Dilute Acid Hydrolysis of Paper Birch: Kinetics Studies of Xylan and Acetyl-Group Hydrolysis

Mark T. Maloney and Thomas W. Chapman
Chemical Engineering Department, University of Wisconsin-Madison

Andrew J. Baker
Forest Products Laboratory, Forest Service, U.S. Department of Agriculture, Madison, Wisconsin 53706

Batch hydrolysis kinetics of paper birch (*Betula papyrifera*) xylan and its associated acetyl groups in dilute sulfuric acid have been measured for acid concentrations of between 0.04 and 0.18M and temperatures of between 100 and 170°C. Only 5% of the cellulose was hydrolyzed for up to 85% xylan removal. Rate data were correlated well by a parallel reaction model based on the existence of reactive and resistant xylan portions. The resulting rate equation predicts the experimental xylan concentrations in the residue to within 10%. Hydrolysis of xylan-associated acetyl groups was found to occur at the same rate as that of xylan, except at 100°C. where acetyl is released preferentially. No effect of acid concentration on the rate of acetyl removal relative to that of xylan was evident.

INTRODUCTION

Many studies have been performed on the kinetics of acid-catalyzed hydrolysis of plant hemicelluloses, particularly glucuronoxylan, the principal hemicellulose present in hardwoods. In most early studies, such as those of Baker and Krcmar[1] and Springer et al.,[2,3] conversion data were obtained at various reaction conditions, but no unifying kinetic model was developed. Early work[2-4] did indicate that the hydrolysis of glucuronoxylan, often simply called xylan, occurs much more readily than that of cellulose and that the hydrolysis rate increases with acid concentration and temperature. Furthermore, the results suggested that the first 60-70% of the xylan hydrolyzes according to apparent first-order reaction kinetics with respect to the mass of xylan in the residue, whereas the remaining xylan is hydrolyzed at a decidedly slower rate. Because the mechanism of the solid-phase acid-catalyzed hydrolysis has not been elucidated, no satisfactory basis for explaining the observed rate behavior is yet available.

With the current interest in chemical production from biomass [5,6] and in modified pulping processes,' there is renewed interest in the hydrolysis of wood and other biomass. In lieu of a detailed theoretical model capable of predicting reaction behavior *a priori,* the process engineer needs extensive data and empirical rate models to explore possible processing schemes. Recent studies aimed at providing such information include the work of Beck and Wang[8] on the hydrolysis of cotton gin residues by dilute sulfuric acid and those of Veeraraghavan et al.[9] and Cahela et al.[10] on the acid hydrolysis of oak hemicellulose.

In addition to xylose, acid hydrolysis of hardwood hemicellulose yields large quantitites of acetic acid. In paper birch there are 6 or 7 acetyl groups substituted on every 10 xylose units in the xylan.[11] The potential yield of acetic acid is therefore about 6 g/100 g dry wood, and the potential xylose yield is about 25 g. An interesting question with process implications is how the rate of acetyl hydrolysis compares with that of the xylan backbone of hemicellulose.

Very few workers have conducted research on the kinetics of wood deacetylation or its relation to hemicellulose hydrolysis. Work by Erins et al.[12] on the deacetylation of spruce in dilute alkali, however, did indicate several interesting characteristics of deacetylation kinetics. The rate of acetyl removal from the wood was found to follow the same general trend seen for acid-catalyzed xylan hydrolysis. That is, the first 70% or so of the acetyl groups is removed according to an apparent first-order reaction, while the remaining acetyl groups are removed much more slowly, following different pseudo-first-order kinetics. Deacetylation by alkali of isolated hemicellulose, on the other hand, was found to follow a single first-order reaction rate law.

The purposes of this study are to provide a rate model for hardwood hemicellulose hydrolysis by dilute acid and to determine the relative rate of acetyl group hydrolysis.

KINETICS MODELS

Most rate studies with hemicellulose hydrolysis have been conducted as two-phase isothermal batch ex-

periments in which xylan dissolution is followed as a function of time. Typical results are found to follow the form shown in Figure 1, which shows some data from this study plotted as the log of the percent of original xylan remaining in the solid residue as a function of time. If the xylan were completely accessible to water (and acid) such that no diffusional restrictions affected the rate and if the local rate of xylan dissolution were proportional to the mass of xylan present, the kinetics should be first order in xylan, and the data in Figure 1 should fall on a straight line. It is seen that such is not the case; rather, there is a distinct slowing of the rate at about 70% conversion.

One may consider at least three possible explanations of the observed rate behavior. First, there may be transport limitations within the reaction mass that cause local concentration and rate variations during the course of the reaction. Second, different portions of the xylan may possess different intrinsic reactivities that can change during hydrolysis. Finally, the reaction may not be homogeneous in nature but may occur at a xylan–water interface. In the last case the rate would be proportional to interfacial area and depend on changing structural features during hydrolysis.

Although all three of these possibilities deserve more thorough study, the second is the one that has most commonly been used to correlate experimental rate data. For example, both Conner[13] and Veeraraghavan et al.[9] viewed the xylan to be composed of two fractions, each of which reacted according to a homogeneous, first-order kinetics law. That is, the rate of dissolution of xylan would be expressed as

$$R_X = \frac{-dX}{dt} = zk_fX_f + (1 - z)k_sX_s \qquad (1)$$

where R_X is the rate of removal of xylan from the solid, X is the fraction of original xylan remaining in the solid residue, X_f and X_s are the fractions of the

fast- and slowly-reacting xylan remaining in the solid residue, z is the fraction of original xylan identified as the fast-reacting form, and k_f and k_s are rate constants. The rate constants are each assumed to have an Arrhenius temperature dependence and an acid concentration dependence,

$$k_f = k_{f0}\exp(-E_f/RT)C_H^m \qquad (2)$$

and

$$k_s = k_{s0}\exp(-E_s/RT)C_H^n \qquad (3)$$

where E_f and E_s are activation energies for the fast- and slowly-reacting xylan portions, C_H is the hydrogen ion concentration, and m and n are empirical rate parameters.

The concept of fast and slowly hydrolyzing hemicellulose was recently used by Beck and Wang[8] to develop a kinetics model, intended for reactor design purposes, for the hydrolysis of cotton gin residues in dilute sulfuric acid. Hemicellulose present in cotton gin residue is composed primarily of pentosans which, unlike hardwood hemicellulose, include a substantial amount of arabinan in addition to xylan. Based on limited kinetic data, they determined best-fit parameters for the following pentosan hydrolysis model:

$$R_P = -\frac{dP}{dt} = k_{f0}\exp\left(\frac{-E_f}{RT}\right)C_A^m P^2 \\ + k_{s0}\exp\left(\frac{-E_s}{RT}\right)C_A^n P \qquad (4)$$

where P is the weight fraction of pentosan in the solid residue and C_A is the sulfuric acid concentration. The values of E_f and E_s determined from multiple regression analysis were 18,000 and 5600 cal/mol, respectively, while the values determined for m and n were 1.36 and 0.36, respectively.

EXPERIMENTAL PROCEDURE

A detailed description of the batch reaction procedures used here is given by Springer.[2] White birch samples were kept frozen and green until they were sliced into cross-sectional wafers 0.01 in. thick. These slices were then stacked, frozen, and bored on a lathe to fill 5 mm o.d. pyrex tubes with about 0.25 g wood. After oven drying and weighing, 1 ml dilute sulfuric acid was added to achieve about a 4:1 liquid-to-solid ratio, the minimum amount of liquid required to wet the wood completely, and the tube was sealed. Reactions were run in duplicate in a constant-temperature oil bath. The contents of the tube have been shown to attain 99% of the temperature change within 25 s of immersion in the oil bath.[14]

Batch hydrolysis reactions were conducted at 100, 130,150, and 170°C in 0.09M sulfuric acid, and at 130°C in 0.040, 0.090, and 0.18M sulfuric acid, with all acid concentrations calculated based on solution densities
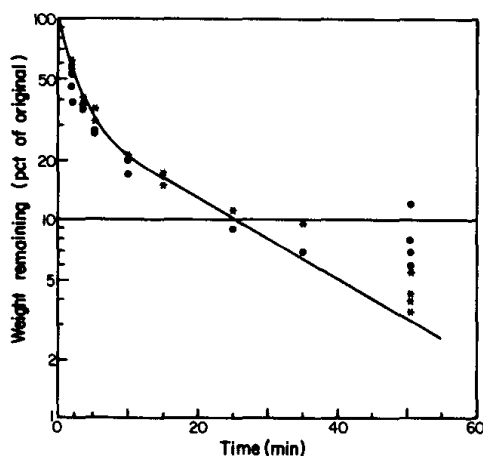

Figure 1. Typical conversion data for xylan and acetyl group hydrolysis, obtained at 150°C in 0.090M sulfuric acid ($C_H = 0.082M$) with a 4:1 liquid-to-solid ratio: (") acetyl, (*) xylan; –, model prediction for xylan removal [eq. (6)].

at room temperature. After a prescribed reaction time the tubes were rapidly cooled and broken open. The hydrolysate (about 1 ml) was separated from the residue on a filter crucible by thorough rinsing and then diluted to 10 ml. Monomeric xylose and glucose concentrations of the hydrolysate were determined by high-performance liquid chromatography. The residue was analyzed for xylan and glucan content by the method of Scott.[15] The acetic acid content of the hydrolysate was determined by gas chromatography. The amount of potential acetic acid bound to solubilized xylan was determined by reacting a portion of the diluted hydrolystate at 200°C for 20 min, analyzing it for acetic acid, and comparing its acetic content with that of the original hydrolysate. The acetyl group content of the residue was determined by hydrolyzing a portion of the residue at 200°C for 40 min in 0.04M sulfuric acid and then analyzing the resultant hydrolysate for acetic acid. Ash analyses were done on unreacted wood samples and on a composite sample of hydrolyzed wood. The ash samples obtained were analyzed for calcium, magnesium, and manganese by atomic absorption.

RESULTS

From chemical analysis of paper birch samples the maximum yield of xylose/100 g dry wood was found to be 24.7 g while that of acetic acid was found to be 6.9 g. These yields correspond to maximum concentrations in undiluted hydrolysate of about 6.0 and 1.5% for xylose and acetic acid, respectively, for a 4:1 tiquid-to-solid ratio.

Hydrolysis data from the experiments at 150°C in 0.090M sulfuric acid have been presented in Figure 1. Residual amounts of both xylan and acetyl, each expressed as a percent of the amount present in the original sample, are shown as a function of reaction time. Values for both components were obtained by chemical analysis of the residue.

Figure 2 presents the xylan dissolution data for the experiments done with 0.090M sulfuric acid at temperatures of 100, 130, 150, and 170°C. Figure 3 presents
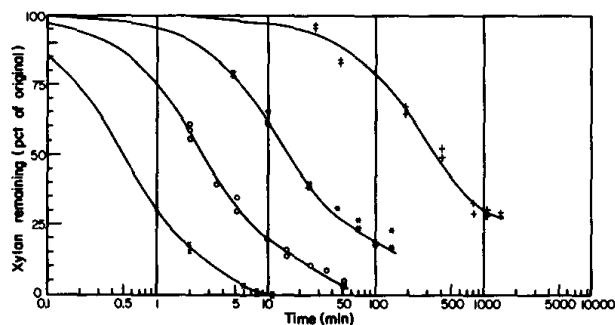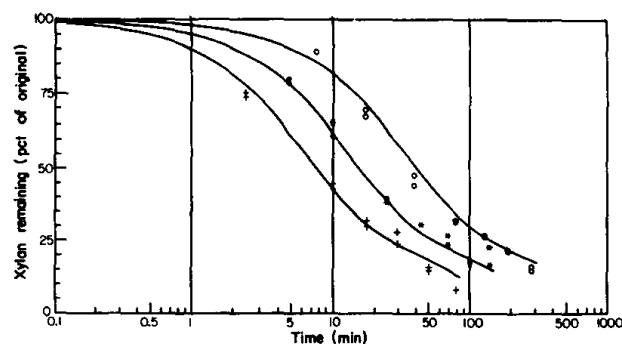

Figure 3. Experimental and predicted xylan conversion rates at 130°C with a 4:I liquid-to-solid ratio of various sulfuric acid concentrations: (!) 0.040M (C_H = 0.032M), (*) 0.090M (C_H = 0.082M). (+) 0.18M (C_H = 0.17M); –, model prediction [eq. (6)].

the xylan residue data for the 130°C experiments at sulfuric acid concentrations of 0.040, 0.090, and 0.18M. These conversion data have been plotted against a logarithmic time scale to allow convenient comparison of the times required for hydrolysis under various conditions.

The cellulose and lignin contents of the original wood were found to be 40.5 and 19.0%, respectively, on an oven-dry basis. During hydrolysis approximately 95% of the cellulose present in the wood remained intact for up to 85% xylan removal. For virtually complete xylan removal 85% of the cellulose remained. No lignin analyses were performed on the hydrolyzed wood samples.

Figures 4 and 5 indicate the relative rate of acetyl release from hemicellulose as plots of the fraction of acetyl removed from the residue versus the amount of xylan removed, expressed as percentages of original amounts. Figure 4 shows the data obtained with 0.090M sulfuric acid at various temperatures. Figure 5 shows the results at 130°C with three different acid concentrations. For moderate degrees of hydrolysis, i.e., when more than 50% of the original acetyl remained intact,
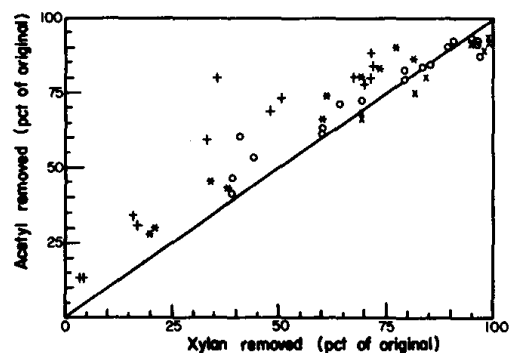

Figure 2. Experimental and predicted xylan conversion rates in 0.090M sulfuric acid (C_H = 0.082M) for a 41 liquid-to-solid ratio at various temperatures: (+) 100°C, (*) 130°C, (!) 150°C, (×) 170°C; –, model prediction [eq. (6)].

Figure 4. Hydrolytic removal of acetyl groups from paper birch relative to that of xylan in 0.090M sulfuric acid (C_H = 0.082M) for a 4:1 liquid-to-solid ratio at various temperatures: (+) 100°C. (*) 130°C. (!) 150°C, (×) 170°C; –, equal rate of acetyl group and xylan removal.
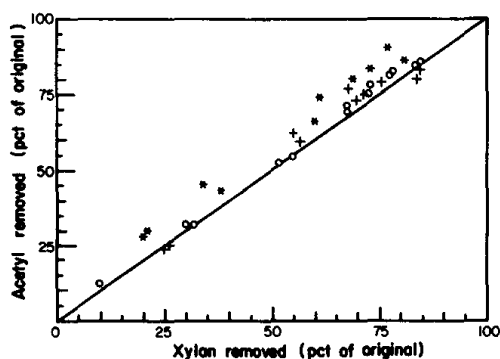
Figure 5. Hydrolytic removal of acetyl groups from paper birch relative to that of xylan at 130°C for a 4:1 liquid-to-solid ratio at various sulfuric acid concentrations: (!) $0.040M$ ($C_H = 0.032M$). (*) $0.090M$ (C, = $0.082M$), (+) $0.18M$ ($C_H = 0.17M$), −, equal rate of acetyl group and xylan removal.

as much as one-half of the acetyl present in the hydrolysate was bound to solubilized xylan.

Table I presents the results of the ash analysis as concentrations of calcium, magnesium, and manganese in the dry unreacted birch and in the dry hydrolysis residue.

DISCUSSION OF RESULTS

The removal of paper birch xylan as a function of time follows the general trend discussed earlier. As shown in Figure 1, the first 70% or so of the xylan is removed according to apparent first-order kinetics, whereas the remaining xylan is removed at a much slower rate that can also be modeled according to a first-order law. As indicated in Figures 2 and 3, increased temperature and acid concentration both cause an increase in the rate of xylan dissolution.

The xylan hydrolysis data were found to be reproducible within a 5% relative error, except at very low residual xylan levels, while acetyl hydrolysis data typically varied 5–15% between replicates. An acetyl mass balance was performed for each experiment from the analyses of free soluble and bound soluble acetyl in the hydrolysate and of the acetyl content of the hydrolyzed residue. Good closure was obtained on the

Table I. Cation analysis of unreacted and hydrolyzed white birch samples.

Cation	Concentration in unreacted air-dried wood (ppm)	Concentration[a] in hydrolyzed oven-dried wood (ppm)
Ca^{+2}	550	35
Mg^{+2}	60	<10
Mn^{+2}	45	1.2

[a] In neutralization calculations the residue weight was assumed to be 70% of the unreacted wood weight.

total amount of acetyl present, corresponding to 6.9 ± 0.5 mg acetic acid obtained from 100 mg dry wood, indicating consistency in separation and analysis procedures.

Hydrolysate sugar analyses indicated that the yield of monomeric xylose is highly dependent on the extent of xylan hydrolysis. For low extents of xylan removal (<40%) a significant portion of the solubilized xylan was present as oligomers, whereas for intermediate extents of removal, nearly quantitative yields of monomeric xylose were obtained. Reaction conditions that provided extensive xylan removal also resulted in somewhat reduced yield due to xylose degradation.

The degree of cellulose degradation was found to depend only on the fraction of original xylan removed and not on the conditions of hydrolysis, which is in agreement with earlier findings of Hams et al.[16] on dilute acid hydrolysis. The results obtained are also comparable to those obtained by Karlivan[17] for hydrolysis in 90% sulfuric acid, although he suggests that much greater cellulose degradation would be expected with dilute acid hydrolysis.

Modeling of the xylan hydrolysis data was attempted with the two different kinetics expressions presented above, each of which is based on the existence of two types of xylan that differ in their susceptibility to hydrolysis. One model, that of Beck and Wang[8] [presented here as eq. (4)], includes a second-order dependence on the residue xylan concentration for which there appears no obvious theoretical basis. This model does not fit the experimental data well. The other model, that of Veeraraghavan et al.[9] and of Conner[13] [given in eq. (1)], provides a much better fit to the experimental data. This model is based on the presence of two types of xylan that hydrolyze via parallel first-order reactions. A nonlinear regression routine was used to determine the best values of z, k_f, and k_s, in the integrated form of equation (1),

$$X = z \exp(-k_f t) + (1 - z)\exp(-k_s t) \qquad (5)$$

to fit the xylan dissolution data for each set of reaction conditions.

As shown in Table II, the value obtained for z, the fraction of xylan identified as the fast-reacting form, is virtually independent of reaction conditions. The average value of z, 0.684, was substituted into the model, and best-fit values for k_f and k_s were redetermined, resulting in only minor changes in the model's effectiveness. These values of k_f and k_s (presented in Table 11) were then used to determine the temperature and acid concentration dependencies of the rate constants.

Best-fit k_f and k_s values obtained for reactions in $0.090M$ sulfuric acid at four different temperatures were used to calculate preexponential factors and activation energies for the fast- and slowly-reacting portions by assuming an Arrhenius temperature dependence,

The activation energies were determined to be 30,620

Table II. Rate constants for hydrolysis of xylan in white birch.

Temperature (°C)	Corrected sulfuric acid concentration[a] (M)	Best-fit values for weight fraction of fast-reacting xylan, z	Experimental best-fit rate constants[b] (min⁻¹)		Rate constants calculated from global rate expression (min⁻¹)	
			k_f	k_s	k_f [eq. (7)]	k_s [eq. (8)]
100	0.082	0.701	3.35×10^{-3}	1.14×10^{-4}	3.45×10^{-3}	1.17×10^{-4}
130	0.032	0.647	3.12×10^{-2}	2.09×10^{-3}	2.78×10^{-2}	1.92×10^{-3}
130	0.082	0.638	6.99×10^{-2}	4.44×10^{-3}	7.21×10^{-2}	5.00×10^{-3}
130	0.17	0.595	1.51×10^{-1}	1.20×10^{-2}	1.50×10^{-1}	1.04×10^{-2}
150	0.082	0.724	4.27×10^{-1}	4.18×10^{-2}	4.31×10^{-1}	4.55×10^{-2}
170	0.082	0.703	2.10×10^{0}	3.34×10^{-1}	2.19×10^{0}	3.39×10^{-1}

[a] **Acid concentrations were corrected for incomplete sulfuric acid dissociation and for neutralization by ash.**

[b] **An average value for z, the weight fractions of fast-reacting xylan, of 0.684 was used in determining these rate constants.**

± 120 cal/mol and 37,400 ± 750 cal/mol for the fast- and slowly-reacting portions, respectively. These values are much higher than those cited earlier from the work of Beck and Wang with cotton gin residues. A comparison of the activation energies obtained for the slow-reacting hemicellulose portion is particularly interesting, since the low value (5600 cal/mol) obtained by Beck and Wang suggests that diffusional effects are responsible for the reduced hydrolysis rate. The higher value obtained for E, in this study indicates that the slower hydrolysis rate may not be due to diffusional limitations. Diffusional control of the reaction rate also seems unlikely according to geometric considerations. For the 0.2–0.3-mm slices of wood used, the dimensionless time parameter, Dt/y^2, for the diffusion of xylose or water is of order 10 after about 1 min of reaction, indicating that significant gradients within the wood pores would not be expected after this time.

The acid dependence of the xylan hydrolysis rate was determined according to equation (2) and (3), in which the hydrogen ion concentration was calculated from the neutralizing ability of the wood and the degree of dissociation of sulfuric acid at elevated temperatures. Within the temperature and pH ranges of this study, more than 97% of the sulfate present is in the form of bisulfate[18]; it was therefore assumed that only 1 mol of hydrogen ions was obtained from each mol of sulfuric acid. The neutralizing ability of the wood was calculated from the difference in cation content of the original and hydrolyzed wood, as listed in Table I. One mol of hydrogen ions (and sulfuric acid) was assumed to be neutralized for each equivalent weight of cations dissolved during hydrolysis. The calculated neutralizing ability of the wood, about 3.5 mg sulfuric acid/g dry wood, is considerably lower than the value of 8–9 mg sulfuric acid/g dry wood determined for red oak by Veeraraghavan et al.[9]

Neutralization of the acid was assumed to occur immediately upon contact with the wood. That is, the acid concentration during hydrolysis was assumed to be constant at its neutralization-adjusted value. As a result of the dissociation and neutralization considerations, nominal sulfuric acid concentrations of 0.040, 0.090, and 0.18M correspond to actual hydrogen ion concentrations of 0.032, 0.082, and 0.17M in the experiments. Based on these adjusted concentrations, the acid dependence of the rate constants obtained at 130°C yields the values of 0.93 ± 0.05 for m and 1.02 ± 0.16 for n in equation (2) and (3). The rates of hydrolysis for both xylan portions are both essentially first order with respect to hydrogen ion concentration, which is in agreement with proposed homogeneous hydrolysis mechanisms. [19]

Combination of equations (1), (2), and (3) with the experimentally determined parameters yields a global rate model for hydrolysis of birch xylan. The integrated form for isothermal batch hydolysis becomes

$$X = 0.684 \exp(-k_f t) + (1 - 0.684)\exp(-k_s t) \quad (6)$$

where

$$k_f = 2.267 \times 10^{16} \ (\text{min}^{-1}/\text{mol L}^{-1}) \times \exp\left(\frac{-30,260 \ \text{cal/mol}}{RT}\right) C_H \quad (7)$$

and

$$k_s = 1.163 \times 10^{19} \ (\text{min}^{-1}/\text{mol L}^{-1}) \times \exp\left(\frac{-37,400 \ \text{cal/mol}}{RT}\right) C_H \quad (8)$$

and T is in kelvins, t is in minutes, and C_H is the hydrogen ion concentration in mols per liter corrected for ash neutralization and incomplete sulfuric acid dissociation. A comparison of the rate constants predicted by this global model to those that best fit the experimental data is given in Table II. The fit of the model to the experimental data is shown in Figure 2 for reactions at various temperatures in 0.090M sulfuric

acid and in Figure 3 for reactions at 130°C in different acid solutions; the curves drawn in these figures are computed from equation (6). The model approximates the experimental results quite well, with a typical relative error of less than 10% in xylan conversion under all reaction conditions. This model may be combined with an existing model for acid-catalyzed xylose degradation" to predict the hydrolysate xylose concentration as a function of time.

Modeling of the temperature dependence of the xylan hydrolysis rate was considerably more successful than modeling of the acid dependence, as can be seen by comparing the agreement in Figure 2 with that in Figure 3. Difficulties in modeling the acid dependence probably arise from uncertainties in describing the neutralizing behavior of the wood.

Because of the greater scatter in the acetyl group hydrolysis data, separate modeling of the deacetylation kinetics proved to be impractical. However, important conclusions on the rate of acetyl removal can be made by comparing the rate of acetyl removal with that of xylan. As illustrated in Figures 4 and 5, the acetyl removal rate is comparable to the xylan removal rate under the reaction conditions studied, although the relative hydrolysis rate is seen to have some temperature dependence. Data obtained in 0.090M sulfuric acid at 100 and 130°C, shown in Figure 4, indicate that deacetylation at lower temperatures occurs at a somewhat faster rate than xylan removal, whereas the two removal rates are nearly equal at the higher temperatures of 150 and 170°C. These results suggest that at low temperatures acetyl groups are removed from the wood at a significant rate by two pathways: by direct hydrolysis of acetyl groups substituted on the solid xylan backbone and by hydrolytic dissolution of small fragments of the xylan chain that are still acetyl substituted. Acetyl removal by xylan hydrolysis has been substantiated by the detection of acetyl-substituted xylose in the hydrolysate. Since at higher temperatures (150 and 170°C) the deacetylation rate is nearly equal to the xylan hydrolysis rate, it appears that the rate of acetyl removal by direct hydrolysis is negligible compared to that occurring by xylan removal. This suggests that the temperature dependence of the xylan hydrolysis rate is greater than that of the direct deacetylation rate in solid wood.

The effect of acid concentration on the relative rate of direct deacetylation is less clear. As shown in Figure 5, no distinct trend in relative removal rates is observed with varying acid concentration at 130°C.

CONCLUSIONS

An empirical rate model for birch hydrolysis has been developed in terms of first-order homogeneous hydrolysis of two xylan fractions. The model is adequate for the range of temperatures and acid concentrations studied, predicting experimental conversion data within

a 10% relative error. When combined with a rate model for xylose degradation," a rate model of this type is useful for process calculations, providing a conversion rate function for reactor design. Such an application has been demonstrated by Maloney et al.[21] in the modeling of a percolation reactor for paper birch hemicellulose hydrolysis.

Significant difference between the rate of acetyl removal and that of xylan was seen only at low temperatures (100 and 130°C) where some preferential removal of acetyl takes place. No effect of acid concentration on the relative removal rate was observed at 130°C. According to these results, a process that would selectively remove acetyl from wood by means of dilute acid catalysis while leaving the xylan backbone primarily intact does not seem to be feasible. At temperatures below 130°C, the only reaction conditions found to result in selective acetyl removal, reaction times of several hours would be required to obtain significant acetic acid production.

NOMENCLATURE

C_A	sulfuric acid concentration (mol/L)
C_H	corrected hydrogen ion concentration (mol/L)
D	mass diffusivity of xylose (cm²/s)
E_f, E_s	activation energies for rate constants k_f and k_s (cal/mol)
k_f, k_s	first-order rate constants for hydrolysis of fast- and slow-reacting xylan portions (min^{-1})
k_{f0}, k_{s0}	frequency factors for rate constants k_f and k_s (min^{-1}/mol/L)
m, n	order of hydrogen ion concentration dependence for rate constants k_f and k_s
P	pentosan concentration (weight fraction in solid)
R	universal gas constant (= 1.987 cal/mol K)
R_X, R_P	reaction rates for xylan, pentosan hydrolysis
t	time (min)
T	temperature (K)
X	fraction of original xylan remaining
X_f, X_s	fraction of original fast- and slowly-reacting xylan remaining
y	half-thickness of wood slice (cm)
z	fraction of original xylan identified as the. fast-reacting form

References

1. A. J. Baker and G. F. Krcmar, U.S. Forest Products Laboratory, Madison, WI, 1956, unpublished report.
2. E. L. Springer, Ph.D. thesis, University of Wisconsin, Madison, 1961.

3. E. L. Springer, J. F. Harris, and W. K. Neill, *Tappi*, **46**, 551 (1963).
4. F. A. Simmonds, S. M. Kingsbury, and J. S. Martin, *Tappi*, **38**, 178 (1955).
5. H. R. Bungay, *Science*, **218**, 643 (1982).
6. R. B. Shah, E. C. Clausen, and J. L. Gaddy, *Chem. Eng. Prog.* **80**(1), 76 (1984).
7. E. Sjöström, "Production of Chemicals from Wood as an Integrated Part of the Pulping Process," presented at 1983 International Symposium on Wood and Pulping Chemistry, Tsukuba Science City, Japan (1983).
8. S. R. Beck and Ta-Sheng Wang, "Kinetic Analysis of Hemicellulose Hydrolysis in Cotton Gin Residue," presented at AIChE National Meeting, Orlando, FL, February 1982.
9. S. Veeraraghavan, R. P. Chambers, M. Myles, and Y. Y. Lee, "Kinetic Modeling and Reactor Development for Hemicellulose Hydrolysis," presented at AIChE National Meeting, Orlando, FL, February 1982.
10. D. R. Cahela, Y. Y. Lee, and R. P. Chambers, *Biotechnol. Bioeng.*, **25**, 3 (1983).
11. B. Lindberg, K. Rosell, and S. Svensson, *Svensk Papperstidning*, **76**, 30 (1973).
12. P. Erins, V. Cinite, M. Jakobsons, and J. Gravitis, *Applied Polymer Symposium No. 28*, p. 1117 (1976).
13. A. H. Conner, *Wood and Fiber Science*, **16**, 268 (1984).
14. R. Tomlin and J. Baumgartner, U.S. Forest Products Laboratory, Madison, WI, 1956, unpublished report.
15. R. W. Scott, *Anal. Chem.*, **48**, 1919 (1976).
16. J. F. Harris, J. F. Saeman, and E. G. Locke, "Wood as a Chemical Raw Material," in *Chemistry of Wood*, B. L. Browning, Ed. (Wiley, New York, 1963), Chap. 11, p. 535.
17. V. P. Karlivan, "New Aspects of the Production of Chemicals from Biomass," presented at World Conference on Future Sources of Organic Raw Materials, Toronto (1978).
18. W. L. Marshall and E. V. Jones, *J. Phys. Chem.*, **70**, 4028 (1966).
19. A. F. Bochkov and G. E. Zaikov, *Chemistry of the O-Glycosidic Bond: Formation and Cleavage* (Pergamon Press, Oxford, 1979).
20. D. F. Root, Ph.D. Thesis, University of Wisconsin, Madison, 1956.
21. M. T. Maloney, T. W. Chapman, and A. J. Baker, "Numerical Percolation Reactor Model for Xylan and Acetyl-Group Hydrolysis," presented at AIChE Summer National Meeting, Philadelphia, PA, August 1984.