

# KINETIC MODELING OF HARDWOOD PREHYDROLYSIS. PART II. XYLAN REMOVAL BY DILUTE HYDROCHLORIC ACID PREHYDROLYSIS<sup>1</sup>

*Anthony H. Conner, Kimball Libkie,  
and Edward L. Springer*

Research Chemist, Physical Science Technician, and Chemical Engineer  
Forest Products Laboratory,<sup>2</sup> Forest Service  
U.S. Department of Agriculture  
Madison, WI 53705

(Received May 1984)

## ABSTRACT

Knowledge of prehydrolysis kinetics has applicability to the design, development, and modeling of processes to separate wood into its basic chemical constituents (i.e., cellulose, hemicellulose, and lignin). The kinetics of xylan hemicellulose removal with 0.10 M HCl at 120 C from quaking aspen, paper birch, American elm, red maple, and southern red oak was studied. The mathematical model developed in Part I to describe the kinetics of xylan removal by water prehydrolysis of these species could be used to model xylan removal with dilute hydrochloric acid. Xylan removal could thus be modeled as the sum of two parallel first-order reactions—one fast and one slow. However, unlike the case with water prehydrolysis where the rate constants for the fast ( $k_f$ ) and slow ( $k_s$ ) reaction processes could be correlated with each other, they could not be correlated for HCl prehydrolysis. Instead the  $k_f$  and  $k_s$  values determined for each species clustered about average  $k_f$  and  $k_s$  values for all the species as a whole. A single set of parameters determined from a nonlinear least squares fit of the experimental prehydrolysis data for all the species as a whole to the model could be used to reasonably describe the course of xylan removal from all the species. The fact that one set of parameters could be used suggests that the same reactions are taking place on prehydrolysis and that the chemical structure and physical morphology of the xylan hemicellulose were essentially the same in the species studied and probably in all temperate hardwood species. The model thus provides a good approximation of xylan removal from any temperate hardwood with dilute hydrochloric acid at the reaction conditions studied.

*Keywords:* Xylan, prehydrolysis, hydrochloric acid, kinetics, hardwoods, aspen (*Populus tremuloides*), birch (*Betula papyrifera*), elm (*Ulmus americana*), maple (*Acer rubrum*), southern red oak (*Quercus falcata*).

## INTRODUCTION

The hemicelluloses in wood are more readily hydrolyzed than is cellulose, affording a means of selectively removing the hemicellulose as sugars. Many recent schemes for utilizing wood as a source of chemicals and liquid fuels, therefore, include a prehydrolysis step to hydrolyze the hemicelluloses to water-soluble monomeric sugars and oligosaccharides prior to a main (cellulose) hydrolysis step. The milder conditions used in prehydrolysis result in higher yields of the hemicellulose-derived sugars than would occur during the harsher conditions of the

---

<sup>1</sup> This article was written and prepared by U.S. Government employees on official time, and it is therefore in the public domain (i.e., it cannot be copyrighted).

<sup>2</sup> The Forest Products Laboratory is maintained by the U.S. Department of Agriculture, Forest Service, in cooperation with the University of Wisconsin-Madison, Madison, WI.

main hydrolysis. The lignocellulosic residue remaining after prehydrolysis is hydrolyzed in the main hydrolysis step to give glucose and a lignin residue. In hardwoods the predominate hemicellulose is *O*-acetyl-(4-*O*-methylglucuronoxylan, which hydrolyzes mainly to xylose, one of the more easily degraded sugars.

Prehydrolysis is catalyzed by dilute mineral acids, or in the absence of added mineral acid, by the acetic acid released on hydrolysis of the acetyl groups from the hemicellulose polymer (autohydrolysis). Knowledge of the kinetics of prehydrolysis has a broad range of applicability to present wood utilization processes (e.g., prehydrolysis kraft pulping (Richter 1956), Masonite fiberboard and hardboard production (Mason 1921), Iotech steam explosion (1980), and the Stake process (Bender 1979)) and is of importance in the design, development, and modeling of new processes to separate wood into its basic chemical constituents (i.e., cellulose, hemicellulose, and lignin).

Previous research on hardwood prehydrolysis has shown that based on a plot of the logarithm of the fraction of xylan remaining in the solid phase versus reaction time, the removal of xylan hemicellulose from wood appears to occur with an initial fast phase followed by a slower second phase (Simmonds et al. 1955; Kobayashi and Sakai 1956; Springer et al. 1963; Springer and Zoch 1968). Kobayashi and Sakai (1956), Kamiyama et al. (1974), Kang and Yoo (1976), Conner (1981, 1984), and Veeraraghavan et al. (1982) have suggested that these two phases are due to the simultaneous removal of an easily hydrolyzable hemicellulose fraction and a difficult to hydrolyze hemicellulose fraction.

Springer et al. (1963) and Springer and Zoch (1968) obtained estimates of the pseudo first-order rate constants for the initial fast removal of xylan from various hardwoods ( $k_i$ ). These estimates were obtained from the initial slope of the semilog plot of xylan remaining versus time. Individual rate constants for the fast and slow phases were not determined, nor were the experimental data modeled to demonstrate their fit to any kinetic system. Conner (1984) showed that xylan removal from hardwoods (aspen, birch, elm, maple, and red oak) by water prehydrolysis (autohydrolysis) could be modeled as the sum of two parallel first-order reactions—one fast and one slow. Thus the fraction of xylan  $X_t/X_T^0$ , remaining after any reaction time,  $t$ , was described by:

$$X_t/X_T^0 = (1 - X_S^0/X_T^0)EXP[-k_f(t - \Delta t)] + (X_S^0/X_T^0)EXP[-k_s(t - \Delta t)] \quad (1)$$

where

$X_T^0$  = total xylan in wood at  $t = 0$

$X_S^0$  = slow reacting xylan in wood at  $t = 0$

$X_F^0$  = fast reacting xylan in wood at  $t = 0$  ( $X_F^0 = X_T^0 - X_S^0$ )

$X_t$  = total xylan in wood at any  $t$

$k_s$  = apparent psuedo first-order rate constant for removal of slow reacting xylan

$k_f$  = apparent psuedo first-order rate constant for removal of fast reacting xylan

$\Delta t$  = empirical time correction to isothermal reaction conditions

In addition it was shown that the rate constant for initial xylan removal ( $k_i$ ) is a

TABLE 1. Reaction rate constants for xylan removal from various hardwoods with 0.10 M HCl at 120 C.

Species	Calculated <sup>1</sup>					Reported <sup>2</sup> k <sub>r</sub> (Min <sup>-1</sup> )
	k <sub>r</sub> (Min <sup>-1</sup> )	k (Min <sup>-1</sup> )	X <sub>0</sub> /X <sub>t</sub> <sup>0</sup> (Pct)	Δt (Min)	k (Min <sup>-1</sup> )	
Paper birch	0.0482 ± 0.0075	0.0035 ± 0.0007	37.9 ± 5.0	0.93 ± 1.00	0.0313	0.0231
Quaking aspen	0.0372 ± 0.0022	0.0025 ± 0.0004	28.5 ± 2.3	1.09 ± 0.44	0.0273	0.0229
Southern red oak	0.0351 ± 0.0033	0.0033 ± 0.0008	25.7 ± 4.2	0.48 ± 0.70	0.0269	—
Red maple	0.0336 ± 0.0029	0.0030 ± 0.0006	29.3 ± 3.8	1.01 ± 0.63	0.0246	0.0210
American elm	0.0284 ± 0.0033	0.0031 ± 0.0007	34.0 ± 5.3	0.79 ± 0.83	0.0198	0.0174
Overall <sup>3</sup>	0.0358 ± 0.0026	0.0031 ± 0.0005	31.2 ± 3.0	0.77 ± 0.53	0.0256	—

<sup>1</sup> From nonlinear least squares fit of data to Eq. (1) using the Statistical Analysis System (SAS) at the University of Wisconsin-Madison. Data are reported ± standard error (asymptotic).

<sup>2</sup> Springer and Zoch (1968).

<sup>3</sup> From nonlinear least squares fit of the data from all the species to Eq. (1) using SAS at the University of Wisconsin-Madison. Data are reported ± standard error (asymptotic).

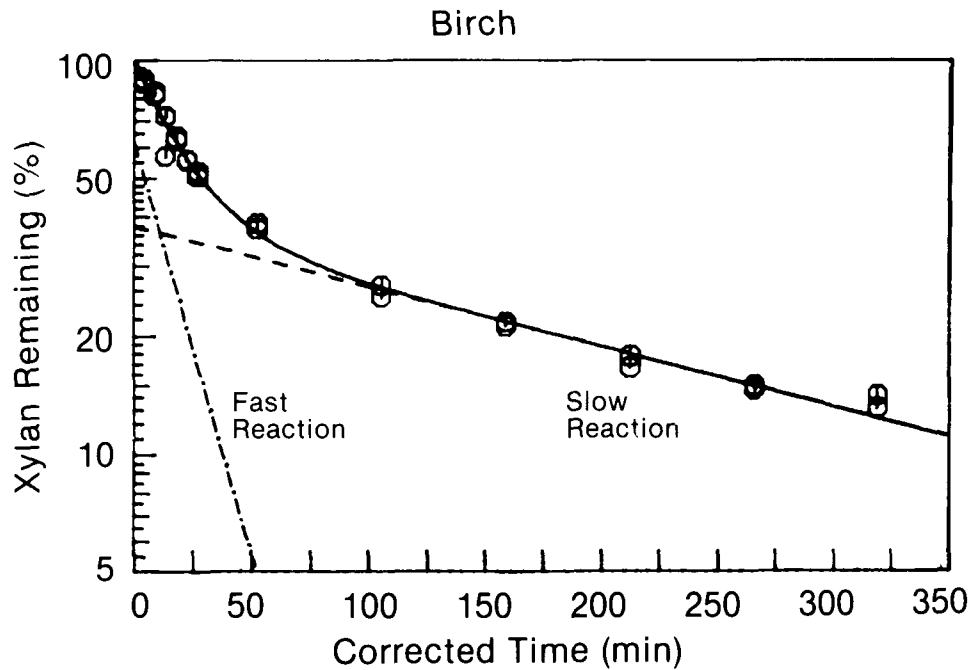


FIG. 1. Semilog plot of xylan remaining versus time (corrected) for prehydrolysis of paper birch with 0.10 M HCl at 120 C. The open circles are experimental data. The solid line is the curve for a nonlinear least squares fit of the data to Eq. (1). The progress of the separate fast (---) and slow (-·-) reactions are indicated by the broken lines.

complex function of the rate constants for the fast ( $k_f$ ) and slow reactions ( $k_s$ ). The initial rate could be calculated from  $k_f$  and  $k_s$  by the following:

$$k_i = k_f(1 - X_S^0/X_T^0) + k_s X_S^0/X_T^0 \quad (2)$$

We wish to report here that these equations also describe the prehydrolysis of quaking aspen (*Populus tremuloides* Mich.), paper birch (*Betula papyrifera* Marsh), American elm (*Ulmus americana* L.), red maple (*Acer rubrum* L.), and southern red oak (*Quercus falcata* Michx.) with 0.10 M HCl at 120 C. The experimental data for the prehydrolysis of aspen, birch, elm, and maple are those reported previously by Springer and Zoch (1968) and those for red oak are newly acquired data.

#### RESULTS AND DISCUSSION

The derivation of Eq. (1) and (2) was described previously (Conner 1984). Equation (1) was fitted by a nonlinear least squares method to the experimental data reported by Springer and Zoch (1968) for the prehydrolysis of aspen, birch, elm, and maple and to experimental data obtained on the prehydrolysis of red oak with the Statistical Analysis System (SAS) version 79.3A (Helwig and Council 1979). The results of this analysis are presented in Table 1. Figures 1 and 2 show that in all cases the calculated values of xylan remaining after various reaction

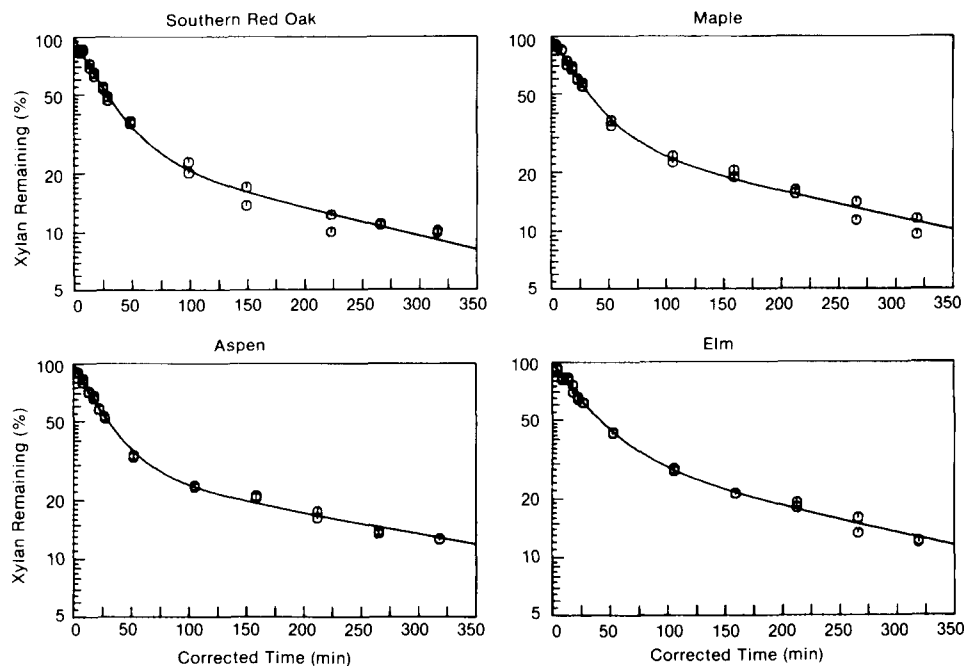


FIG. 2. Semilog plots of xylan remaining versus time (corrected) for prehydrolysis of southern red oak, red maple, quaking aspen, and American elm with 0.10 M HCl at 120 C. The open circles are experimental data. The solid line is the curve for a nonlinear least squares fit of the data to Eq. (1).

times, using the least squared values of  $k_s$ ,  $k_f$ ,  $\Delta t$ , and  $X_S^0/X_T^0$  in Eq. (1), are in good agreement with the experimental data.

The graphical interpretation of Eq. (1) for the prehydrolysis of birch is illustrated in Fig. 1. The percentage of slower reacting xylan,  $(X_S^0/X_T^0) \times 100$ , is found by extrapolating the slow reaction process to  $t = 0$ . This extrapolated line represents the course of the slow reaction process and its slope is the apparent pseudo first-order rate constant for the slow reaction process,  $k_s$ . If at each reaction time the portion of the slower reacting xylan is subtracted from the total xylan remaining at that time, then one obtains the second dashed line in Fig. 1, which represents the course of the fast reaction process. The slope of this second dashed line is the apparent pseudo first-order rate constant for the fast reaction process,  $k_f$ .

The initial rate constant,  $k_i$ , calculated from Eq. (2) and that determined graphically by Springer and Zoch (1968) are compared in Table 1. The differences between the calculated values and those estimated by Springer and Zoch are due to the two different methods used to obtain these values and in part to experimental errors associated with the data that made it difficult to establish precisely the parameters of the model and the slope of the initial curve. Thus the calculated  $k_i$  values were obtained from Eq. (2), which was derived from Eq. (1) by differentiation explicitly at time zero. Springer and Zoch's  $k_i$  values were obtained from the best slope of a semilog plot of the xylan removal data versus time over the interval from time zero to the time at approximately 50% xylan removal; and

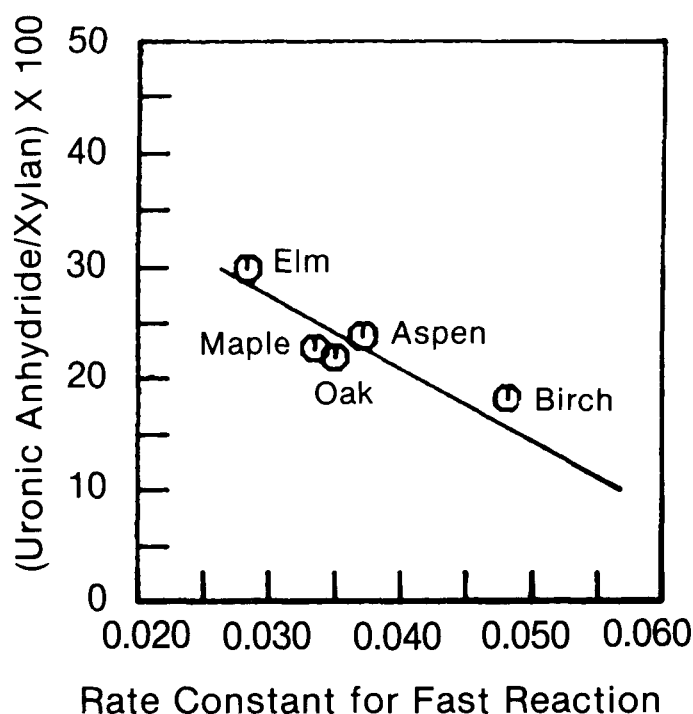


FIG. 3. Plot of (uronic anhydride content/xylan content)  $\times$  100 versus  $k_f$ .

are, therefore, influenced by a contribution from the slow reaction process on the initial slope. The initial slope can be used to predict xylan removal from time zero to the time for approximately 50% remaining xylan. Equation (1) predicts xylan removal both initially as well as at times beyond those for 50% remaining xylan.

Springer and Zoch (1968) observed that there appeared to be an inverse relationship between  $k_i$  and the uronic acid content of the various hardwoods. Conner (1984) showed that as expected this inverse relationship also applied to  $k_f$  for water prehydrolysis and the uronic acid content of these hardwoods. Our data indicate that the  $k_f$  data from hydrochloric acid catalyzed prehydrolysis of these hardwoods also fit into this trend (Fig. 3). The uronic acid content of the southern red oak was determined by a spectrophotometric procedure (Scott 1979) and by the Browning method (1949). The uronic acid contents of the other species were determined by the Browning method. From literature data (Scott 1979; Whistler *et al.* 1940), it appears that the Browning method gives a higher value than the spectroscopic method because of the release of  $\text{CO}_2$  from components other than uronic acid in the wood. For purposes of comparison between species, only the Browning values have been used. This, however, is a source of possible deviation about the line in Fig. 3.

While  $k_f$  and  $k_s$  for the water prehydrolysis of these hardwood species were highly correlated (Conner 1984), no statistically significant correlation between

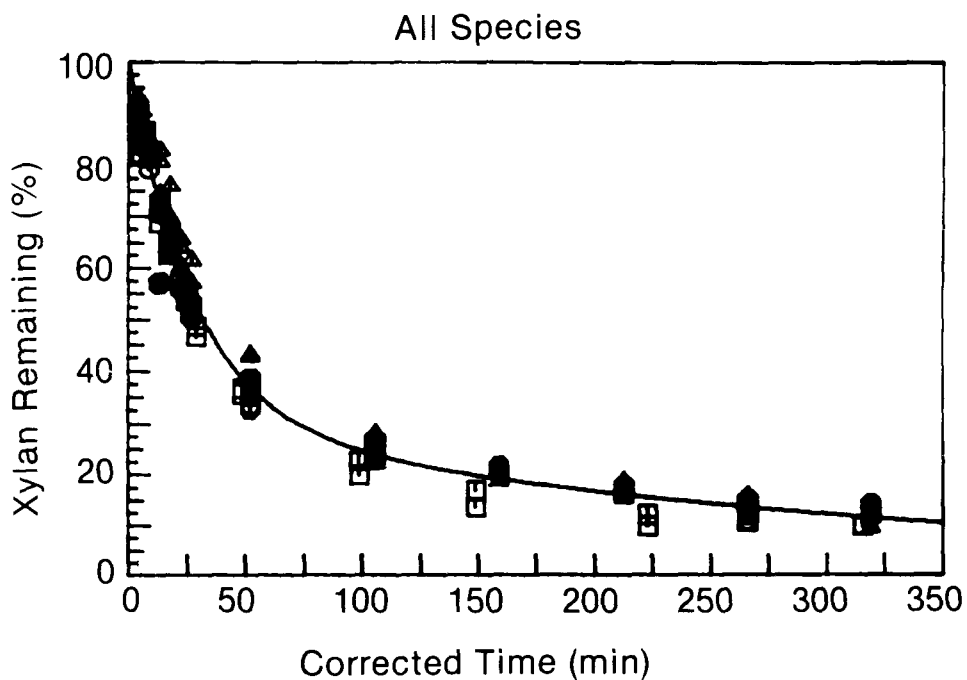


FIG. 4. Linear plot of xylan remaining versus time (corrected) for prehydrolysis of all the species ( $\circ$  = aspen,  $\bullet$  = birch,  $\triangle$  = elm,  $\blacktriangle$  = maple,  $\square$  = southern red oak). The solid line is the curve for a nonlinear least squares fit of all the prehydrolysis data for all the species as a group to Eq. (1).

$k_f$  and  $k_s$  for prehydrolysis with 0.10 M HCl was found. For 0.10 M HCl prehydrolysis the slow rate constant,  $k_s$ , was essentially constant for all the species. Except possibly for birch and elm, the  $K_f$  values also tend to cluster about an average  $k_f$  value. To test whether there was a significant difference in the fit of the data for individual species to Eq. (1) as opposed to an overall fit of the data, the total data for the prehydrolysis of all the hardwood species studied were fit as a single group to Eq. (1) using the SAS nonlinear least squares method. The values for  $k_f$ ,  $k_s$ ,  $\Delta t$ , and  $X_S^0/X_T^0$  for this overall fit are listed in Table 1. Although statistically the fit of all the prehydrolysis data to Eq. (1) was not as good as the individual fits of data for each species, it can be seen from Fig. 4 that the overall fit is quite satisfactory. That one set of parameters can be used to reasonably fit all the prehydrolysis data for the species studied suggests that the same reactions are taking place on prehydrolysis and that, as expected, the chemical structure of the xylan polymer is essentially the same in these and all temperate hardwood species. The differences in xylan removal as evidenced by the scatter of the sets of data points for the various species about the curve in Fig. 4 are no doubt due at least in part to differences in their uronic acid contents as previously discussed. Because these differences are not extremely large, Fig. 4 is probably a good approximation of the xylan removal curve for any temperate hardwood at the reaction conditions studied.

On water prehydrolysis of these species at 170 C, the  $k_f$  and  $k_s$  values varied

over a 4- to 5-fold range ( $k_f$ : 0.019 to 0.081  $\text{min}^{-1}$ ;  $k_s$ : 0.0009 to 0.0049  $\text{min}^{-1}$ ) and could be correlated with each other (correlation coefficient = 0.993). The reason(s) for the clustering of the  $k_f$  and  $k_s$  values for 0.10 M HCl prehydrolysis as opposed to the wider distribution of and the apparent correlation between  $k_f$  and  $k_s$  observed with water prehydrolysis, are not known. It is possible that this difference is due to the fact that HCl, a strong mineral acid, swamps the effect of the liberated acetic acid, a weak organic acid, and effectively establishes an equal acidity for all the woods. When no mineral acid is present, the acidities although much lower range more widely, being established as acetic acid is produced by hydrolysis. Inorganic ash forming constituents present in wood are known to neutralize significant proportions of dilute mineral acid solutions added to wood (Saeman 1945; Springer and Harris 1984). This effect was not quantified in the present work; however, given the quantity of acid added in each case and the usual level of ash present in each species studied, the reduction in acidity was small and was probably about equal in all species. At the higher temperature used for water prehydrolysis (170 C), the lignocellulosic structure of the wood may be more open than at the temperature used for hydrochloric acid prehydrolysis (120 C), allowing the acid more ready access to the hemicellulose polymer. At 120 C the rate limiting step in the prehydrolysis of the slow reacting xylan may be either penetration of the lignocellulosic structure by the acid or removal of the polymeric fragments rather than hydrolysis of acetal linkages in the polymer. Thus, in this case, one would also expect a leveling effect upon the rates as observed. Further studies comparing water and HCl prehydrolysis over a broader range of conditions would be useful to determine the exact causes for the clustering of the  $k_f$  and  $k_s$  values for the HCl prehydrolysis of hardwood species. Further work is needed to establish a mathematical model describing the effects of significant independent variables (such as hydrogen ion concentration, reaction temperature, reaction time, and uronic acid to xylan ratio) on the rate constants  $k_f$  and  $k_s$ .

#### EXPERIMENTAL

The experimental techniques used in the study of the prehydrolysis of southern red oak are those used by Springer and Zoch (1968) and Conner (1984). The experimental data for the prehydrolysis of aspen, birch, elm, and maple were those obtained by Springer and Zoch (1968).

##### *Prehydrolysis*

Rate data were taken on heartwood in the form of thin disks approximately 3 mm in diameter, 0.25 mm thick. The disks were prehydrolyzed at a liquor to wood ratio of 6:1 in small reaction vessels made from 15-cm sections of 5 mm o.d. Pyrex glass tubing.

##### *Sugar analyses*

Sugar analyses were performed by ASTM method D 1915 (1979). Uronic anhydride was determined by a dehydration procedure (Scott 1979), and by the Browning method (1949). For the southern red oak heartwood used in these experiments, the uronic acid content by Scott's newer method was 3.4%, and by the older Browning method was 4.7%. Both values are based on extractives-free dry wood weight.



## ACKNOWLEDGMENTS

The following Forest Products Laboratory employees made special contributions to this report: Carol Link of the Laboratory Statistics Group fit the data using SAS at the University of Wisconsin-Madison; Virgil Schwandt and Marilyn Efland performed sugar analyses.

## REFERENCES

- AMERICAN SOCIETY FOR TESTING MATERIALS. 1979. Standard method for chromatographic analysis of chemically refined cellulose. ASTM D 1915-63. Philadelphia, PA.
- BENDER, R. 1979. U.S. Patent 4,136,207.
- BROWNING, B. L. 1949. Apparatus for determination of polyuronide carboxyl. *Tappi* 32(3):119-120.
- CONNOR, A. H. 1981. Acetic acid prehydrolysis of hardwoods. 181st Amer. Chem. Soc. Natl. Mtg., Atlanta, GA.
- . 1984. Kinetic modeling of hardwood prehydrolysis. Part I. Xylan removal by water prehydrolysis. *Wood Fiber Sci.* 16(2):268-277.
- HELWIG, J. T., AND K. A. COUNCIL (EDS.). 1979. SAS user's guide, 1979 edition. SAS Institute, Inc., Cary, NC.
- IOTECH CORPORATION. 1980. Final report: Optimization of steam explosion pretreatment. U.S. Department of Energy, Fuels from Biomass Program.
- KAMIYANA, Y., V. HIRABAYASHI, Y. SAKAI, AND T. KOBAYASHI. 1974. Xylose production by hydrolysis of corncobs with dilute sulfurous acid. *J. Ferm. Technol. (Japan)* 52(9):669-675.
- KANG, Y., AND M. YOO. 1976. Saccharification of sawdust. Part I, Hydrolysis rate of lauan wood xylan. *Hwahak Konghak* 14(2):97-103.
- KOBAYASHI, T., AND V. SAKAI. 1956. Hydrolysis rate of pentosan of hardwood in dilute sulfuric acid. *Bull. Agric. Chem. Soc. Japan* 20:1-7.
- MASON, W. H. 1921. U.S. Patent 1,399,976.
- RICHTER, G. A. 1956. Some aspects of prehydrolysis pulping. *Tappi* 39(4):193-210.
- SAEMAN, J. F. 1945. Kinetics of wood saccharification-hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperatures. *Ind. Eng. Chem.* 37(1):43-52.
- SCOTT, R. W. 1979. Colorimetric determination of hexuronic acids in plant materials. *Anal. Chem.* 51:936-941.
- SIMMONDS, F. A., R. M. KINGSBURY, AND J. S. MARTIN. 1955. Purified hardwood pulps for chemical conversion. II. Sweetgum prehydrolysis-sulfate pulps. *Tappi* 38(3):178-186.
- SPRINGER, E. L., AND J. F. HARRIS. 1984. Effect of neutralizing capacity of wood on hydrogen ion concentration during prehydrolysis with mineral acid (in process).
- , AND L. L. ZOCH. 1968. Hydrolysis of xylan in different species of hardwoods. *Tappi* 51(5):214-218.
- , J. F. HARRIS, AND W. K. NEILL. 1963. Rate studies of the hydrotropic delignification of aspenwood. *Tappi* 46(9):551-555.
- VEERARAGHAVAN, S., R. P. CHAMBERS, AND Y. Y. LEE. 1982. Kinetic model and reactor development in hemicellulose hydrolysis. *AIChE Natl. Mtg.*, Orlando, FL.
- WHISTLER, R. L., A. R. MARTIN, AND M. HARRIS. 1940. Determination of uronic acids in cellulosic materials. *J. Res. Nat. Bur. Std.* 24:13-23.