the main hydrolysis of the cellulose to glucose. Kinetic data are required to model the reactions that occur during prehydrolysis so that optimum conditions and product mixes can be predicted. Two promising prehydrolysis methods, the Iotech steam explosion process and the Stake process, are based on water prehydrolysis (autohydrolysis). The kinetics of water and of dilute (5%) acetic acid prehydrolysis of southern red oak wood over the temperature range of 170 to 240 C were investigated. Kinetic parameters were determined that permitted modeling not only of xylan removal from the wood but also of the occurrence of xylan oligosaccharides, free xylose, furfural, and further degradation products in the prehydrolyzate. At lower temperatures (approximately 170 to 200 C), xylan removal could be modeled as the sum of two parallel reactions (one for an easily hydrolyzed portion and one for a more resistant portion of xylan) using the equation derived in Part I. At the highest temperature studied (236.9 C), the removal of xylan from the wood was best modeled as a single reaction with a small fraction of the xylan being essentially nonreactive. The occurrence of xylan oligosaccharides, xylose, furfural, and further degradation products in the prehydrolyzate was modeled as consecutive, irreversible pseudo first-order reactions. A timelag associated with the de-polymerization of the xylan oligosaccharides to xylose was accounted for in the model by allowing the apparent rate constant for the formation of xylose to increase exponentially with time to a maximum value. Increasing the temperature decreased the time required for the overall reactions to occur, increased the portion of xylan removed from the wood, and increased the yield of total anhydroxylose units (xylose + xylan oligosaccharides) that were recovered in the prehydrolyzate. Prehydrolysis with dilute acetic acid does not greatly affect the maximum yields of products in the prehydrolyzate over those observed with water prehydrolysis; however, the time to maximum yield decreased. The data presented in this report indicate that, at higher temperatures, water or dilute acetic acid prehydrolysis gives yields comparable to those for dilute sulfuric acid prehydrolysis at 170 C recently reported in the literature. Preliminary results with lignin isolated from the water and acetic acid prehydrolysis residues confirm recent reports that lignins of this type are useful as phenol substitutes in phenol-formaldehyde adhesives.

Keywords: Prehydrolysis, autohydrolysis, water prehydrolysis, acetic acid prehydrolysis, kinetics, modeling, southern red oak, *Quercus falcata* Michx.

INTRODUCTION

The hemicelluloses in wood are more readily hydrolyzed than is cellulose. This fact affords a means of removing the hemicellulose selectively by a hydrolysis step (prehydrolysis) prior to further processing of the lignocellulose. Prehydrolysis

can be effected by dilute mineral acid or by the acetic acid released on water prehydrolysis (autohydrolysis) from labile acetyl groups attached to the hemicellulose polymer. Prehydrolysis is not a new process. Based largely on the pioneering work of Richter (1956), prehydrolysis is presently used to remove hemicelluloses prior to the production of kraft-dissolving pulps, especially those produced from hardwoods. The Masonite process (Mason 192 1) uses a prehydrolysis step in the production of fiberboard and hardboard products.

The U.S. Forest Products Laboratory (FPL) in cooperation with the Tennessee Valley Authority (TVA) has studied a two-stage dilute acid process for producing ethanol from hardwoods (Harris et al. 1984), specifically southern red oak *(Quercus falcata* Michx.). Dilute sulfuric acid prehydrolysis at about 170 C removes the hemicellulosic sugars in the first stage. The lignocellulosic residue remaining after prehydrolysis is hydrolyzed to free glucose with dilute sulfuric acid at about 230 C in the second stage.

Other recent processes proposed for utilizing wood as a source of chemicals and liquid fuels include a prehydrolysis step in which the hemicellulose is removed by water prehydrolysis prior to chemical or enzymatic hydrolysis of cellulose to glucose. Water prehydrolysis is the fundamental basis of the Ioteeh steam-explosion process (Marchessault and St.-Pierre 1978; Marchessault et al. 1979; Foody et al. 1980) and the Stake process (Bender 1979), which are under active study either as stand-alone processes or in combination with other processes for utilizing wood to produce chemicals, liquid fuels, and animal feed.

A variety of studies have investigated the prehydrolysis of wood hemicelluloses with dilute mineral acid (e.g., Conner et al. 1984; Kang and Yoo 1976; Kobayashi and Sakai 1956; Lee et al. 1979; Simmonds et al. 1955; Springer 1966; Springer and Harris 1982; Springer et al. 1963; Springer and Libkie 1980; Springer and Zoch 1968; Veeraraghavan et al. 1982) and with water (e.g., Bender 1979; Casebier 1973a, b; Casebier et al. 1969; Conner 1984; Dietricks et al. 1978; Foody et al. 1980; Klemola and Nyman 1966; Marchessault and St.-Pierre 1978; Marchessault et al. 1979; Sears et al. 1971; Springer and Harris 1982; Springer and Zoch 1968). For the most part these studies investigated primarily hemicellulose removal and did not focus in any systematic manner on the amounts of hemicellulosic sugars in the prehydrolyzate or on further reactions of and reaction products from the solubilized sugars.

Studies such as those above indicate that water prehydrolysis is an attractive alternative to dilute mineral acid prehydrolysis as a method for separating the hemicellulosic sugars from hardwoods since the costs of the mineral acid and its neutralization are avoided. Because limited information was available on the amounts and types of hemicellulosic components appearing in the hydrolyzate as a function of time and temperature and because knowledge about the kinetics of water prehydrolysis is applicable to a number of wood utilization processes, we studied the kinetics of hardwood (specifically southern red oak) prehydrolysis with water and with dilute (5 %) acetic acid. Kinetic data are required to model the reaction processes that occur during prehydrolysis so that optimum prehydrolysis conditions and product mixes can be predicted and compared with other processes.

The investigations of the kinetics of water and dilute acetic acid prehydrolysis of southern red oak, reported here, cover the temperature range from about 170 to 240 C. In terms of reaction conditions, these temperatures span the range from

those used in previous studies on water prehydrolysis conducted at FPL (Conner 1984; Springer et al. 1963; Springer 1966; Springer and Hams 1982) to those of the Iotech steam-explosion process and Stake process.

RESULTS AND DISCUSSION

The hemicelluloses in hardwoods are predominately O-acetyl -(4 -O- methylglu-curono)xylan. For the purposes of our investigations, we have defined "xylan" as the total, potential xylose anhydride units in a wood or residue sample determined by the analytical methods.

Prehydrolysis of southern red oak will give rise to xylose, xylose degradation products, and variously substituted xylan oligosaccharides. In addition prehy-drolysis removes various lignin degradation products as well as small amounts of other hemicellulosic sugars. Wayman and Lora (1980) have studied extensively the nature of the lignin produced on prehydrolysis of hardwoods.

The removal of xylan from wood by prehydrolysis and the appearance of prod-ucts in the prehydrolyzate can be considered the consequence of a series of con-secutive, irreversible reactions:

$$X_W \xrightarrow{k_1} X_O \xrightarrow{k_2} X \xrightarrow{k_3} F \xrightarrow{k_4} D \tag{1}$$

where

$$
\begin{aligned}
X_W &= \text{xylan in the wood} \\
X_O &= \text{xylan oligosaccharides in the prehydrolyzate} \\
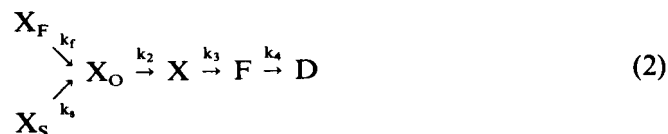X &= \text{xylose in the prehydrolyzate} \\
F &= \text{furfural in the prehydrolyzate} \\
D &= \text{further degradation products} \\
k_1, k_2, k_3, k_4 &= \text{apparent pseudo rate constants for the reactions indicated}
\end{aligned}
$$

Xylan removal

Conner (1984) showed that xylan removal (i.e., $X_W \rightarrow X_O$) from hardwoods by water prehydrolysis at 170 C could be modeled kinetically as the sum of two parallel pseudo first-order reactions instead of a single reaction as indicated in Eq. (1). Thus the reactions occurring on prehydrolysis may be represented as:

$$
\begin{array}{c}
X_F \\
\quad \searrow^{k_f} \\
\qquad X_O \xrightarrow{k_2} X \xrightarrow{k_3} F \xrightarrow{k_4} D \\
\quad \nearrow \\
X_S \;^{k_s}
\end{array}
\tag{2}
$$

where

$$
\begin{aligned}
X_F &= \text{a more reactive xylan fraction in the wood} \\
X_S &= \text{a less reactive xylan fraction in the wood} \\
k_f, k_s &= \text{pseudo first-order rate constants}
\end{aligned}
$$

TABLE 1. *Apparent reaction rate constants for xylan removal from southern red oak at various temperatures with water and dilute (5%) acetic acid.*

Prehydrolysis reaction conditions temperature	k_f	k_s	X_s^0/X_w^0	Δt
°C	min^{-1}		%	min
Water				
171.1[a]	0.0807 ± 0.0061	0.0049 ± 0.0008	26.1 ± 2.5	2.6 ± 0.3
185.5[a]	0.2842 ± 0.0746	0.0263 ± 0.0236	31.5 ± 13.1	1.2 ± 0.2
201.5[a]	0.8484 ± 0.0554	0.0766 ± 0.0217	18.5 ± 2.9	0.7 ± 0.0
236.9[b]	3.6948 ± 0.2580	—	3.1 ± 1.4	0.5 ± 0.0
Acetic acid (5%)				
171.1[a]	0.1900 ± 0.0102	0.0095 ± 0.0010	28.6 ± 1.1	2.3 ± 0.1
201.7[a]	1.4431 ± 0.0298	0.0942 ± 0.0049	17.6 ± 0.5	0.7 ± 0.0
236.9[b]	4.1022 ± 0.3780	—	0.3 ± 2.1	0.3 ± 0.0

[a] From SAS nonlinear least squares fit of experimental prehydrolysis data to Eq. (3). Values are reported ± asymptotic standard error.
[b] From SAS nonlinear least squares fit of experimental prehydrolysis data to Eq. (4). Values are reported ± asymptotic standard error.

At any time, t, $X_W = X_F + X_S$ so that the amount of xylan remaining in the wood can be described by the following equation (Conner 1984):

$$X_W/X_W^0 = (1 - X_S^0/X_W^0)\exp(-k_f(t - \Delta t))$$
$$+ (X_S^0/X_W^0)\exp(-k_s(t - \Delta t)) \qquad (3)$$

where

X_W^0 = xylan in the wood initially

X_S^0 = less reactive xylan in the wood initially

Δt = empirical time correction to adjust experimental data to isothermal, isoacidic conditions

Equation (3) was fitted by a nonlinear least squares method to experimental data obtained on prehydrolysis of southern red oak with water and dilute (5 %) acetic acid using the Statistical Analysis System (SAS) version 79.3A (Helwig and Council 1979). This least squares method provided estimates of k_f, k_s, X_s^0/X_w^0, and Δ t (Table 1) that could be used to model xylan removal from southern red oak at the various conditions investigated (Fig. 1).

These data indicate that the portion of less reactive xylan decreases with increasing temperature, supporting the view that the difference in reactivity between the two xylan fractions is probably not due to gross differences in their chemical structure, but is largely due to physical inaccessibility of a portion of the xylan to the hydrolytic reagent.

At the highest temperature (236.9 C), the removal of xylan from the wood with both water and dilute acetic acid was best modeled as a single reaction in which a small fraction of the original xylan was not reactive. This is in agreement with previous observations that a small fraction of hemicellulose in wood appears to be intimately associated with the cellulose and is only removed at the much slower cellulose removal rate (Harris et al. 1963). The experimental data at the highest temperature were therefore fitted to the following equation:
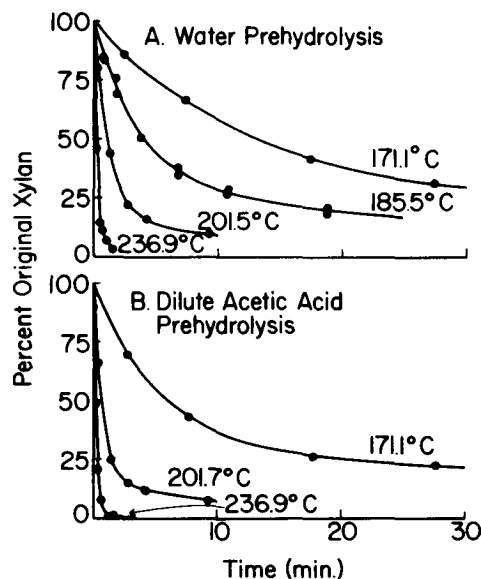
FIG. 1.   Xylan removal from southern red oak wood on prehydrolysis with water or dilute (5%) acetic acid. The closed circles represent experimental data; the time for each data point is corrected by Δt (Table 1) as discussed in the text. The solid lines were calculated from numerical integration of Eqs. (5) and (6) using the parameters listed in Table 1.

$$X_w/X_w^0 = (1 - X_s^0/X_w^0)\exp(-k_f(t - \Delta t)) + X_s^0/X_w^0 \qquad (4)$$

This equation can be derived from Eq. (3) for the special case where $k_s = 0$ (i.e., where the less reactive xylan fraction has no reactivity under the conditions studied).

Xylan removal from southern red oak on water and dilute acetic acid prehydrolysis as a function of temperature and time are compared in Fig. 1. It is readily apparent how rapidly the rate of reaction increases with temperature. At the highest temperature, well over 950/0 of the xylan in the wood can be removed within approximately 1 minute. This figure demonstrates the effectiveness of processes such as the Iotech and Stake process in removing the hemicellulose fraction of wood and also demonstrates why these processes are most efficient at higher temperature conditions.

An Arrhenius plot of k_f versus $1/T$ (where T is the temperature in "K) for water and dilute acetic acid prehydrolysis is shown in Fig. 2. The lines in Fig. 2 were determined from the least squares fit of ln k_f to $1/RT$ (R = universal gas constant). The activation energies for water and dilute acetic acid prehydrolysis can be obtained from the slope ($\Delta E/RT$) of these lines. For water prehydrolysis, the activation energy is 108 kJ/mole; that for acetic acid prehydrolysis is 88 kJ/mole. These values can be compared to the activation energy determined for the dilute hydrochloric acid prehydrolysis of aspen wood, 118 kJ/mole (Springer 1966), over the temperature range 60 to 120 C. If the Arrhenius plot is limited to the lower temperatures (i.e., 171 to 202 C), where two distinct reactions are occurring, then the activation energy of the fast reaction is 116 kJ/mole for acetic acid prehydrolysis, in close agreement with that for dilute hydrochloric acid prehydrolysis,
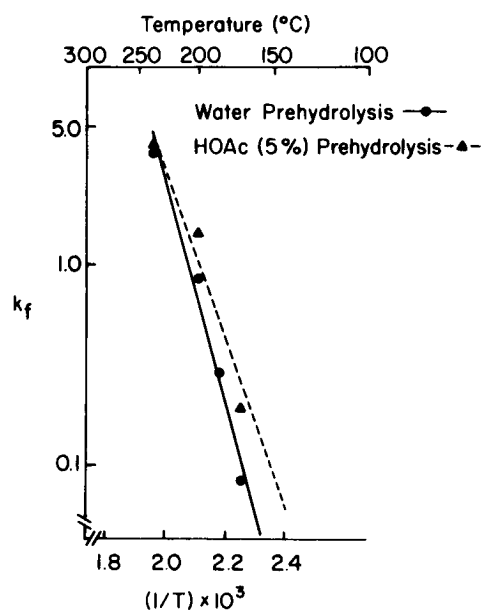
FIG. 2. Arrhenius plot of k_f versus $1/T$ for water and dilute (5%) acetic acid prehydrolysis of southern red oak wood. k_f is the apparent pseudo first-order rate constant for the removal of the easily hydrolyzed xylan. T is the reaction temperature in °K.

and is 136 kJ/mole for water prehydrolysis. These last values are comparable with the values of 127 kJ/mole recently determined for the fast prehydrolysis reaction of paper birch in 0.03 to 0.17 M H_2SO_4 at 100 to 170 C (Maloney et al. 1984).

Reaction products in the prehydrolyzate

Those reactions that are responsible for removing the xylan polymer from the wood give rise to soluble oligosaccharides in the prehydrolyzate that can undergo further depolymerization eventually to free xylose. Xylose is unstable in acidic conditions dehydrating to furfural. Furfural can polymerize with itself and its precursors giving rise to what we call degradation products. Like the reactions involved in xylan removal, the reactions that lead to further reaction products are extremely complex, have not been well studied (especially at the reaction conditions used in our investigations), or may involve more than one reaction step (as in the case of xylose conversion to furfural), or maybe catalyzed not only by the hydronium ion but by the hydroxide ion as well (as in the case of furfural disappearance (Root et al. 1959)). It would be of considerable interest to identify the individual reactions involved and to investigate the influence of changing reaction conditions on individual reaction rates. However, the overall chemical complexity of a heterogeneous reaction such as hardwood prehydrolysis makes it almost impossible positively to isolate an individual reaction and measure its rate. It is, however, possible to measure with reasonable accuracy the amounts of various reaction products after different prehydrolysis times. The amount of products formed may then be modeled using apparent rate constants, if it is borne in mind that the apparent rate constants are a complex function of the rate constants for all the individual reactions that might produce a given product. In

TABLE 2. *Apparent reaction rate constants for the formation of further reaction products in the prehydrolyzates from water and dilute (5%) acetic acid prehydrolysis of southern red oak at the conditions indicated.*[a]

Prehydrolysis reaction conditions temperature	k_2	k_3	k_4
°C		min^{-1}	
Water			
171.1	0.022 ± 0.002	0.012 ± 0.001	0.006 ± 0.001
185.5	0.075 ± 0.003	0.057 ± 0.006	0.228 ± 0.061
201.5	0.110 ± 0.005	0.152 ± 0.018	0.236 ± 0.055
236.9	0.784 ± 0.034	1.508 ± 0.143	3.010 ± 0.538
Acetic acid (5%)			
171.1	0.036 ± 0.001	0.016 ± 0.000	0.010 ± 0.002
201.7	0.205 ± 0.010	0.178 ± 0.016	0.144 ± 0.026
236.9	1.250 ± 0.079	1.540 ± 0.157	1.491 ± 0.222

[a] From SAS nonlinear least squares fit of experimental prehydrolysis data to the simultaneous differential Eqs. (5) to (8). Rate constants are reported ± asymptotic standard error.

spite of these limitations, the apparent rate constants can provide a better understanding of the overall reaction processes that are involved in prehydrolysis and can be used to model the prehydrolysis system.

The appearance of xylan oligosaccharides, xylose, furfural, and degradation products in the prehydrolyzate from the xylan in the wood can be described [in the context of Eq. (2)] by the following simultaneous differential equations for a series of consecutive, irreversible pseudo first-order reactions:

$$dX_F/dt = -k_f[X_F] \tag{5}$$

$$dX_S/dt = -k_s[X_S] \tag{6}$$

$$dX_O/dt = k_f[X_F] + k_s[X_S] - k_2[X_O] \tag{7}$$

$$dX/dt = k_2[X_O] - k_3[X] \tag{8}$$

$$dF/dt = k_3[X] - k_4[F] \tag{9}$$

$$dD/dt = k_4[F] \tag{10}$$

Experimental data for the amounts of oligosaccharides (X_o), xylose (X), furfural (F), and degradation products (where $D = X_w^o - X_F - X_S - X - F$) were fitted to this system of differential equations with SAS to determine the apparent rate constants k_2, k_3, and k_4. The apparent rate constants k_f and k_s the values X_F^o and X_s^o, and Δt as determined for the removal of xylan from the wood (Table 1) were specified as known parameters. The rate constants determined by this fit are given in Table 2.

The rate constants determined by this fitting process (Table 2) and the rate constants and parameters determined for the removal of xylan (Table 1) were substituted into Eqs. (5) to (10). Numerical integration of this set of simultaneous differential equations gave calculated values for each component in the model [Eq. (2)] as a function of time. The software routine DEPC (Madison Academic Computing Center, University of Wisconsin-Madison 1972) was used for nu-
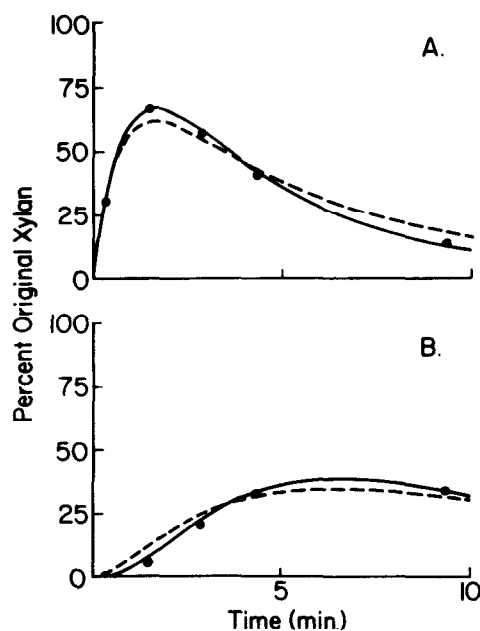
FIG. 3. Appearance of (A) xylan oligosaccharides and (B) free xylose in the prehydrolyzate of southern red oak wood. Prehydrolysis was conducted at 201.7 C with dilute (5%) acetic acid. The closed circles represent experimental data; the time for each data point is corrected by Δt (Table 1) as discussed in the text. The dashed lines (k_2 invariant) and the solid line (k_2 varies with time) are calculated as described in the text. This figure illustrates the improved fit of the model to the experimental data by allowing the apparent rate constant k_2 to vary with time.

merical integration by the fourth-order predictor-corrector Hammig method (1959). The calculated values for each component agree fairly well with the experimental data and thus describe in general the overall reactions that occur on prehydrolysis; however, as illustrated in Fig. 3 (dashed line), the appearance/disappearance of the oligosaccharides and xylose were not accurately described. Thus, for example, at short reaction times the oligosaccharides were underpredicted but were over-predicted at longer reaction times.

This discrepancy between the calculated values for the oligosaccharides and the xylose is apparently due to a timelag associated with the depolymerization of the xylan oligosaccharides to xylose. Indeed one might expect a timelag since the hydrolysis of the xylan oligosaccharides is a random process leading indirectly to xylose via progressively shorter oligosaccharides. Thus random hydrolysis of the xylan oligosaccharides liberated from the wood gives, after short reaction times, predominately xylan oligosaccharides of reduced DP and not free xylose. However, after longer reaction times, hydrolysis is increasingly more likely to lead to free xylose. In effect it would appear as if the *apparent* rate constant for the formation of xylose from oligosaccharides (k_2) was increasing with time.

To test this hypothesis, the experimental data were again fitted to Eqs. (5) to (10). During this second fitting process, k_2 was allowed to vary exponentially according to the following equation:

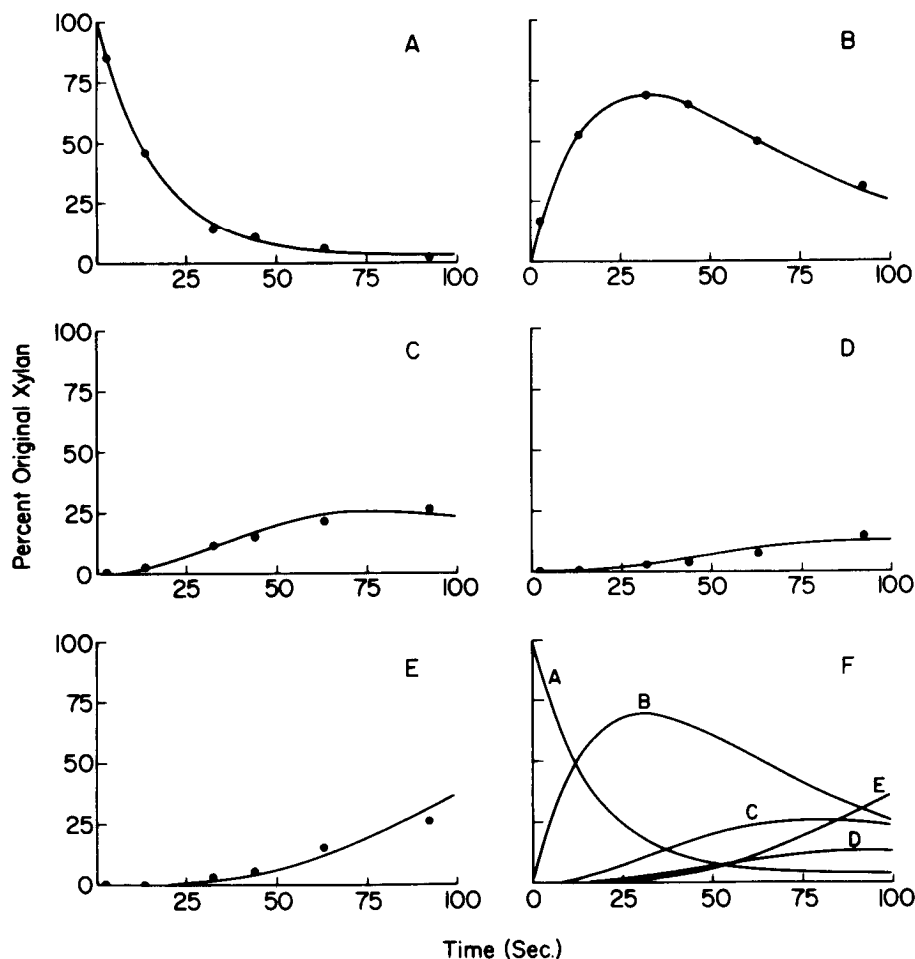$$k_2 = k_2{}^{max}(1 - \exp(-\beta t))$$ (11)

FIG. 4. Water prehydrolysis of southern red oak wood at 236.9 C. Comparison of experimental data (closed circles) with predictions (solid lines) for appearance/disappearance of (A) xylan from the wood, (B) oligosaccharides in the prehydrolyzate, (C) free xylose in the prehydrolyzate, (D) furfural in the prehydrolyzate, and (E) degradation products. Predictions formed by numerical integration of Eqs. (5) to (11) using the parameters listed in Table 3. Insert F shows a composite of the various reaction processes (A–E). The time for each data point is corrected by Δt (Table 1) as discussed in the text.

where k_2^{max} and β are constants to be determined in the fitting process. The experimental data were fitted to these equations with the NREG 77 nonlinear least squares procedure (Madison Academic Computing Center 1982) in conjunction with the IMSL (1982) differential equation routine DGEAR. For prehydrolysis with water at 171.1 C, a high correlation existed between (β and k_3 so that the program did not converge. For prehydrolysis with acetic acid at 171.1 C, β could be varied over wide limits with minimal changes in the residual sum of squares. Therefore, in both cases β was fixed prior to fitting the data. The values of β for these conditions were set to be slightly smaller than the value of ,β at the next highest temperature studied.

The values of the rate constants and the constants k_2^{max} and β determined by

TABLE 3. *Final parameters used to model the water and dilute (5%) acetic acid prehydrolysis of southern red oak.*[a]

Prehydrolysis reaction conditions temperature	X_s^0/X_w^0 [b,c]	k_f [b,c]	k_s [b,c]	β	k_2^{max}	k_3	k_4	Overall standard deviation of model
°C	%			⸺ min ⸺				%
Water								
171.1	26.1	0.081	0.005	0.10[c]	0.023	0.012	0.005	±3.8
185.5	31.5	0.284	0.026	0.13	0.125	0.065	0.215	±2.1
201.5	18.5	0.848	0.077	0.65	0.133	0.165	0.250	±2.2
236.9	3.1	3.695	—	1.55	1.392	1.848	3.438	±1.5
Acetic acid (5%)								
171.1	28.6	0.190	0.010	0.60[c]	0.036	0.016	0.008	±1.9
201.7	17.6	1.443	0.094	0.63	0.284	0.186	0.146	±1.5
236.9	0.3	4.102	—	1.88	2.022	1.716	1.608	±2.6

[a] Parameters obtained from NREG fit of experimental data to Eqs. (5) to (11) except as noted.
[b] Obtained from SAS fit for xylan removal data (Table 1).
[c] Fixed prior to fitting with NREG.

this second method (Table 3) and the rate constants and parameters determined for the removal of xylan (Table 1) were substituted into Eqs. (5) to (11). Numerical integration (with DEPC) of these equations gave calculated values for each component in the model [Eq. (2)] as a function of time. Figures 3 (solid line) and 4 illustrate the improved fit of the calculated values to the experimental data when k_2 vanes with time. Table 3 contains the overall standard deviation for the fit of the calculated values to the experimental data.

Yields of reaction products

Figures 4 and 5 show the appearance and disappearance of the components derived from xylan by water and dilute acetic acid prehydrolysis. Table 4 lists the times to maximum yields and the maximum amounts of xylan oligosaccharides, free xylose, and total anhydroxylose units (i.e., oligosaccharides + xylose) in the prehydrolyzate. The maximum amount of oligosaccharides in the prehydrolyzate solution increases with increasing temperature, while the amount of free xylose decreases. The maximum yield of total anhydroxylose units, which occurs at a time that is between the time for maximum oligosaccharide yield and the time for maximum xylose yield, also increases with temperature. Thus increasing the prehydrolysis temperature decreases reaction times, increases the amount of xylan removed from the wood, and increases the maximum amount of anhydroxylose units that can be recovered in the prehydrolyzate. Interestingly, addition of dilute acetic acid to the prehydrolysis system does not greatly affect the maximum yields obtained, only the time to maximum yield.

These data demonstrate that water prehydrolysis or dilute acetic acid prehydrolysis can be an effective means of removing hemicellulose from wood. They also demonstrate that high temperatures and good control of reaction times are required to ensure optimum yields of recoverable anhydroxylose units in the prehydrolyzate. Thus, the Iotech process rapidly prehydrolyzes the raw material with high-pressure steam at about 240 C followed by an explosive rapid discharge
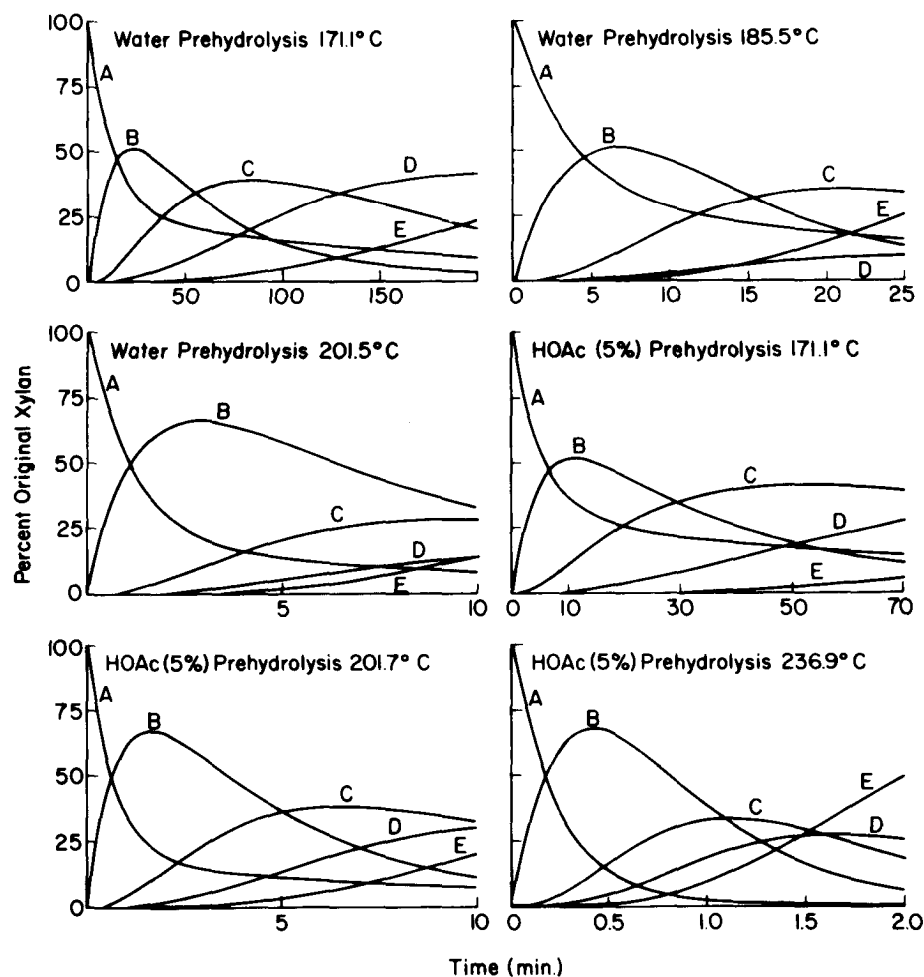
FIG. 5.   Composite graphs showing the appearance/disappearance of (A) xylan from the wood, (B) oligosaccharides in the prehydrolyzate, (C) free xylose in the prehydrolyzate, (D) furfural in the prehydrolyzate and (E) degradation products for water and dilute acetic acid (HOAc) prehydrolysis of southern red oak wood at the temperatures indicated. The various curves were calculated by numerical integration of Eqs. (5) to (11) using the parameters in Table 3.

of the material which fragments the residue but more importantly affords a means for cooling the residue rapidly.

Springer and Harris (1982) concluded that at 170 C water prehydrolysis of aspen wood was not as effective as dilute (0.4 %) sulfuric acid prehydrolysis. They report that for dilute sulfuric acid prehydrolysis of aspen wood approximately 83% of the total potential anhydroxylose is found in the prehydrolyzate after 12 minutes, with 6% of the original xylan remaining in the wood. However, our data on southern red oak show that at higher temperatures water or dilute acetic acid prehydrolysis can be as effective as dilute sulfuric acid prehydrolysis at 170 C. Table 4 shows that at 236.9 C water and dilute acetic acid prehydrolysis give similar results in about 30 seconds to 1 minute.

Water and dilute acetic acid prehydrolysis give predominately xylan oligosac-

TABLE 4. *Maximum yields[a] of xylan oligosaccharides, free xylose, and total anhydroxylose in the prehydrolyzate of southern red oak.*

Prehydrolysis reaction conditions temperature	Xylan oligosaccharides		Free xylose		Total anhydroxylose[b]		
	Time[c]	Maximum yield	Time[c]	Maximum yield	Time[c]	Maximum yield	Xylan remaining[d]
°C		%		%		.... %	
Water							
171.1	23.0 M	51.2	83.0 M	39.2	41.0 M	70.4	24.0
185.5	6.6 M	51.3	20.9 M	35.4	10.9 M	67.2	26.8
201.5	2.9 M	66.2	9.5 M	28.7	4.3 M	79.6	15.6
236.9	31.0 S	69.3	77.5 S	25.2	41.0 S	82.0	10.8
Acetic acid (5%)							
171.1	11.2 M	51.5	52.5 M	41.8	21.5 M	71.2	24.5
201.7	1.6 M	67.0	6.5 M	38.2	2.7 M	80.8	15.4
236.9	25.0 S	66.9	66.0 S	33.2	35.5 S	83.1	9.1

[a] Percent of original xylan.
[b] Note that total anhydroxylose at any reaction time is the sum of the xylan oligosaccharides and free xylose at that set of experimental conditions. The maximum total anhydroxylose yield occurs at the time this *sum* reaches a maximum.
[c] M = minutes, S = seconds.
[d] At the time for maximum total anhydroxylose yield.

charides, whereas dilute sulfuric acid prehydrolysis yields predominately xylose. But for most purposes this may not be an important distinction since the xylan oligosaccharides could be readily converted to xylose enzymatically (Brice and Morrison 1982), could be used directly in animal feeds, or could be converted to chemical intermediates. In water prehydrolysis the hydrolysis catalyst is produced *in situ.* Water or acetic acid prehydrolyzates would not require neutralization prior to their use as animal feed or for simultaneous enzymatic fermentation to chemical intermediates (e.g., ethanol), thus avoiding possible scaling problems within the recovery systems, such as occur, for example, with sulfuric acid neutralization lime.

A major fraction of the lignin can be extracted from water and acetic acid prehydrolyzed wood residues, especially from residues produced at the higher prehydrolysis temperatures, with organic solvents (e.g., ethanol) or with aqueous alkalies. Our preliminary results have confirmed a recent report (Forintek 1982) that lignins of this type can be used as a substitute for phenol in phenol-formaldehyde plywood adhesives (Table 5). Utilization of the lignin fraction of wood, like that of the hemicellulose fraction, is an important determinant in the economic utilization of wood as a source of chemicals, energy, or animal feed.

EXPERIMENTAL

Air-dried whole wood chips of southern red oak *(Quercus falcata* Michx.) were ground in a Wiley mill to pass a 4-millimeter screen. The fraction having a 20- to 30-mesh size was used for all experiments. The summative analysis of this material is presented as Table 6.

Prehydrolysis

All reactions were conducted in a reaction bomb made from a 152-millimeter section of 316 stainless steel tubing (⁻9.8-mm outside diameter by 0.8-mm wall)

TABLE 5. *Preliminary test results of wood veneers bonded with phenol-formaldehyde (p/f) modified with lignin (l) extracted from prehydrolyzed southern red oak wood.*[a]

Species[b]	Bonding system	Bonding conditions			Shear strength[c]	
		Temperature	Time	Pressure	Dry	Wet
		°C	Min	MPa	············· MPa ·············	
Yellow birch	p/f[d]	150	5	1.2	13.5	8.2
Yellow birch	p/f/l[e]	160	20	1.5	10.9	8.3
Yellow birch	p/f/l[e]	185	20	1.5	10.6	7.7
Douglas-fir	p/f[d]	150	5	1.2	8.0	5.2
Douglas-fir	p/f/l[e]	185	5	1.6	5.8	4.2
Douglas-fir	p/f/l[e]	185	20	1.6	7.6	5.0

[a] Southern red oak chips (⅜ in.) were prehydrolyzed with steam at 170 C for 30 minutes. The prehydrolyzed chips were thoroughly washed with hot water. The lignin was extracted from the washed chips with 95% ethanol in a soxhlet apparatus during a 24-h period.
[b] Veneers (150 mm long, 150 mm wide, and 3 mm thick) were used to form a two-ply panel with the adhesive indicated and at the conditions indicated.
[c] The bonded veneer panels were conditioned at 27 C and 30% relative humidity before they were cut into two-ply lap shear specimens. The lap shear specimens were tested for shear strength either dry or wet after a standard vacuum-pressure soak (National Bureau of Standards, U.S. Product Standard for Construction Plywood, 1974) using a universal testing machine at a loading rate of 1 cm/min.
[d] A commercial phenol-formaldehyde resin.
[e] A resin formulated in the laboratory with phenol, formaldehyde, and prehydrolysis lignin in the approximate mole ratio of 1:2.3: 1.5 (assuming the monomeric formula weight for lignin = 180).

sealed at one end by welding a small section of a stainless steel rod into place. The open end was sealed with a stainless steel Swagelock cap. The cap had a small hole drilled through the top. A silicon rubber septum was placed between the reaction vessel and the cap.

About 600 milligrams of wood meal of known moisture content was weighed accurately and placed in the tared reaction bomb. A vacuum was drawn on the sealed bomb using a hypodermic needle passed through the septum and connected to an aspirator. Sufficient water was introduced into the evacuated bomb with a syringe to give a liquid-to-solid ratio of 3:1 (wt:wt). The reaction vessel was then centrifuged to ensure the movement of the water throughout the sawdust bed. This was facilitated by the vacuum previously drawn on the system.

The reaction vessel was heated in a constant temperature oil bath (*O. 1 C) for the desired length of time. On removal, the reaction vessel was submerged in cold water to stop the reaction. The time from submersion in the oil bath to submersion in the cold water bath was recorded as the reaction time.

Before opening the bomb, any pressure was relieved with a hypodermic needle. The contents were washed from the bomb with hot water onto a tared sintered glass funnel. The residue was washed with approximately 100 milliliters of boiling water and dried in a vacuum oven at 60 C overnight. The filtrate was collected and diluted to a known volume.

Sugar analyses

Sugar analyses were performed by ASTM method D 1915 (1979) except that the individual sugars were determined by HPLC on a Bio-Rad HPX-85 carbohydrate column instead of by paper chromatography. The column temperature was maintained at 85 C. Distilled water was used to elute the column. An RI detector was used to monitor the effluent. Determination of sugars by HPLC was shown to be comparable to paper chromatography and to have the same order of precision (Pettersen et al. 1984).

Uronic anhydride was determined by a dehydration procedure (Scott 1979).

TABLE 6. *Summative analysis of southern red oak wood.*

Component	Percent[a]
Glucan	38.9 ± 0.8
Xylan	19.1 ± 1.2
Mannan	2.1 ± 0.3
Araban	0.9 ± 0.2
Galactan	1.7 ± 0.3
Lignin	21.5 ± 1.4
Extractives[b]	6.7 ± 0.1
Uronic anhydride[c]	3.0 ± 0.2
Acetyl	3.5
Ash	0.3
Other	2.3

[a] Based on oven-dried wood weight.
[b] Extracted with benzene/alcohol.
[c] Determined as in Scott (1979).

Acetyl analysis

The acetyl content was determined by an alkaline hydrolysis procedure (Wiesenberger 1947).

Ash analysis

The ash analysis was determined by ASTM method D 1102 (1978).

Lignin analysis

The lignin was determined as the insoluble residue obtained after the primary hydrolysis with 72 % sulfuric acid in the sugar analyses (Effland 1977).

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