Prehydrolysis of Hardwoods with Dilute Sulfuric Acid

Edward L. Springer

Forest Products Laboratory, † *Forest Service, U.S. Department of Agriculture, Madison, Wisconsin 53705*

The effects of temperature, time, acid concentration, wood species, liquor-to-wood ratio, particle size, and drying on hemicellulose hydrolysis and sugar yields during hardwood prehydrolysis were investigated. A full factorial design was used to study the effects of liquor-to-wood ratio, particle size, and drying on prehydrolysis of southern red oak. Liquor-to-wood ratio and drying had no significant effects. Wood particle size affected the rate of hydrolysis due to poor impregnation of large particles with acid. The remaining variables were studied by using dried wood, thin, easily impregnated disks, and a high liquor-to-wood ratio (3.9:1). A factorial design was used to study the effects of temperature and acid concentration on the maximum quantity of xylose and its oligomers found in solution during prehydrolysis of red oak. Maximum potential xylose increased with increasing temperature and acid concentration: 87% was obtained at 190°C and 0.80% H_2SO_4. Wood species had little effect upon results.

Introduction

Most work on prehydrolysis has focused on prehydrolysis prior to kraft pulping in production of dissolving-grade pulps (Rydholm, 1965). The primary objective of these studies was to efficiently remove the hemicellulose polymers from the wood by means of water or dilute mineral acid hydrolysis. After prehydrolysis, the remaining lignocellulosic substrate was kraft pulped and bleached. This gave a relatively pure cellulose having the desired characteristics for conversion to rayon, cellophane, and other products. The composition of the prehydrolysate received little to no attention in these studies because the prehydrolysate was considered a waste stream suitable only for disposal. Recently some Finnish workers studied both the characteristics of the prehydrolysis pulp and the composition of the prehydrolysate (Arhippainen, et al., 1981). Their objective was to produce a superior quality dissolving-grade pulp from silver birch together with a valuable coproduct, such as xylitol, from the prehydrolysate. Unfortunately, due to experimental difficulties, the results on composition of the prehydrolysates were only approximations, and the influence of prehydrolysis conditions on composition was not precisely defined.

Some previous work on prehydrolysis was concerned with the kinetics of the hydrolysis and removal of the xylan polymer from hardwoods without a specific focus on either dissolving-pulp production or prehydrolysate utilization (Springer, 1966; Springer and Zoch, 1968). These studies considered only the composition of the initial wood and of the solid residues remaining after prehydrolysis; prehydrolysate compositions were not determined. Three other studies on prehydrolysis have considered production of chemical products from hardwood prehydrolsates (Springer and Libkie, 1980; Limbaugh et al., 1979; Lee et al., 1979). The prehydrolysate solutions were analyzed in these studies. In the note to the editor by Springer and Libkie (1980) on prehydrolysis of paper birch with sulfur dioxide, only two reaction conditions were considered. The effect of a range of reaction conditions on solution composition was not determined. The papers by Limbaugh et al. (1979) and Lee et al. (1979) on prehydrolysis of southern red oak with sulfuric acid contain considerable data on the influence of reaction conditions on the yield of xylose in the prehydrolsates and some data on other solution component-s. These data, however, have not been confirmed. The values for maximum xylose yields and the yield trends with temperature and acid concentration diverge widely from the findings of the present work and from the findings of Scott et al. (1983). The reasons for these differences are not known.

The present work on prehydrolysis of hardwoods with dilute sulfuric acid was performed as part of a program, at the Forest Products Laboratory, to evaluate the possibility of developing a two-stage dilute acid hydrolysis process. The goal of this process was to convert the carbohydrate fraction of hardwoods to monomeric sugars. The readily fermentable sugars (glucose and mannose) were then to be converted to ethanol and the difficult to

† The Laboratory is maintained in cooperation with the University of Wisconsin, Madison, WI.

ferment sugars (xylose, arabinose, and galactose) converted to other chemical products. Two stages of hydrolysis were contemplated to separate the hydrolysis of the easily hydrolyzable hemicellulose (prehydrolysis) from that of the difficulty hydrolyzable cellulose. Establishing optimum conditions in each stage would result in maximum sugar yields. The reaction conditions investigated in the present work were selected on the basis of work by Harris and co-workers (1984). In that work, unpublished data on xylan removal from finely divided hardwoods at various temperatures and acid concentrations (Baker and Krcmar, 1956) and the best available data on xylose degradation in solution (Root et al., 1959) were used to calculate maximum yields of xylose in solution. It was assumed that all xylan put into the solution was present as xylose (i.e., no oligomers were present). The calculations indicated that a reaction temperature of about 170°C, an acid concentration of about 0.40% H_2SO_4, and a time of about 5 min were near optimum. Because the calculations involved several assumptions and could be in error, it was necessary to experimentally study the prehydrolysis of hardwoods over a range of practical reaction conditions.

Previous studies on prehydrolysis, wherein the prehydrolysates were analyzed, investigated the effects of the variables: reaction temperature, reaction time, and acid concentration. Invariably only one liquor-to-wood ratio and one wood particle size were used. In addition only ovendried wood was employed. Because fresh, never-dried wood would be employed in any commercial scale hydrolysis process, it was essential in this study to investigate the effect of drying the wood. Because low liquor-to-wood ratios were contemplated in the proposed process and larger wood particle sizes would be easier to use and require less chipping and milling energy, it was also vital to study the effects of liquor-to-wood ratio and wood particle size. The work of this study was divided into three parts. In the first part the effects of drying, liquor-to-wood ratio, and wood particle size were studied. In part two the effects of reaction temperature, acid concentration, and reaction time were investigated, and in part three the effect of wood species was examined.

Due to the urgency of the wood hydrolysis program, a pilot-scale study on dilute sulfuric acid prehydrolysis of southern red oak was carried **out** simultaneously with the present study. The results of this pilot-scale study have been published (Scott et al., 1983) and were compared with present results.

In prehydrolysis of hardwoods the xylan hemicellulose polymer is hydrolyzed to xylose, xylose oligomers (mainly xylobiose), and xylose-uronic acid oligomers (mainly xylose-uronic acid dimer). The glucomannan hemicellulose polymer is hydrolyzed to glucose, mannose, and various oligomers (mainly dimers such as cellobiose), and some easily hydrolyzable cellulose is also hydrolyzed to glucose and oligomers (mainly cellobiose). The indexes used for determining the extent of the prehydrolysis in the first part of this study were (1) yield of solid residue, (2) percent of the original xylan (determined as anhydroxylose) remaining in the solid residue, and (3) percent of the total potential anhydroxylose units of the wood found as xylose, xylose oligomers, and xylose-uronic acid dimer in the prehydrolysate. In the second and third parts the removal of all carbohydrate constituents was followed.

Effects of Drying, Liquor-to-Wood Ratio, and Particle Size

Experimental Design. A two-level full factorial experiment was set up to evaluate the influences of wood drying, liquor-to-wood ratio, and particle size on the rate

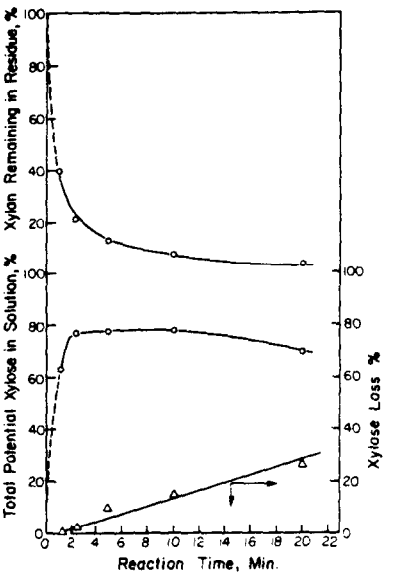

Figure 1. Xylan removal from the solid phase. xylose and xylose oligomer appearance in the prehydrolysate, and xylose loss for 170 °C, 0.40% sulfuric acid.

of prehydrolysis of southern red oak (*Quercus **falcata*** Michx.) heartwood. For this experiment, a reaction temperature of 170°C and a concentration of added acid of 0.40% H_2SO_4 were chosen on the basis of the previously discussed calculation procedure. Because of the uncertainties involved in the calculations, the reaction time was established by a preliminary experiment.

The optimum reaction time for maximizing the quantity of xylose and xylose oligomers put into solution was determined by taking data on oven-dried southern red oak heartwood in the form of 2.9 mm diameter, 0.38 mm thick disks by the use of 0.40% H_2SO_4 at a liquor-to-wood ratio 3.9:1, a temperature of 170°C, and various reaction times. The techniques used are described in the Experimental Techniques section. The results are shown in Figure 1. Percent of total potential xylose found in solution is defined as the sum of the anhydroxylose units found as xylose, xylose oligomers, and xylose-uronic acid dimer in solution divided by the total potential anhydroxylose units in the original wood and multiplied by 100. A long relatively flat maximum occurred for percent of total potential xylose found in the solution. This was due to the near balancing of xylose input from the hydrolyzing solid hemicellulose and xylose degradation in the solution. A 5.0-min reaction time was at or close to the highest value and was chosen for the reaction time in part one.

The levels of the three variables used in the full factorial experiment were as follows: never-dried wood vs. wood dried overnight at 70°C in a vacuum oven; wood disks 2.9 mm in diameter and 0.38 mm long in the fiber direction compared with those of the same diameter but 2.54 mm long; and liquor-to-wood ratios of 3.9:1 for thin disks and 3.6:1 for thick disks contrasted with 1.7:1 for thin disks and 1.3:1 for thick disks.

To assure equal acid concentrations at high and low liquor-to-wood ratios all reaction tubes were filled at the high level and allowed to equilibrate for several weeks. After that time, all ambient temperature neutralization due to wood ash constituents was assumed to have occurred. All possible free liquid was then removed from the low liquor-to-wood ratio tubes.

Results and Discussion. The results of the factorial experiment are given in Figure 2. The values shown are averages of at least three determinations; pooled 95%

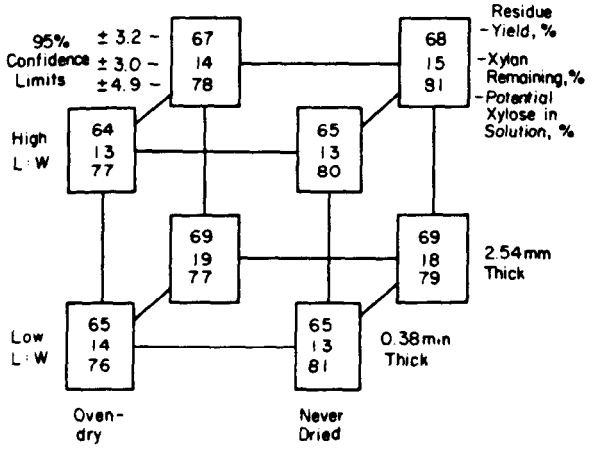

Figure 2. Effects of liquor-to-wood ratio, wood particle size, and wood drying on prehydrolysis results.

confidence limits are also given. These results indicate that drying the wood produced no significant effect on residue yield, xylan remaining in the residue, or potential xylose in the hydrolysate. It is, however, known from a previous study (Springer, 1983) that drying results in a slight decrease in residue yield. This is caused by a small increase in the content of easily hydrolyzed cellulose. Prehydrolysis of the hemicelluloses was found to be unaffected by drying. In that study several more replicate determinations were made, and thus the data were of somewhat greater precision.

Changing the particle size had no statistically significant effect at high liquor-to-wood ratio, although small increases in all indexes were found. At low liquor-to-wood ratio the residue yield and percent xylan remaining in the residue increased significantly as particle size increased. These increases can be explained by inadequate impregnation of the thick disks. Although the thick disks were held in the acid catalyst solution for very long periods of time, entrained air may have prevented thorough impregnation. Comparison of the pilot-scale results with results from the second phase of this study substantiates this explanation.

Changing the liquor-to-wood ratio produced no statistically significant effect on any of the three indexes for the thin disks. For the thick disks, only the amount of xylan remaining in the residue significantly increased when the ratio decreased. The reason for these increases is probably as follows. As noted above, the large particles were probably not thoroughly impregnated with acid catalyst solution. Consequently a substantial fraction of the ash-forming constituents of the wood that neutralize applied mineral acid were not neutralized in large wood particles. Since both high and low liquor-to-wood ratio samples were treated with acid solution at the high ratio for several weeks, an equal quantity of neutralizing capacity would be present in both samples of wood just prior to reaction at 170°C. It is known from previous work (Springer and Harris, 1985) that considerable neutralization takes place under reaction conditions. At low liquor-to-wood ratio, which was produced by sucking out all free liquid from the tubes just before reaction, this neutralization would reduce the hydrogen ion concentration of the acid solution more than at high liquor-to-wood ratio because less total acid would be present. As a result of lower hydrogen ion concentration, the rate of xylan hemicellulose hydrolysis would be decreased and the xylan remaining increased, as was found. It is thus concluded on the basis of this hypothesis and the thin disk results that in thoroughly impregnated particles which have been thoroughly deashed (i.e, at equal hydrogen ion concentrations) differences in liquor-to-wood ratio, in the range studied, would have no significant effect on prehydrolysis. For wood particles, especially large particles, that have not been completely neutralized, liquor to wood ratio will have an effect due to neutralization of the applied acid during reaction.

No statistically significant differences were observed in percent of potential xylose found in solution for any combination of the independent variables (drying, liquor-to-wood ratio, and particle size). The probable reason for this can be understood by again referring to Figure 1. The percent total potential xylose found in solution remains relatively constant over a reasonably wide range of percent xylan remaining in the solid phase and thus also of residue yield. Consequently, residue yield and xylan remaining in the residue are much better indexes for the extent of prehydrolysis.

Because wood particle size had a significant effect on rate of prehydrolysis, it was decided to conduct the second and third parts of the study by using thin (0.38 mm) disks. This eliminated the effects of inadequate impregnation. It was also decided to use high liquor-to-wood ratios since, for the thin disks, liquor-to-wood ratio had no significant effect. In addition the effect of the neutralizing capacity of the wood is reduced by using high liquor-to-wood ratios (Springer and Harris, 1985). Because drying the wood had little effect on prehydrolysis and it was experimentally difficult to work with never-dried wood, vacuum oven-dried wood samples were used.

Effects of Reaction Temperature, Reaction Time, and Acid Concentration

Experimental Design. Most hardwoods contain about 20% xylan hemicellulose, only about 3% glucomannan hemicellulose, and approximately 5% easily hydrolyzable cellulose. Therefore, this part of the work was mainly concerned with following the removal of xylan from the wood and the appearance of xylose, xylose oligomers, and xylose-uronic acid oligomers in the prehydrolysate. Removal of the other constituents and the appearance of glucose, mannose, and their oligomers in the solution was also followed and reported. The data on these minor constituents are, however, subject to large errors because their quantities are so small.

The main purpose of this part of the work was to investigate the influence of the known important reaction variables, temperature, time, and acid concentration. on the quantity of anhydroxylose units from the xylan hemicellulose polymer that can be found as xylose, xylose oligomers, and xylose-uronic acid dimer (total potential xylose) in the prehydrolysate from the unextracted southern red oak (*Quercus falcata* Michx.) heartwood. Because the prehydrolysate solution was analyzed only for combined uronic anhydride, all xylose-uronic acid oligomers in the solution were calculated as xylose-uronic acid dimer. The higher oligomers would, however, be present only in very small quantities and would hydrolyze to xylose and xylose-uronic acid dimer in the secondary hydrolysis procedure. The additional xylose was thus determined and counted as xylose oligomer. The analytical methods used and the calculations employed are given in the Experimental Techniques section and in Table VI.

Reaction conditions determine the rate of hydrolysis of the solid xylan polymer and the rates of degradation of xylose and its oligomers. As shown in Figure 1, for fixed values of reaction temperature and acid concentration a maximum total potential xylose in solution occurs at a given reaction time. The objective here was to determine the influence of reaction temperature and acid concen-

Table 1. Composition of Original Woods

component	southern red oak heartwood, unextracted, %	quaking aspen sapwood, extracted, %	paper birch sapwood, extracted, %
lignin	21.8	18.4	19.2
glucan	40.3	52.2	44.2
mannan	2.9	2.7	2.4
xylan	19.3	19.7	22.6
bronic anhydride	2.9	3.1	2.9
acetyl	3.7	*a*	*a*
extractives (ethanol-benzene)	5.5	*a*	*a*
ash	0.24	*a*	*a*
unaccounted for	3.4	3.9	8.7
total	100.0	100.0	100.0

[a] Not measured.

tration on the value of this maximum.

In the third part of the work the same type of data ***were*** also taken by using ethanol-benzene- and hot-water-extracted quaking aspen (*Populus tremuloides* Michx.) sapwood and ethanol-benzene and hot-water-extracted paper birch (*Betula papyrifera* Marsh.) sapwood. The compositions of the original woods are given in Table I.

Reaction conditions employed for each wood species are given in Table II. For each combination of temperature and acid concentration several reaction times were used ranging from 0.33 to 180 min. The longest time for each condition was such that it was near or beyond the maximum for percent potential xylose in solution. A two-level factorial design was used to study the effects of temperature and acid concentration on maximum percent potential xylose in solution for prehydrolysis southern red oak heartwood. The upper level of temperature, 190°C, was such that accurate reaction time data could still be obtained at an acid concentration of 0.80% H_2SO_4. In earlier work, using the 5 mm outside diameter Pyrex tube reactors. the heatup time of the tube contents was determined and a time correction calculated to compensate for the time that the tube contents were not at the isothermal reaction temperature (Springer et al., 1963). For the present work this time correction was 20 s. The isothermal reaction times reported here are thus the actual time in the oil bath minus 20 s. Data on aspen and birch were taken at the reaction conditions (190°C, 0.80% H_2SO_4) where southern red oak gave maximum percent potential xylose in solution. Some additional data were taken on aspen by using 0.40% H_2SO_4 and several reaction temperatures.

As was previously discussed, inorganic ash-forming constituents (i.e., cations) present in wood exchange with hydrogen ions and thus neutralize part of the mineral acid added to wood to catalyze hydrolysis. A practical procedure was developed for determining the neutralizing capacity of wood so that hydrogen ion concentration can be accurately determined in hydrolysis solutions at reaction conditions (Springer and Harris, 1985). This method was used to determine the average molality of hydrogen ion during reaction for each of the reaction conditions used in the present work. The hydrogen ion concentrations are given in Table II. Cation contents of the original woods and the prehydrolyzed solid residues were determined by solubilizing the samples with a nitric-perchloric acid mixture and determining the individual cations in the resulting solutions by using plasma emission spectrophotometry (Liegel et al., 1980).

Results and Discussion. The results from the two-level factorial design for prehydrolysis of southern red oak heartwood are given in Table III. Sugars in solution are reported as anhydrides because the original wood and residue compositions are reported on that basis. The xylose, xylose in oligomers, and xylose in xylose-uronic acid dimers (as anhydrides) in the table were summed, multiplied by 100, and divided by the xylan (anhydroxylose) content of the original wood to give the percent of the total potential xylose found in the solution. Figure 3 shows this value plotted against isothermal reaction time for all the reaction conditions and the wood species used. The data points connected by the solid lines are for southern red oak. The percent of the total potential xylose of the wood found in the prehydrolysate solution increased with both increasing acid concentration and increasing temperature. At 190°C and 0.80% added H_2SO_4 (0.074 molal hydrogen ion concentration), a maximum of 87% of the potential xylose of the wood was found in the solution. The maximum occurred at an isothermal reaction time of about 40 s. Since shorter reaction times are considered to be impractical, these reaction conditions are thought to be near optimum for dilute sulfuric acid prehydrolysis of thoroughly impregnated southern red oak.

The data for southern red oak for potential xylose in solution at the near optimum conditions are plotted in Figure 4. Here we see that at the maximum, 75% of the potential xylose of the wood appears as xylose in the perhydrolysate solution, 8% appears as xylose oligomers, 4% as xylose-uronic acid dimers, 7% remains as xylan in the solid residue, and 6% has been lost through xylose degradation (primarily dehydration to furfural) in the solution. Going to higher reaction temperatures and higher acid concentrations might somewhat reduce both the xylan remaining in the residue and the loss. Considerably shorter reaction times would, however, have to be employed. Such reaction times are outside the range where reasonably accurate data can be obtained by using present experimental techniques.

Effect of Wood Species

After the data on southern red oak were obtained, the two other hardwoods, quaking aspen and paper birch, were studied. Both woods were prehydrolyzed by using the

Table II. Reaction Conditions Employed and Actual Acid Concentrations during Prehydrolysis

	reaction conditions			initial cation content of wood, mequiv/g	cations released to soln, av during reaction, mequiv/g of wood	av *m* of $[H^+]$ during reaction
wood species	concn of applied H_2SO_4, %	reaction temp, °C	liquor-to-wood ratio			
southern red oak	0.40	170	3.9:1	0.040	0.032	0.033
	0.40	190			0.033	0.033
	0.80	170			0.033	0.074
	0.80	190			0.034	0.074
quaking aspen	0.40	140	5.0:1	0.078	0.072	0.027
	0.40	170			0.072	0.027
	0.40	190			0.072	0.027
	0.80	190			0.072	0.068
paper birch	0.80	190	3.9:1	0.035	0.030	0.075

Table III. Results (g/100 g of Original Wood) from Prehydrolysis of Southern Red Oak

reaction conditions			residue composition						sugar in soln (as anhydride)						
temp, °C	actual acid condn, *m*	isothermal time,[a] min	yield	xylan	glucan	mannan	uronic anhydride	lignin	xylose	xylose in oligomers	xylose-uronic dimers	glucose	glucose in oligomers	mannose	mannose in oligomers
			100[b]	19.3[b]	40.3[b]	2.9[b]	2.9[b]	21.8[b]							
170	0.033	0.92	73.6	7.6	40.5	1.2	1.5	20.2	5.1	6.1	0.9	0.6	0.1	1.1	0.5
		2.2	67.7	4.1	39.5	0.7	0.8	20.0	9.5	4.3	1.0	0.8	0.1	1.6	0.4
	*	4.7	63.7	2.5	37.8	0.4	0.6	19.7	11.8	2.2	0.9	0.8	0.3	1.3	0.4
		9.7	62.4	1.4	38.4	0.6	0.2	20.7	13.8	0.7	0.5	1.3	0.1	1.6	0.3
		19.7	60.7	0.7	38.0	0.3	0.1	20.9	12.6	0.7	0.1	2.7	0.3	1.7	0.2
	0.074	0.92	67.4	4.5	38.9	0.8	1.1	18.7	9.0	4.5	1.0	0.8	0.1	1.7	0.4
	x	2.2	63.9	2.4	39.1	0.5	0.5	19.6	13.5	1.5	1.0	1.2	0.1	1.6	0.6
		4.7	61.6	1.6	37.9	0.6	0.3	20.4	15.3	0	0.7	2.0	0.3	2.1	0.3
		9.7	59.4	0.7	35.9	0.2	0.2	20.6	12.6	1.1	0.2	2.7	0.3	1.6	0.2
190	0.033	0.33	67.8	4.1	39.1	1.9	1.1	19.0	8.0	6.1	1.1	0.8	0.3	0.9	1.1
	v	0.67	63.2	2.2	39.1	0.6	0.5	18.6	11.7	3.7	1.0	1.4	0.4	1.5	0.8
		1.7	60.6	1.0	38.8	0.2	0.2	18.9	15.7	0	0.4	1.8	0.4	1.7	0.3
		2.7	59.8	0.6	36.8	0.3	0.2	19.4	13.4	2.1	0.2	2.5	0.7	1.5	0.6
	0.074	0.33	62.7	1.8	38.8	0.3	0.6	19.2	12.7	2.1	1.2	1.0	0.4	1.7	0.8
		0.67	60.0	1.2	38.4	0.3	0.3	18.8	14.5	1.6	0.8	1.6	0.4	2.1	0.1
		1.2	59.0	1.0	37.0	0.1	0.3	18.6	13.8	0.7	0.5	3.0	0.2	2.0	0.1
			95% Confidence Limits												
	*		±3.4	0.4	2.4	0.2	0.1	1.4	1.4	1.0	0.1	0.2	0.2	0.2	0.2
	x		±0.7	0.2	2.2	0.2	0.1	1.8	0.9	0.1	0.1	0.4	0.2	0.4	0.4
	v		±0.8	0.3	2.1	0.8	0.1	0.3	1.9	1.6	0.2	2.2	0.4	0.2	0.3

[a] 20-s heatup period subtracted from actual time. [b] Unextracted original wood.

Table IV. Results (g/100 g of Original Wood) from Prehydrolysis of Quaking Aspen

reaction conditions			residue composition						sugar in soln (as anhydride)						
temp, °C	actual acid condn, *m*	isothermal time,[a] min	yield	xylan	glucan	mannan	uronic anhydride	lignin	xylose	xylose in oligomers	xylose-uronic dimers	glucose	glucose in oligomers	mannose	mannose in oligomers
			100[b]	19.7[b]	52.2[b]	2.7[b]	3.1[b]	18.4[b]							
140	0.027	40	73.7	4.9	49.7	1.1	0.8	16.6	10.6	1.4	1.0	0.2	0.2	1.0	0
	*	110	70.1	3.1	48.3	0.9	0.5	16.4	13.7	0	0.8	2.0	0	1.3	0.1
		180	69.1	1.9	49.7	0.6	0.2	16.9	13.7	0	0.3	0.9	0.4	1.1	0.6
170	0.027	1.7	74.8	5.0	51.6	0.6	1.4	15.6	5.2	6.1	1.0	0.1	0.4	0.6	0.6
		3.7	70.4	2.9	50.3	0.4	0.8	15.4	9.0	3.9	1.0	0.8	0.3	1.1	0.3
		7.7	67.6	1.5	48.7	0.1	0.4	15.8	12.3	1.3	0.6	0.9	0.4	1.0	0.2
		11.7	66.2	1.3	49.2	0.1	0.4	15.9	13.1	1.0	0.4	1.9	0.4	1.3	0.2
190	0.027	0.67	68.2	1.9	48.8	1.1	0.6	15.0	8.7	5.9	0.9	0.8	0.5	1.2	0.5
		1.7	64.8	1.3	44.9	1.6	0.3	14.7	13.1	2.5	0.7	2.2	0.4	1.5	0.4
	0.068	0.33	65.2	1.5	45.0	1.5	0.6	15.8	12.3	2.2	0.6	1.4	1.8	1.6	0.2
		0.67	66.9	1.9	45.9	0.9	0.3	15.6	11.2	4.2	1.2	1.6	0.4	1.7	0.4
		1.2	62.1	0.9	44.3	0.4	0.2	15.2	12.6	1.2	0.5	3.6	0.8	1.8	0.1
			95% Confidence Limits												
	*		±0.7	0.5	2.7	0.1		0.5	0.6		0.1	0.3		0.2	0.2

[a] 20-s heatup period subtracted from actual time. [b] Extracted original wood.

Table V. Results (g/100 g of Original Wood) from Prohydrolysis of Paper Birch

reaction conditions			residue composition						sugar in soln (as anhydride)						
temp. °C	actual acid condn. *m*	isothermal time,[a] min	yield	xylan	glucan	mannan	uronic anhydride	lignin	xylose	xylose in oligomers	xylose-uronic dimers	glucose	glucose in oligomers	mannose	mannose in oligomers
			100[b]	22.6[b]	44.2[b]	2.4[b]	2.9[b]	19.2[b]							
190	0.075	0.33	65.1	3.9	42.0	0.3	0.9	16.2	11.2	5.1	1.2	0.8	0.4	0.7	0.5
	*	0.67	61.4	1.8	41.4	0.3	0.4	16.3	15.4	2.8	1.0	1.7	0.3	1.1	0.3
	1	1.2	58.8	1.3	40.0	0.2	0.3	16.1	15.3	1.9	0.8	2.6	0.4	1.1	0.2
			95% Confidence Limits												
	*		±0.6	0.3	1.1	0.3	0.1	0.5	1.2	1.3	0.3	0.4	0.2	0.4	0.2
	x		±2.8	0.5	1.3	0.2	0.1	0.3	0.7	2.0	0.3	0.7	0.5	0.2	0.1

[a] 20-s heatup period subtracted from actual time. [b] Extracted original wood.

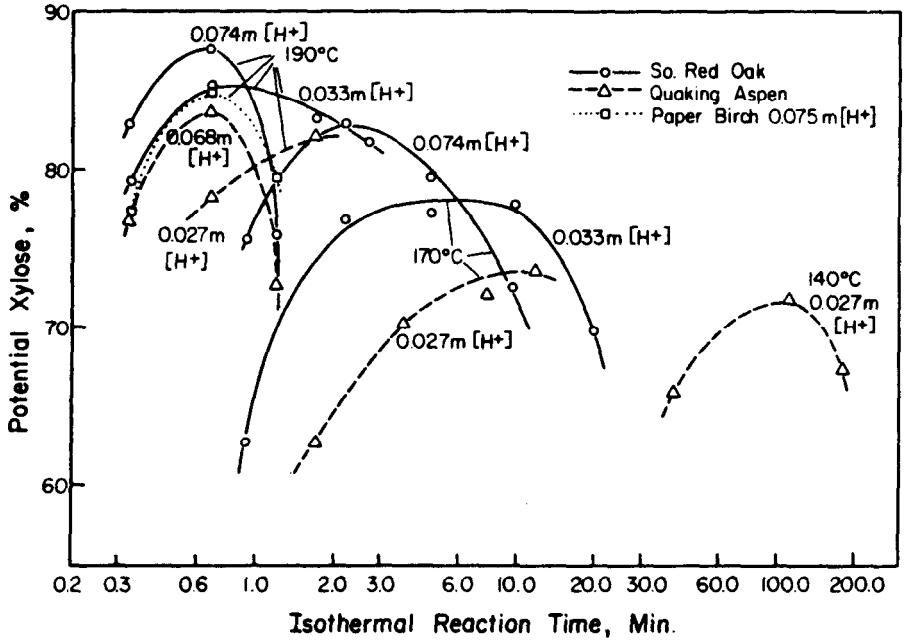

Figure 3. Effects of reaction temperature, acid concentration, and reaction time on the percent of the total potential xylose in the wood found as xylose and its oligomers in the prehydrolysate.

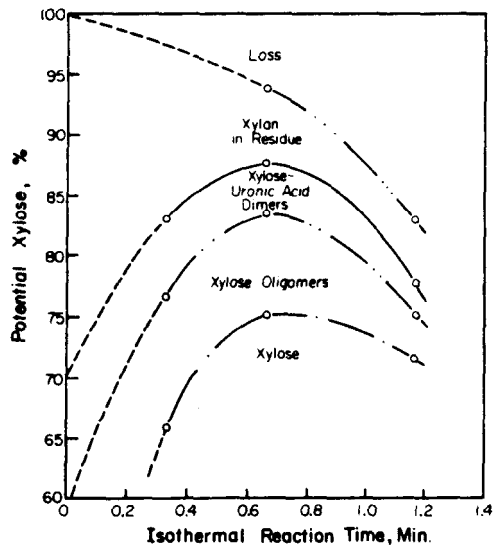

Figure 4. Distribution of xylose and xylose anhydride units in the prehydrolysate and the solid residue for southern red oak prehydrolyzed at 190°C by using 0.80% sulfuric acid.

optimum condition (190°C, 0.80% added H_2SO_4) for southern red oak, and several other conditions were studied for aspen. The results are given in Tables IV and V and in Figure 3. Very similar results were obtained for all three wood species. The aspen and birch wood samples had been extracted with ethanol-benzene followed by hot water prior to prehydrolysis; the southern red oak was unextracted. The hot-water extraction may have slightly reduced the xylan contents of the aspen and birch samples, and this may have slightly reduced the maximum potential xylose in solution. The higher cation content of the aspen wood (Table II) significantly reduced actual hydrogen ion concentrations during reaction, causing the percent potential xylose in solution to be lower for each reaction condition than the values for southern red oak. This agrees with the observed effect of acid concentration in the prehydrolysis of southern red oak.

On the basis of these data, it appears that all temperate hardwood species will respond in a nearly identical fashion to dilute sulfuric acid prehydrolysis. The data for prehydrolysis of southern red oak should thus be a close approximation to those for any other temperature hardwood and also to those for mixtures of temperature hardwoods. These data should thus be extremely useful in the design of practical prehydrolysis processes for hardwoods.

Comparison to Pilot-Scale Prehydrolysis

The pilot-scale study of Scott et al. (1983) was carried out simultaneously with the present work. In this pilot-scale study, 650-g batches of fresh chips were impregnated with dilute sulfuric acid, drained, placed in a 0.01-m^3 digester, and prehydrolyzed at 170°C by direct steaming of the chips. Chips 9.5 mm in length and about 2 mm thick were used. Although an entirely different method (Scott, 1976) was used for analyzing the wood, solid residues. and solutions than in the present work, the results agree quite closely with the 170°C data reported here. Because some steam condensed on the chips and, simultaneously, some liquid was expelled from the chips during heatup, liquor-to-wood ratio decreased during reaction. Average liquor-to-wood ratios were about 1:1. Since the pilot-scale results agree reasonably well with the present results obtained at a liquor-to-wood ratio of 3.9:1, it appears that liquor-to-wood ratio does not significantly affect the rates of prehydrolysis of thoroughly impregnated wood. In addition, because the present results and the pilot-scale results agree fairly well, it seems that at least for well-impregnated particles having particle sizes of the pilot-scale chip size and below, particle size has a negligible effect on results. The particle-size effect found in the first phase of the present work was thus probably entirely due to inadequate impregnation of the large particles.

In the pilot-scale study, the analytical method used determined only the total anhydroxylose units present in the prehydrolysate solution. In the present study the various forms in which anhydroxylose units appeared in the solution (i.e., xylose, xylose oligomers, and xylose-uronic acid dimer) were determined.

Conclusions

Drying never-dried wood had no significant effect on prehydrolysis of the hemicellulose polymers in southern

red oak. Varying the liquor-to-wood ratio over the experimentally accessible range (3.9:1 to 1.3:1) also had no significant effect on prehydrolysis. Increasing the particle size by lengthening the 2.9-mm diameter wood disks reduced the rates of prehydrolysis. Inadequate impregnation of acid solution into the thick disks, even after prolonged soaking, appears to be the cause of the reduced rates.

As is well-known, reaction temperature, reaction time, and hydrogen ion concentration greatly influence rates of prehydrolysis. For given conditions of reaction temperature and acid concentration, the percent of the total potential xylose of the wood that is present in the prehydrolysate solution as xylose, xylose oligomers, and xylose-uronic acid dimer attains a maximum value at a given reaction time. This maximum value increases with increasing reaction temperature and acid concentration. The highest maximum value attained in the present study was 87%.

For temperate hardwoods, prehydrolysis results appear to be relatively independent of wood species. Prehydrolysis of southern red oak, quaking aspen, and paper birch under nearly identical reaction conditions gave nearly identical percentages of total potential xylose in solution. Absolute quantities of sugars in solution differed somewhat due to differing initial quantities of xylan hemicellulose in the woods.

Experimental Techniques

Reaction Conditions. Pyrex glass tubes of 5-mm o.d. were utilized as the reaction vessels in this work. Never-dried wood was introduced into the reactors in the form of 2.9-mm-diameter disks. Previously described experimental techniques were used (Springer et al., 1963). Particle size was varied by varying disk thickness. Wood grain (fiber length) was parallel to the thickness dimension. Thus for the 0.38-mm disks every fiber lumen was cut open, whereas for the 2.54-mm disks most of the fibers were uncut.

In the first part of the work the reactor tubes were filled with wood in pairs; care was taken to assure that identical wood-moisture contents were present in both tubes. One tube of each pair was then dried for 16 h in a vacuum oven at 70°C. The fresh wood weights and the oven-dried weight of wood in the dried tube were used to calculate the weight of oven-dry wood in the undried tube. A solution containing 0.40% H_2SO_4 was then added to the tubes containing the dried wood. For each tube containing never-dried wood an exact quantity of an acid solution was added, having such a concentration that when accounting for wood-moisture content a final concentration of 0.40% H_2SO_4 was present in the tube. In the second and third parts of the work, all wood was dried and it was thus unnecessary to fill the tubes in pairs. Applied acid concentrations of 0.40% and 0.80% H_2SO_4 were used in parts two and three.

A liquor-to-wood ratio of 3.91 was used for the 0.38-mm disks and of 3.6:1 for the 2.54-mm disks. Slightly more solution was required to cover the thin disks. In the first part of the work, half the reactor tubes were then sealed and the other half carefully stoppered, and all were stored for several weeks to allow the acid solution to uniformly distribute itself by diffusion throughout the disks. After storage, all free liquor was carefully sucked out of the stoppered tubes by using a long, thin hypodermic needle. The tubes were then sealed. The low liquor-to-wood ratio for the tubes containing the 0.38-mm disks was about 1.7:1 and that for the tubes with the thick disks was about 1.3:1. Apparently the increased number of interfaces between the thin disks retained additional liquor. In the second and third parts of the work only thin disks and a 3.9:1 liquor-to-wood ratio were used.

The tubes and their contents were reacted in an oil bath maintained within ±0.1°C of the reaction temperature.

Analytical Methods. After cooling, each tube, was opened and its contents filtered by using a sintered glass bottom crucible. The solid residue was thoroughly washed with hot distilled water and dried in a vacuum oven at 70 °C. The original wood and each solid residue were analyzed for total potential xylose, glucose, and mannose by using TAPPI Provisional Method T250 PM-75. For each tube the filtrate and washings were quantitatively collected and made up to a standard volume of 25.0 mL. Xylose, glucose, and mannose in the combined filtrate and washings were determined by quantitative paper chromatography as per the above TAPPI method. Because oligomers were present, an aliquot of each hydrolysate solution was subjected to a secondary hydrolysis procedure using an acid concentration of 4.0% H_2SO_4 at 120°C for 1.0 h. Xylose, glucose, and mannose in the hydrolyzed solution were again determined by using paper chromatography. The quantity of uronic anhydride present in the original wood, in each residue, and each hydrolysate solution (before secondary hydrolysis) was determined by using the method of Scott (1979). Since uronic anhydride was present in the hydrolysate both as free uronic arid and combined with xylose and xylose oligomers (predominantly as the dimer), a procedure was developed to determine the combined uronic anhydride in solution. To a 0.125-mL aliquot of the hydrolysate 2 mg of $NaBH_4$ was added. After a reaction time of at least 20 min at room temperature, 0.05 mL (1 drop) of glacial acetic acid was added to destroy the unreacted $NaBH_4$. The solution was then analyzed by using the method of Scott. The $NaBH_4$ reduced the free uronic acid contained in the solution, leaving only the combined uronic acid to be determined as uronic anhydride by the method of Scott (1979).

Calculations and Correction Factors. The sugar content (anhydride basis) of each residue and each hydrolysate sample from a given reaction were calculated from the analytical data by using the Fortran computer program given in Table VI. In the method used for analyzing the wood and solid residues, about 60% of the bonds between the uronic acid groups of the xylan hemicellulose polymer and the adjacent anhydroxylose units remain intact. Thus in the secondary hydrolysate from the solid residues 60% of the uronic acid units have an attached xylose anhydride unit. Since these xylose units were not accounted for in the paper chromatography, it was necessary to add them to the total xylose (corrected for analytical losses) to arrive at the total potential xylose in the solid samples. This was done by analyzing the wood and solid residues for uronic anhydride content and increasing the analyzed xylose content by an amount equivalent to 60% of the uronic anhydride content.

Hydrolysate solution analyses were also corrected to account for the xylose units bonded to uronic acid units. Here the fraction of combined uronic acid units varied since prehydrolysis conditions varied. The previously described analytical procedures for determining the fraction of combined uronic anhydride units were employed. The "fraction combined" and "total uronic anhydride" values were used to calculate the combined xylose in the prehydrolysate. Because the prehydrolysate was subjected to the secondary hydrolysis procedure (to determine the oligomers present), it was necessary to account for the xylose in the secondary hydrolysate which derived from hydrolysis of the xylose-uronic acid dimers. On secondary

Table VI. Fortran Program for Computing Residue and Solution Components

```
      C     RESIDUE AND SOLUTION COMPONENTS-G PER 100G WOOD-ANHYDRIDE BASIS
            READ(5,110)A,B,C,D,E,F,G,H
            READ(5,110)ZC,VC,WC,XC
        110 FORMAT(8F9.5)
            PRINT 122
        122 FORMAT(1H1)
            PRINT 123
        123 FORMAT(1X'%xR TEM  H+  TIME  YIELD x-RES G-RES M-RES UA-RE L-RES
           .K-RE %F-SO %O-SO %U-SO %L-SO GF SO GO-SO GL-SO MF-SO MO-SO ML-SO
           .M-SO %Px'//)
            PRINT 124
        124 FORMAT(19x,'100    19.3  40.3   2.9   2.9  21.8  12.8')
        114 READ(5,113,END=1000)I,J,K,M,AC,TI,S,Q,P,R,T,U,Z,UA
        113 FORMAT(I2,I3,I2,I3,F4.2,F7.0,F6.2,3F7.2,2F6.4,F6.2,F5.2)
        116 READ(5,115)I,J,VS,WS,XS,VM,WM,XM,US,FU
        115 FORMAT(I2,I3,8F6.3)
            V=(0.9*S)/(A*(1.0-B*F+(1.0-F)*(((B*P)/(C*Q))+((D*R)/(E*Q)))))
            W=V*(((A*(1.0-F))/G)*((P/(C*Q))+(F/(1.0-F))))
            XU=0.97778*V*A*(1.0-F)*R/(H*E*Q)
            XA= UA*0.60*132/176
            X=XU+XA
            YD=(U*100.0)/T
            XWA=X*(YD/100.0)
            XCA=XC*(132.0/150.0)
            XZA=XCA-XWA
            XL=2.5*XS/T
            XLA=XL*(132.0/150.0)
            XK=2.5*XM/T
            UL=2.5*US/T
            XI=FU*UL*(150.0/176.0)
            XIA=XI*(132.0/150.0)
            XF=XK-XI*0.40*((0.897+1.0)/2)
            XT=(XF/0.897)+XI
            XTA=XT*(132.0/150.0)
            XO=(XF/0.897)-XL
            XOA=XO*(132.0/150.0)
            XLOA=XZA-XTA
            PX=100.0*((XLA+XOA+XIA)/XCA)
            XR=100.0*(XWA/XCA)
            VWA=V*(YD/100.0)
            VCA=VC*(162.0/180.0)
            VZA=VCA-VWA
            VL=2.5*VS/T
            VLA=VL*(162.0/180.0)
            VK=2.5*VM/T
            VT=VK/0.987
            VO=VT-VL
            VOA=VO*(162.0/180.0)
            VTA=VT*(162.0/180.0)
            VLOA=VZA-VTA
            WWA=W*(YD/100.0)
            WCA=WC*(162.0/180.0)
            WZA=WCA-WWA
            WL=2.5*WS/T
            WLA=WL*(162.0/180.0)
            WK=2.5*WM/T
            WT=WK/0.968
            WTA=WT*(162.0/180.0)
            WO=WT-WL
            WOA=WO*(162.0/180.0)
            WLOA=WZA-WTA
            FZ=Z*(YD/100.0)
            UAA=UA*(YD/100.0)
            UK=YD-(VWA+WWA+XWA+FZ+UAA)
            UKL=100.0-YD-(VTA+WTA+XTA+VLOA+WLOA+XLOA)
            PRINT 120,XR,M,AC,TI,YD,XWA,VWA,WWA,UAA,FZ,UK,XLA,XOA,XIA,XLOA,
           .VLA,VOA,VLOA,WLA,WOA,WLOA,UKL,PX
        120 FORMAT(1X,F4.1,I4,F4.2,F6.0,18F6.2,F5.1)
            GO TO 114
       1000 STOP
            END
```

hydrolysis, 40% of these dimers are hydrolyzed yielding xylose. Some degradation of the liberated xylose occurs during the hydrolysis so a factor of (0.897 + 1.0)/2 was multiplied by the total liberated xylose to account for this loss. The factor 0.897 is the fraction of xylose surviving the secondary hydrolysis procedure. The average was used because xylose liberation took place throughout the procedure. This calculated xylose from xylose-uronic acid dimers was subtracted from the total xylose in the secondary hydrolysate to obtain the total xylose in the hydrolysate from xylose and xylose oligomers. This figure was then corrected for hydrolysis losses to give the total xylose and xylose oligomers in the prehydrolysate. The xylose was then subtracted from this to give the xylose present as oligomers. The total undegraded anhydroxylose units present in all forms (xylose, xylose oligomers, xylose-uronic acid dimers) in the prehydrolysate solution were used as the principal index for effectiveness of the prehydrolysis.

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Kimball A. Libkie for his assistance in carrying out the experimental work.

Nomenclature for Fortran Program

A = fraction of glucose surviving the total two-stage hydrolysis and neutralization procedure (0.947)
B = relative reducing power of mannose to glucose determined by the titration method (0.921)
C = relative reducing power of mannose to glucose determined by the photometric method (0.854)
D = relative reducing power of xylose to glucose determined by the titration method (0.969)
E = relative reducing power of xylose to glucose determined by the photometric method (0.969)
F = fraction of glucose eperimized to mannose in the two-stage hydrolysis and neutralization procedure (0.0016)
G = fraction of mannose surviving the total two-stage hydrolysis and neutralization procedure (0.940)
H = fraction of xylose surviving the total two-stage hydrolysis and neutralization procedure (0.873)
ZC = grams of lignin in the original wood sample per 100 g of oven-dry wood
VC = grams of potential glucose in the original wood sample per 100 g of oven-dry wood
WC = grams of potential mannose in the original wood sample per 100 g of oven-dry wood
XC = grams of potential xylose in the original wood sample per 100 g of oven-dry wood
I = series identification number
J = reaction vessel (tube) number
K = solvent concentration, %
M = reaction temperature, °C
AC = acid concentration, %
TI = reaction time, s
S = total reducing sugar as grams of glucose per 100 g of oven-dry sample
Q = weight of glucose in the glucose spot after separation of the neutralized concentrated hydrolysate by paper chromatography, μg
P = weight of mannose expressed as equivalent weight of glucose in the mannose spot after separation of the neutralized concentrated hydrolysate by paper chromatography, μg
R = weight of xylose expressed as equivalent weight of glucose in the xylose spot after separation of the neutralized concentrated hydrolysate by paper chromatography, μg
T = weight of wood sample, g
U = weight of solid residue after reaction, g
Z = lignin content of the solid residue in grams per 100 g of oven-dry residue
UA = uronic anhydride content of the solid residue in grams per 100 g of oven-dry residue
VS = milligrams of glucose per milliliter of the 25.0 mL total perhydrolysate plus washings sample
WS = milligrams of mannose per milliliter of the 25.0 mL total prehydrolysate plus washings sample
XS = milligrams of xylose per milliliter of the 25.0 mL total prehydrolysate plus washings sample
VH = milligrams of glucose per milliliter of the secondary hydrolyzed 25.0-mL total prehydrolysate plus washings sample
WH = milligrams of mannose per milliliter of the secondary hydrolyzed 25.0-mL total prehydrolysate plus washings sample
XH = milligrams of xylose per milliliter of the secondary hydrolyzed 25.0-mL total prebydrolysate plus washings sample
US = milligrams of uronic anhydride per milliliter of the 25.0-mL total prehydrolysate plus washings sample
FU = fraction of uronic anhydride combined with xylose in the prehydrolysate plus washings sample
V = grams of glucose anhydride per 100 g of oven-dry solid sample
W = grams of mannose anhydride per 100 g of oven-dry solid sample
XU = grams of xylose anhydride uncorrected for unhydrolyzed xylose-uronic acid linkages per 100 g of solid sample
XA = grams of xylose anhydride in unhydrolyzed xylose-uronic acid dimers per 109 g of solid sample
X = total grams of xylose anhydride per 100 g of solid sample
YD = yield of solid residue, %
XWA = grams of xylose anhydride in the solid residue from 100 g of original oven-dry wood
XCA = grams of xylose anhydride in 100 g of original oven-dry wood
XZA = grams of xylose anhydride put into solution per 100 g of original oven-dry wood
XL = grams of free xylose found in the prehydrolysate solution per 100 g of original oven-dry wood
XLA = grams of xylose anhydride found in the prehydrolysate solution per 100 g of original oven-dry wood
XK = grams of xylose found in the secondary hydrolyzed prehydrolysate solution per 100 g of original oven-dry wood
UL = grams of uronic anhydride found in the prehydrolysate solution per 100 g of original wood
XI = grams of xylose in the prehydrolysate solution combined with uronic anhydride as dimers per 100 g of original wood
XIA = grams of xylose anhydride in the prehydrolysate solution combined with uronic anhydride as dimers per 100 g of original wood
XF = grams of xylose in the secondary hydrolyzed prehydrolysis solution excluding xylose from hydrolysis of xylose-uronic acid dimers hydrolyzed during secondary hydrolysis per 100 g of original wood
XT = total grams of xylose in all forms in the prehydrolysis solution per 100 g of original wood
XTA = total grams of xylose anhydride in all forms in the prehydrolysis solution per 100 g of original wood
XO = grams of xylose in oligomers in the prehydrolysate solution per 100 g of original wood
XOA = grams of xylose anhydride in oligomers in the prehydrolysate solution per 100 g of original wood
XLOA = xylose anhydride loss, grams per 100 g of original wood
PX = percent of the total xylose anhydride in the original wood found in all forms of xylose anhydride in the prehydrolysate solution
XR = percent of the total xylose anhydride in the original wood found as xylose anhydride in the solid residue
VWA = grams of glucose anhydride in the solid residue from 100 g of original oven-dry wood
VCA = grams of glucose anhydride in 100 g of original oven-dry wood
VZA = grams of glucose anhydride put into solution per 100 g of original oven-dry wood
VL = grams of free glucose found in the prehydrolysate solution per 100 g of oven-dry wood
VLA = grams of glucose anhydride found in the prehydrolysate solution per 100 g of original oven-dry wood
VK = grams of glucose found in the secondary hydrolyzed prehydrolysate solution per 100 g of original oven-dry wood
VT = total grams of glucose in all forms in the prehydrolysate solution per 100 g of original oven-dry wood
VO = grams of glucose in oligomers in the prehydrolysate solution per 100 g of original oven-dry wood
VOA = grams of glucose anhydride in oligomers in the prehydrolysate solution per 100 g of original oven-dry wood
VTA = total grams of glucose anhydride in all forms in the prehydrolysate solution per 100 g of original oven-dry wood

VLOA = glucose anhydride loss, grams per 100 g of original oven-dry wood
WWA = grams of mannose anhydride in the solid residue from 100 g of original oven-dry wood
WCA = grams of mannose anhydride in 100 g of original oven-dry wood
WZA = grams of mannose anhydride put into solution per 100 g of original oven-dry wood
WL = grams of free mannose found in the prehydrolysate solution per 100 g of original oven-dry wood
WLA = grams of mannose anhydride found in the prehydrolysate solution per 100 g of original oven-dry wood
WK = grams of mannose found in the secondary hydrolyzed prehydrolysate solution per 100 g of original oven-dry wood
WT = total grams of mannose in all forms in the prehydrolysate solution per 100 g of original oven-dry wood
WTA = total grams of mannose anhydride in all forms in the prehydrolysate solution per 100 g of original oven-dry wood
WO = grams of mannose in oligomers in the prehydrolysate solution per 100 g of original oven-dry wood
WOA = grams of mannose anhydride in oligomers in the prehydrolysate solution per 100 g of original oven-dry wood
WLOA = mannose anhydride loss, grams per 100 g of original oven-dry wood
FZ = grams of lignin in the solid residue from 100 g of original oven-dry wood
UAA = grams of uronic anhydride in the solid residue from 100 g of original oven-dry wood
UK = grams of unknown material in the solid residue from 100 g of original oven-dry wood
UKL = grams of unknown material in the prehydrolysate solution from 100 g of original oven-dry wood

Registry No. H_2SO_4, 7664-93-9; D-xylose, **58-86-6; D-glucose,** 50-99-7; D-mannose, 3458-28-4; xylan, 9014-63-5; D-glucan, 9012-72-0; D-mannan, 9036-88-8; hemicellulose, 9034-32-6.

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