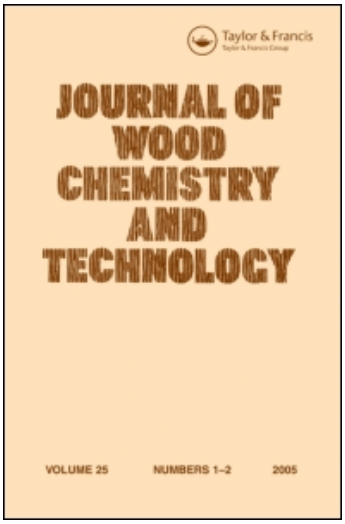

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Ralph W. Scott[a]; Theodore H. Wegner[a]; John F. Harris[a]
[a] U.S. Department of Agriculture, Forest Products Laboratory, 1 Forest Service, Madison, Wisconsin

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DILUTE SULFURIC ACID PREHYDROLYSIS OF SOUTHERN RED OAK CHIPS BY DIRECT STEAM HEATING

Ralph W. Scott, Theodore H. Wegner, and John F. Harris

Forest Products Laboratory,[1] Forest Service
U.S. Department of Agriculture
Madison, Wisconsin 53705

ABSTRACT

Design of commercial scale processes for acid prehydrolysis of wood to useful products requires information on expected product yields under practical operating conditions. In this study, 650-gram batches of green southern red oak chips were hydrolyzed at 170°C. Particular attention was directed to conserving acid by low liquor-to-wood ratios, and to uniform acid distribution by vacuum impregnation. Carboxylate groups within the wood caused a significant, but unavoidable, loss of acid strength. As a consequence of this and other losses, satisfactory hydrolyses required 2.0 to 2.5% H_2SO_4 for 5-minute impregnations. Long impregnations, which provided partial neutralization of the carboxylate groups, were hydrolyzed at equivalent rates by 0.47 to 0.73% H_2SO_4.

A 5-minute vacuum impregnation of green chips with 2.5% H_2SO_4 followed by a 6-minute hydrolysis, removed 81% of the wood xylose as xylose and xylose oligomers, and 10% as furfural. Hydrolyses after long acid impregnations produced more xylose and less furfural. From 75 to 85% of the wood acetyl was recovered as acetic acid.

INTRODUCTION

There is a continuing need to determine product yields under conditions applicable to commercial scale processing. Springer[2] was able to study prehydrolysis kinetics by closely controlling acidity and temperature of thinly sliced wood samples in small

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tubes. However, the use of wood chips and commercial equipment causes less uniform acid impregnation and slower heat-up time than possible in the laboratory. Current studies on wood hydrolysis at the Forest Products Laboratory were planned to provide practical knowledge on the chemical conversion of wood to useful products.

Certain considerations are necessary for economy in any wood prehydrolysis process. Minimal use of water and acid is important. This necessitates use of a liquor-to-wood ratio in the range 1.0 to 1.3 and a low acid concentration. The use of a strong acid, such as sulfuric acid, is supported by higher yields of xylose below 200°C than is possible with water or weak acids.[3,4] In isolated instances it has been recognized that a knowledge of the neutralizing capacity of biomass is important because of acid loss.[5]

Our use of the term, prehydrolysis, is limited to a dilute acid hydrolysis which separates water soluble hemicellulose fragments from insoluble lignocellulose. In this study, we determined the product yields from the acid prehydrolysis of southern red oak under practical operating conditions. Specifically, product yields from wood chips after short acid impregnation times were determined in a batch digester operation. The effects of long acid impregnations and of the neutralizing capacity of wood are also included.

EXPERIMENTAL

Wood Supply

Southern red oak logs (*Quercus falcata* Michx.) from Georgia were debarked and chipped in the green condition into 9.5 mm chips. The well-mixed chips, containing about 34% moisture, were stored at 4°C in sealed plastic bags to prevent moisture loss and fungal action.

A uniform analytical sample was obtained by grinding and mixing 850 g of green chips. The large sample was necessary to

TABLE 1

Chemical Analysis of Southern Red Oak

Anhydride	%	Other	%
glucose	37.8	Klason lignin	21.9
mannose	2.1	extractives[b]	6.7
xylose	18.4	acetyl	4.3
galactose	1.1	ash	.7
arabinose	.7		
4-O-methyluronic	3.3[a]	total	97.0

[a] This assumes all uronic acid is 4-O-methylglucuronic acid.

[b] 6.7% is the sum of ethanol-benzene and hot water extractions.

eliminate variations, such as an observed low ash content of the heartwood. The chemical analysis is shown in Table 1.

The alkalinity in the ash was found by titration to be 0.118 meq per gram of ovendry (OD) wood. This agreed with the value, 0.124, which was the average of six flame spectrophotometric measurements of the major cations (Ca 0.06686, K 0.03840, Mg 0.01486, Na 0.0013, Mn 0.0022).

Acidification of Wood Chips

Acid impregnation into chips by diffusion, gave a very uniform acid distribution. Sufficient sulfuric acid was added to a 1.950-kg batch of green chips (1.282 kg OD) to give a pH of about 1.4 in solution after dilution by the water in the wood, and after partial neutralization of the acid by the wood alkalinity. After 48 to 72 hours soaking, the acid solution was drained and replaced by the desired percentage of acid for 24 hours. This latter exchange was repeated twice. In each case sufficient acid solution was used to cover the chips, and an aspirator vacuum was pulled to discharge entrapped air. After the equilibration period,

excess acid solution was drained from the chips, which were then blotted with paper toweling, mixed, and divided into three equal portions. Liquor-to-wood ratios were in the range of 1.2 to 1.3 in the blotted chips. The amount of H_2SO_4 in each third was later found by sulfate measurements on the liquors obtained after hydrolysis.

A second method of acidification was used to simulate the more rapid acid impregnations applicable to a larger processing scale, in which the acid distribution would be less uniform throughout the chips. For this purpose 650 g of stored green chips (427 g OD) were submerged in the acid solution and the aspirator vacuum was applied for 5 minutes. The vacuum was then released and the excess liquid was drained from the chips for 20 minutes. The chips were blotted, weighed, and transferred to the digester for immediate hydrolysis. The liquor-to-wood ratios before hydrolysis were about 1.0. The amount of H_2SO_4 in each hydrolysis was measured on the liquors after hydrolysis as described previously.

Digester Operation

Acid-impregnated wood chips were hydrolyzed in a 0.01 m^3, jacketed digester. Within the digester was a removable stainless steel chip container: a cylinder 176 mm across and 216 mm deep, open at the top but closed at the bottom (Fig. 1A). The cylindrical surface of the chip container was primarily stainless steel mesh except for the bottom 76 mm which formed a reservoir for condensate. Chips were supported in the container by a removable perforated circular plate (Fig. 1B) with legs to hold the chip bed above the condensate in the reservoir. A separate, solid metal cover (Fig. 1C) over the container protected the chip bed from any condensate dripping off the digester lid.

In operation, the jacket was preheated with steam. The container and chips were then inserted and the digester lid was sealed. The entire apparatus was preheated by steam through the jacket to 100°C as measured by a thermocouple located next to the chip container. Saturated steam was then directed into the

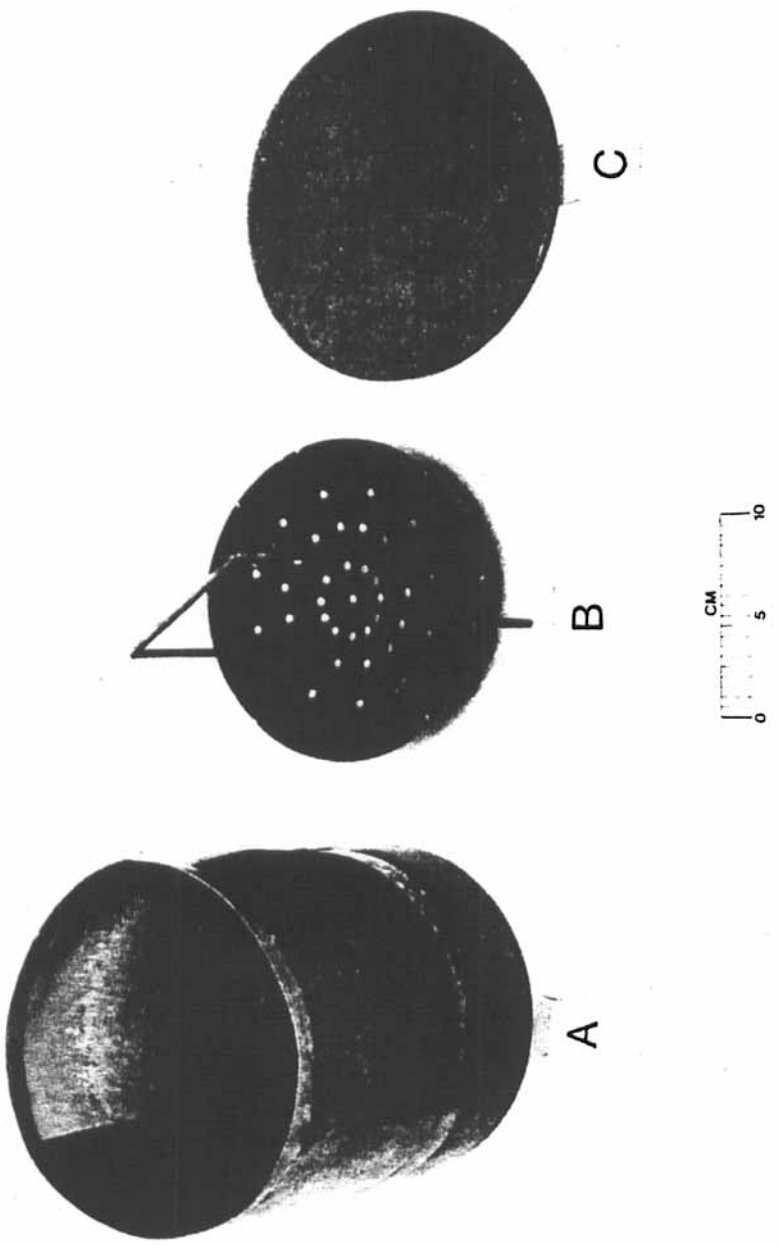

FIGURE 1.--Wood chip container assembly.

digester to raise the digester temperature as rapidly as possible to 170°C. This occurred within 5 seconds as measured by the thermocouple. A baffle in the digester directed incoming steam away from direct impingement on the chips, but the mesh surface permitted immediate accessibility of steam to the chips. Condensate off the chips and the inside surfaces of the chip container drained into the container reservoir. Condensate off the digester walls and lid drained separately into the bottom of the digester below the chip container. This condensate was exhausted through a tube extending from the digester bottom past the chip container and outside the digester where it was directed into an ice bath for collection of its furfural and acetic acid.

The hydrolysis period was terminated by shutting off the exhaust tube and steam, relieving the jacket pressure, and passing water at 10°C into the jacket and onto the digester lid. After rapid cooling to 46°C, the chips and container were removed and placed in a sealed plastic bag for weighing when they reached room temperature. Condensate remaining in the bottom of the digester was added to the ice water containing the previously exhausted condensate.

Brown liquid collected from the container reservoir was weighed and diluted to exactly 1 L. This liquid is termed the "free liquor" to distinguish it from the "condensate" collected separately, and from the "extract" obtained from the residue of hydrolyzed chips.

Residue Extraction

Two methods were used to extract water soluble materials from the hydrolyzed chip residues. The methods gave equivalent results. In the first, the total residue from a hydrolysis was equilibrated for at least 24 hours with 10 L of added distilled water. In the second, chips were soaked for a few hours before they were added to a column and slowly eluted with distilled water until the effluent was free of sulfate.

Chemical Analyses

Glucose, mannose, xylose, and uronic acids in the wood, in the hydrolysis residues, and in the extracts were measured by spectrophotometric methods[6,7] which yielded the sum of oligomeric and monomeric sugars. In some cases paper chromatography or HPLC separations were used to corroborate results. The latter methods also measured the galactose and arabinose not determined by spectrophotometry, and provided data on the amount of free monomeric sugars.

Spectrophotometric values for glucose were corrected for the presence of galactose and those for xylose were corrected for uronic acid, furfural, and arabinose. Negative corrections to xylose quantities were 0.43 times uronic anhydride amounts and 1.469 times furfural amounts; the latter factor was derived from a 93.6% yield of furfural in the analytical reaction.[8] For the purpose of correcting glucose and xylose spectrophotometric analyses it was assumed that all galactose and arabinose of the wood were in the hydrolysates. Assuming that half of the arabinose was converted to furfural, the undetermined weight of arabinose in the hydrolysates would be 2% of the original xylose.

Furfural in extracts and free liquors was measured by a distillation and absorbance method. A measured sample was diluted to about 60 mL and neutralized to phenol red with $NaHCO_3$. The solution was distilled into a 50-mL volumetric flask until only 2-3 mL were required to complete the volume. The neutralization prevented the formation of additional furfural during the distillation. The furfural was measured at peak absorbance, 278 nm on a Beckman DB spectrophotometer, and calculated on the basis of 6.25 mg/mL for an absorbance of 1.00. Furfural in the combined digester condensate and exhausted condensate was measured directly by absorbance at 278 nm.

Acetic acid in solution was determined by gas chromatography on a carbowax-H_3PO_4-coated support, and acetyl in wood and residues by an alkaline hydrolysis followed by acidification, distillation, and titration.[9] Sulfate in solution was precipitated and weighed as $BaSO_4$.

Ash in wood and residues was determined after heating in a muffle furnace up to 575°C for 5 hours. It should be noted that true ash values for hydrolysis residues require that residues be extracted with mineral-free water. The equivalents of alkali in ash samples were found by adding 3 or 5 mL of standard H_2SO_4, warming gently for a few minutes, and back titrating the excess acid with standard NaOH to a phenolphthalein end point. It was necessary to centrifuge oakwood ash from its extract to remove colored particles which interfered with the end point.

Metal cations were determined by atomic emission and atomic absorption flame spectrophotometry (after wet oxidation or after elution by HNO_3 in the case of solid samples).

RESULTS AND DISCUSSION

Products of Hydrolysis

Measured products from several runs are shown in Tables 2 and 3. Maximum yields of xylose, the major product, were about 86% of xylose in the original wood. Different yields of xylose from the equilibrated chips (Table 2) than from the 5-minute vacuum impregnated chips (Table 3) are balanced by the respective furfural yields. The differences are likely due to regions of high acidity in the 5-minute-vacuum impregnated chips. Both higher and lower acidities than the optimum value can decrease xylose yields. The levels of acid chosen for the 5-minute impregnations were calculated to give acid levels comparable to those in the equilibrated chips by taking into account the wood alkalinity, the loss to free liquor, and the estimated water distribution during the heating period. Estimated pH's during hydrolysis are shown in parentheses in Tables 2 and 3.

The best yields of xylose after the 5-minute vacuum impregnations were about 95% of the maximum from the longer acid applications. The yields shown in Tables 2 and 3 include both monomers and oligomers due to the method of analysis. The sum of the yields of xylose and furfural, most of which derived from xylose, accounted for close to 90% of the xylose in the original wood.

TABLE 2

Soluble Products of Hydrolysis at 170°C after a 140-Hour Equilibration of Chips with Acid. Percentage Recovery.

Time, Minutes	Xylose[a]	Furfural[b]	4-O-Methyl-uronic Acid	Acetic Acid	Glucose
		0.47% H_2SO_4 (pH 1.77)[c]			
4	82	2	75	62	2
6	84	3	76	75	3
9	84	6	65	84	4
12	81	9	52	--	5
15	82	11	30	--	5
18	82	11	24	--	6
21	80	14	18	--	6
		0.73% H_2SO_4 (pH 1.40)[c]			
4	86	4	80	76	3
6	86	6	73	84	5
9	81	10	55	85	6
12	80	12	43	--	6

[a] Including both monomeric xylose and xylose in oligomers.
[b] Percentage based upon xylose in the wood, mol per mol.
[c] Calculated pH estimations at 9 minutes.

Furfural is in part a competing product with xylose, permitting some choice of operating conditions for the production of either product. In the hydrolyses with 0.47% H_2SO_4 (Table 2) the increases in furfural yield exceeded the parallel decreases in xylose yield. This is partly due to removal of xylose from the residue so that the yield of soluble xylose tended to remain high. This effect is less apparent at higher acid strengths and after 5-minute impregnations of acid where the loss of soluble xylose was more rapid. Partial conversion of uronic acid and arabinose to furfural increased the furfural yield. An important part of the furfural yield was recovered in the condensate, about 57% at 2.00% H_2SO_4 and 61 to 69% at 2.25% H_2SO_4 (Table 3).

TABLE 3

Soluble Products[a] of Hydrolysis at 170°C after a 5-Minute Vacuum Impregnation of Chips with Acid. Percentage Recovery.

Time, minutes	Xylose	Furfural[b]	4-O-Methyl-uronic Acid	Acetic Acid	Glucose
		2.00% H_2SO_4 (pH 1.49)[c]			
6	79	8	72	78	5
9	78	11	56	80	6
12	76	14	45	84	7
		2.25% H_2SO_4 (pH 1.27)[c]			
6	80	9	68	75	6
9	75	14	52	82	7
12	72	16	42	82	7
		2.50% H_2SO_4 (pH 1.28)[c]			
6	81	10	67	--	6
9	75	15	48	--	7
12	71	18	37	--	9

[a] Nonreducing amounts are: 9 to 10% of the xylose, 26% of the glucose, and decreasing amounts of uronic acid with time from 44 to 33% at 2% H_2SO_4 and from 39 to 30% at 2.25% H_2SO_4.

[b] Percentage based upon xylose in the wood, mol per mol.

[c] Calculated average pH.

The other useful soluble product was acetic acid with 20 to 30% of it in the condensate. Xylose and acetic acid together with furfural (Table 4) sum to about 23% of the original dry wood weight. Also in solution at maximum yields of xylose was a small but significant portion of the glucose, 5 to 9% (Table 3). In Table 5 are total analytical recoveries of constituents in soluble fractions and residues after hydrolyses of the 5-minute acid-impregnated chips. It can be seen that recoveries were good except for uronic acid which was partially destroyed. Included in the material balance for xylose in Table 5 is the small amount of furfural which is actually a product from arabinose and uronic acid.

TABLE 4

Soluble Products[a] of Hydrolysis at 170°C after a 5-Minute Vacuum Impregnation of Chips with Acid. Percentage of the Initial Wood Weight

Time, minutes	Xylose	Furfural	4-O-Methyl-uronic Acid	Acetic Acid	Glucose
			2.00% H_2SO_4		
6	17	1.3	2.8	4.7	2.1
9	16	1.8	2.2	4.8	2.6
12	16	2.4	1.7	5.1	2.9
			2.25% H_2SO_4		
6	17	1.5	2.6	4.5	2.4
9	16	2.5	2.0	4.9	2.8
12	15	2.8	1.6	4.9	2.9
			2.50% H_2SO_4		
6	17	1.7	2.6	--	2.4
9	16	2.5	1.8	--	3.0
12	15	3.1	1.4	--	3.7

[a] Nonreducing amounts are: 9 to 10% of the xylose, 26% of the glucose, and decreasing amounts of uronic acid with time from 44 to 33% at 2% H_2SO_4 and from 39 to 30% at 2.25% H_2SO_4.

It is important to the ease of extraction of hydrolyzed chips that they retained sufficient integrity to be water extracted without fragmentation. The water remaining within the chips after the hydrolysis with 0.47% H_2SO_4 contained 17 to 18% xylose. Such concentrations are the result of low liquor-to-wood ratios and are important to economic recovery and utilization in a commercial operation.

Tables 6 and 7 contain analyses of extracted residues. The analyzed constituents are about 58% of the residue, leaving 42% which would be primarily lignin. About 36% of the original wood as glucose anhydride and 1.5 to 2.0% as xylose anhydride together with a little less than 1% as acetyl remained in the residue.

TABLE 5

Material Balances: Total Measured Percentage Recoveries[a] of Wood Fractions after a 5-Minute Vacuum Impregnation of Chips with Acid and Hydrolysis at 170°C.

Time, minutes	Glucose	Furfural + Xylose	4-O-Methyl-uronic Acid	Acetyl
		2.00% H_2SO_4		
6	99	99	86	97
9	102	98	67	100
12	101	101	54	96
		2.25% H_2SO_4		
6	102	97	80	89
9	103	96	62	93
12	101	97	50	94
		2.50% H_2SO_4		
6	101	101	78	
9	99	94	55	
12	100	95	43	

[a] Molar recoveries in residues and solutions based upon the original wood analysis.

Effective Acid Concentration

The acid concentration (pH) was of primary importance to the overall rate of hydrolysis and to the reaction of xylose to furfural. Previous experience had shown that maximum yields of xylose would be obtained at pH 1.4. Several measurements showed that the desired pH of 1.4 could be experimentally approached, but that it was a variable in time because of gradual acid consumption by the wood and water movement during hydrolysis. The acid consumption was due to carboxylate groups in the wood. Their neutralizing capacity as weak acids was equal to that of their cations which became carbonates in the ash. For calculations of acid re-

TABLE 6

Residue Yields and Compositions after a 140-Hour Equilibration of Chips with Acid and Hydrolysis at 170°C.

Time, minutes	Yield from Wood, %[a]	Percentages of the Residue, as Anhydrides				
		Glucose	Xylose	Acetyl	4-O-Methyl-uronic Acid	Ash
		0.47% H_2SO_4				
4	69	55	4.9	1.3	1.3	0.18
6	66	55	3.6	1.1	.9	.21
9	65	55	2.9	.9	.6	.18
12	65	56	2.3	--	.5	--
15	65	56	2.1	--	.4	.18
18	65	56	1.8	--	--	.20
21	64	56	1.6	--	.3	--
		0.73% H_2SO_4				
4	66	56	3.2	1.0	.8	.25
6	65	56	2.9	.9	.6	.17
9	63	56	1.7	.7	.4	.16
12	62	57	1.6	--	.3	.09

[a] Residues were water-extracted and oven-dried.

quirements the equivalent weight of H_2SO_4 was 98 at pH 1.4 because HSO_4^-, like the carboxyl groups, was largely undissociated.

Of the two methods used to acidify the chips the long term acidification led to the most uniform distribution of acid before hydrolysis. During soaking with 0.47% H_2SO_4 for 140 hours about 1.1% of the dry weight of wood was removed, part of which was due to a decrease in ash content from 0.72% to 0.29-0.24%. This decrease in ash was accompanied by a decrease in alkalinity of the ash from 0.118 to 0.054-0.049 meq per gram of original wood. This loss of about 56% of the wood neutralizing capacity (or alkalinity) was followed by a further 23% loss of original alkalinity during 6 minutes hydrolysis at 170°C, as found by measurement of the alkalinity left in the residue ash. In a separate experiment wood

TABLE 7

Residue Yields and Compositions after a 5-Minute Vacuum Impregnation of Chips with Acid and Hydrolysis at 170°C.

Time, minutes	Yield from Wood, %[a]	Percentages of the Residue, as Anhydrides				
		Glucose	Xylose	Acetyl	4-O-Methyl-uronic Acid	Ash
		2.00% H_2SO_4				
6	67	53	3.4	1.3	0.7	0.25
9	65	56	2.5	1.1	.6	.23
12	65	54	3.1	.8	.5	.19
		2.25% H_2SO_4				
6	67	54	2.4	.9	.6	.28
9	66	55	1.9	.7	.5	.23
12	65	54	2.4	.8	.5	.24
		2.50% H_2SO_4				
6	64	56	2.7	--	.6	.23
9	62	56	1.6	--	.4	.17
12	62	56	2.2	--	.3	.17

[a] Residues were water-extracted and oven-dried.

chips were soaked in 0.34% HCl solution before washing and equilibration with 0.73% H_2SO_4. In this case 74% of the alkalinity was lost during acid treatment and a further 11% during hydrolysis.

The loss of alkalinity during hydrolysis was due to a gradual consumption of the available acid, and was one source of variable acid strength. Following the 5-minute acid impregnations the amounts of wood alkalinity lost during hydrolyses were sufficient to neutralize 50 to 70% of the 2.0 and 2.25% H_2SO_4 taken up by the chips. It is clear that the alkalinity in wood causes a significant loss of acid, a loss which must enter into calculations of acid requirements, and which will increase the cost of large-scale prehydrolysis.

The loss of impregnated H_2SO_4 to the free liquor during hydrolysis was another indication of nonuniform acid distribution. From 38 to 43% of the total sulfate was found in the free liquors of cooks from the 5-minute acid impregnations. Very short cooks showed that most of this acid and most of the free liquor itself were washed into the reservoir within 1 minute. Consequently, this large part of the acid was removed from the chips by the steam condensate and was not available to catalyze hydrolysis.

CONCLUSIONS

In the prehydrolysis of southern red oak chips (well equilibrated with acid) the maximum yield of monomeric and oligomeric xylose was about 86% of the xylose present in the original wood. A 5-minute vacuum impregnation with acid reduced the yield to about 81%, but the decrease was accompanied by a proportionate increase in furfural yield. About 36% by weight of the original wood was removed in each case. At maximum xylose yields 5 to 6% of the glucose present in the original wood was removed.

Neutralization of the acid by carboxylate groups in the wood represents a significant source of acid loss. With equilibrated chips, most of the acid loss occurred during impregnation. With a short impregnation time, most of the acid loss occurred during the prehydrolysis.

Movement of liquor which contained acid was a factor in determining effective acid concentration. During initial heating of the chips, 38 to 43% of the impregnated sulfate was removed by the steam condensate. The movement of liquor and the consumption of acid by the wood during hydrolysis accounted for the much higher levels of acid required by short impregnation times. In a commercial operation, however, the liquor containing the early acid loss could possibly be recycled because it contains only 7 or 8% of the xylose yield.

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