Prehydrolysis of aspen wood with water and with dilute aqueous sulfuric acid

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SUMMARY: Water prehydrolysis of aspen wood was compared with 0.40% sulfuric acid prehydrolysis at a reaction temperature of 170°C. Acid prehydrolysis gave much higher yields of total anhydroxylose units in the prehydrolyzate and removed significantly less anhydroglucose from the wood than did the water treatment. At maximum yields of total anhydroxylose units in the prehydrolyzates, much more monomeric xylose was present in the acid prehydrolyzate than in the water prehydrolyzate.

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In the manufacture of dissolving-grade pulps by the kraft process, a water or dilute mineral acid prehydrolysis is employed to solubilize the hemicelluloses of the wood prior to pulping. For hardwoods, in which the major hemicellulose is 4-*O*-methyl glucuronoxylan, the resulting prehydrolyzate contains large quantities of xylose and its oligomers. Over the years there has been much speculation concerning recovery and utilization of the dissolved substances. Recent efforts directed toward the production of liquid fuels or chemicals from hardwoods have also considered the use of a prehydrolysis step for recovery of xylose and its oligomers prior to hydrolysis of the cellulose to glucose.

In considering any prehydrolysis step, one question that immediately arises is whether the use of dilute mineral acid as a catalyst leads to results different from those of water prehydrolysis. In water prehydrolysis, acetyl groups are cleaved from the wood, mainly from the xylan hemicellulose, and the reactions that occur are catalyzed by the dilute solution of acetic acid thus formed. Use of a mineral acid catalyst will, of course, greatly increase the rate of solubilization of the xylan hemicellulose.

In this study water prehydrolysis of aspen wood was compared with dilute sulfuric acid prehydrolysis at a reaction temperature of 170°C. For the acid prehydrolysis, a sulfuric acid solution with a concentration of 0.40% (0.041 M) was added to the oven dried wood. The study was undertaken to determine whether significant differences occur in the yield of xylose and xylose oligomers in the two prehydrolyzate solutions and in the composition of the solutions.

Results and discussion

Results from both the acid and the water prehydrolysis are given in *table 1.* Anhydroxylose units are present in the prehydrolyzate solutions as xylose, xylose-uronic acid dimers, and other xylose and xylose-uronic acid oligomers. A secondary hydrolysis procedure was used on the prehydrolyzate solutions to convert the xylose oligomers to xylose and the xylose-uronic acid oligomers to xylose and xylose-uronic acid dimer. An analytical correction factor of 1.11 was used to correct for xylose loss during this secondary hydrolysis. It was assumed that 60% of the xylose-uronic acid bonds survived the prehydrolysis. The corrected figure for xylose present after secondary hydrolysis and the uronic anhydride content of the prehydrolyzate were used to calculate the total anhydroxylose units (as xylose) present in the prehydrolyzate. This figure and the amount of monomeric xylose found in the prehydrolyzate were used to calculate the percent of monomeric xylose in each prehydrolyzate (table 1). The percent total potential xylose in each prehydrolyzate was calculated by dividing the total anhydroxylose units present (in all forms) in the prehydrolyzate by the total anhydroxylose units present in the original wood sample and multiplying by 100. Percent loss of xylose was determined by subtracting the sum of the percent total potential xylose in the prehydrolyzate and the percent of original xylan remaining in the solid residue from 100.

The maximum amount of the total potential xylose that can be brought into solution by water prehydrolysis at 170°C is about 20 percentage points less than the amount that can be put in solution by acid

Table 1. Results of water and dilute sulfuric acid prehydrolysis of aspen wood at 170°C

Reaction time, min	Yield of solid residue, %	Original xylan remaining in solid residue, %	Total potential xylose in hydrolyzate, %	Monomeric xylose in hydrolyzate, %	Xylose loss, %
		Water			
37.5	76.2	31	56	8	13
75	72.4	21	61	26	18
125	71.6	17	44	60	39
250	70.8	15	17	95	68
		0.40% H_2SO_4			
2.0	74.8	24	70	41	6
4.0	70.4	14	79	65	7
8.0	67.6	7	82	81	11
12.0	66.2	6	83	86	11

prehydrolysis (table 1; *fig. 1*). This maximum occurs at a point where more xylan remains in the residue than at the maximum for acid prehydrolysis. The true maximum was not quite attained for acid prehydrolysis but is apparently very near 83%. The greater loss of xylose occurring in the water prehydrolysis (table 1) accounts for the reduced xylose yield.

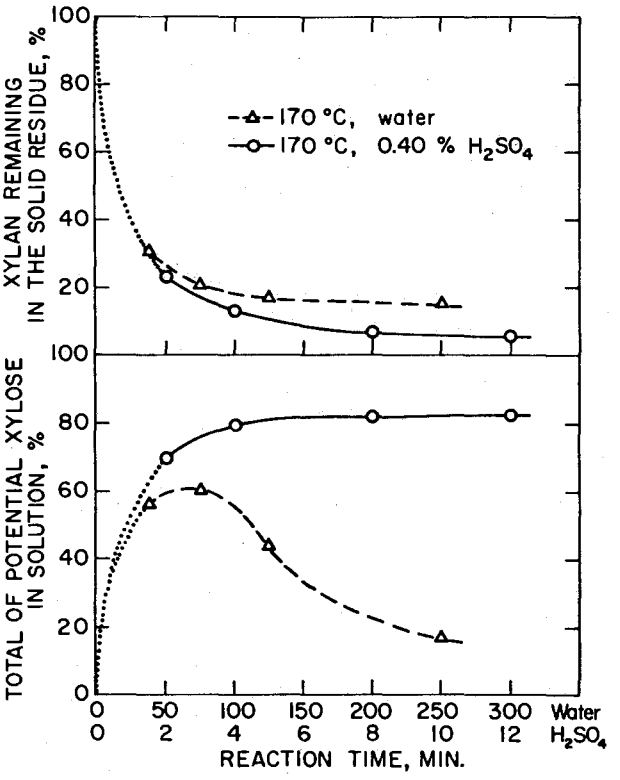

Fig. 1. Comparison of water and dilute sulfuric acid prehydrolysis of aspen wood xylan. Time scales have been adjusted to allow xylan loss comparison.

This greater degradation of xylose in the water prehydrolysis is consistent with the hypothesis that xylose destruction by hydroxyl ions occurs at this acidity (about pH 4). Although the hydroxyl:hydrogen ion ratio is only 10^{-6} at pH 4, the hydroxyl ion is a much more effective catalyst. This is evident from the fact that the maximum stability of sugars is in the range pH 2.5—3.5 (1). Also, the hydroxyl ion is a much more effective mutarotation catalyst (2). There is evidence that the effect of hydroxyl ion catalysis on xylose (3) and glucose (4) degradation is apparent at much higher acidities. In aqueous H_2SO_4, below acid concentrations of about 0.1 N, xylose was found to disappear more rapidly than would be expected by extrapolating the rate constants for higher acidities.

Glycosidic linkages, such as those in the xylan hemicellulose polymer, are known to be stable to hydroxyl ions but easily cleaved by hydrogen ions (5). Given this fact one would expect that as solution acidity decreases, the rate of hydrolysis of the linkages in the xylan hemicellulose polymer (producing soluble fragments consisting of xylose and its oligomers) would proportionately decrease. Due to hydroxyl ion catalysis, the rate of xylose degradation would not, however, decrease proportionately to the acid concentration but would be somewhat higher and would result in greater xylose destruction at low acidities, as was found in the present study. As reaction temperature increases, the phenomenon of increased degradation of xylose at low acidities decreases, and at higher temperatures (around 240°C) the total yields of anhydroxylose units in the water prehydrolyzate might approach those in the acid prehydrolyzate (3, 6).

The percent of monomeric xylose in the prehydrolyzate solutions (table 1) is an index of the quantity of dimers and other oligomers present in the solutions. At the maximum percent potential xylose in solution for water prehydrolysis, only 26% of the anhydroxylose units in the solution were present as xylose. Near the maximum for acid prehydrolysis, 86% of the anhydroxylose units were present as xylose.

Water prehydrolysis at 170°C also differs from dilute sulfuric acid prehydrolysis at 170°C in that less lignin is brought into solution and more glucan is solubilized at a given level of xylan removal (*table 2*).

Table 2. Original wood components remaining in the solid residue after prehydrolysis at 170°C

Reaction time, min	Component remaining, %			
	Lignin	Glucan	Mannan	Xylan
		Water		
37.5	90	92	41	31
75	88	91	43	21
125	96	86	18	17
250	99	87	25	15
		0.40% H_2SO_4		
2.0	84	97	23	24
4.0	82	94	18	14
8.0	84	91	3	7
12.0	85	92	6	6

As xylan removal progresses, the amount of lignin removed increases, goes through a maximum, and greatly decreases (fig. 2). This apparent decrease in lignin removal has been previously observed (7,8), and is due to redeposition of carbohydrate degradation products that are insoluble in 72% sulfuric acid and are thus determined as lignin. At any given level of xylan removal, acid prehydrolysis results in greater lignin removal than does water prehydrolysis.

Water prehydrolysis results in enhanced glucan removal (fig. 3). At 85% xylan removed, water pre-

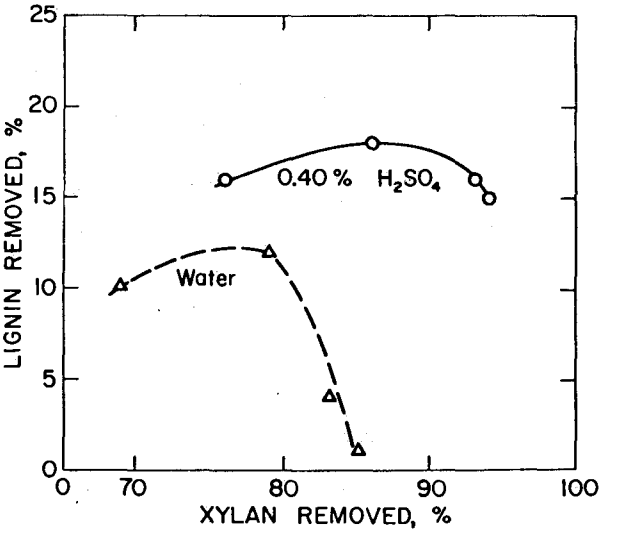

Fig. 2. Lignin removed as a function of xylan removed.

hydrolysis removes more than twice the amount of glucan (about 8 percentage points more) than does the acid prehydrolysis. This greatly enhanced cellulose degradation under near-neutral conditions has also been previously observed (8), but its mechanism has never been satisfactorily explained.

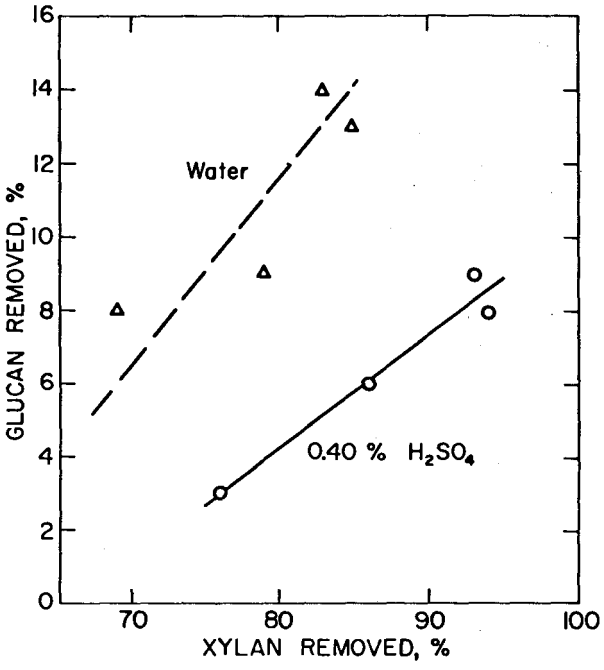

Fig. 3. Glucan removed as a function of xylan removed.

Mannan removal was not plotted because mannan is present in such small quantities that the analytical data could be subject to large random errors. Table 2, however, suggests that xylan and mannan removals go hand in hand in both water and acid prehydrolysis. This might be expected, as both the xylan and glucomannan hemicelluloses are amorphous, easily hydrolyzable, short-chain polymers.

Conclusions

At a reaction temperature of 170°C, water prehydrolysis of aspen wood gives much lower yields of total anhydroxylose units in the prehydrolyzate and removes more glucan from the wood than does prehydrolysis with dilute solutions of sulfuric acid. In addition, at maximum yields, the water prehydrolyzate contains much less monomeric xylose than does the acid prehydrolyzate. In accordance with the known effects of acidity and temperature on xylose degradation, reaction temperatures above 170°C could be expected to cause the yields of total anhydroxylose units in the water prehydrolyzate to begin to approach those in the acid prehydrolyzate.

Experimental

Loss of components from the solid wood phase was determined using previously described techniques (9).

The reaction vessels were Pyrex glass tubes, outside diameter 5 mm. Aspen wood (*Populus tremuloides* Mich.), in the form of ethanol-benzene extracted, ovendry (vacuum oven, 70°C, 16 hr) disks, 0.25 mm thick (in the grain direction), were placed in the tubes (about 0.20 g/tube), and sufficient liquor placed in each tube to give a 5:1 liquor-to-wood ratio. The tubes were sealed with a flame and heated in a constant-temperature oil bath for various time intervals. After cooling, the tubes were opened and the contents filtered using sintered glass-bottom crucibles. The solid residues were thoroughly washed with hot distilled water and dried (vacuum oven, 70°C). For each tube, filtrate and washings were quantitatively collected and made up to a standard volume of 25.0 ml. The original wood and the solid residues were analyzed for potential xylose, glucose, and mannose using a standard hydrolysis procedure followed by paper chromatography (10): *Table 3* gives the composition of the original wood.

Table 3. Composition of original aspen wood

Component	%
Lignin	18.7
Glucan	53.3
Mannan	2.9
Xylan	18.5
Uronic anhydride	3.5
Unaccounted for	3.1
Total	100.0

Monomeric xylose in the filtrate solutions was determined by paper chromatography (10). Because xylose oligomers were present, each hydrolyzate solution was subjected to a secondary hydrolysis (4% H_2SO_4, 1 h, 120°C) and the xylose content of the hydrolyzed solution determined. The quantity of uronic anhydride present in the filtrate solution was determined using a dehydration procedure (1 1).

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The Laboratory is maintained at Madison, Wis., in cooperation with the University of Wisconsin.

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