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U. S. Department of Agriculture, Forest Service
FOREST PRODUCTS LABORATORY

In cooperation with the University of Wisconsin

MADISON, WISCONSIN

R1138

PRETREATMENT OF WOOD WITH HOT DILUTE ACID
AND ITS EFFECT ON LIGNIN VALUES

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Published in
Analytical Edition of
INDUSTRIAL & ENGINEERING CHEMISTRY
May 15, 1937

(PRETREATMENT OF WOOD WITH HOT DILUTE ACID AND
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The influence of pretreatments of wood to remove, by means of hydrolysis, carbohydrate substance which allegedly causes errors in the lignin determination, has been studied to determine whether or not lignin is dissolved during such treatments. Hot water, to some extent, and boiling 3 percent sulfuric acid, to a much greater extent, dissolved lignin from maple wood. An examination of methoxyl contents demonstrated that the substance removed was lignin and not some carbohydrate material which might polymerize to an insoluble residue. All the filtrates gave significant color reactions for lignin with chlorine and sodium sulfite. In addition, the acid filtrates deposited a brown flocculent substance which contained 20.3 percent of methoxyl and which behaved like lignin when chlorinated and subsequently dissolved in sodium sulfite. Spruce wood is reported to be affected in a similar manner. It is recommended that all forms of mild hydrolysis, including treatments with hot water, be avoided when preparing woods for either the determination or isolation of lignin.

For the purpose of removing carbohydrate substances which allegedly polymerize when subjected to the conditions employed in the estimation of lignin, various forms of pretreatments, using hot dilute acid, have been suggested. Norman and Jenkins (4), for example, recommended that the wood be boiled with dilute sulfuric acid for a definite period, making this recommendation with the reservation that nothing was known of the effect of such treatment on lignin as it occurs in the wood.

¹Presented before the Division of Cellulose Chemistry at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937.

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Campbell and Bamford (1) stated that such treatment resulted in the polymerization of some carbohydrate substances with a consequent small but definite increase in the lignin yield. Therefore they recommended that dissolved carbohydrate substances be removed immediately from the sphere of action by the application of several acid treatments, each of only a few minutes' duration. In neither of the above instances was the possibility of an accompanying lignin extraction considered. An investigation of this was therefore initiated and the results are presented in this paper.

Experimental Procedure

Maple wood, ground to 40 mesh in a Wiley mill, was extracted in succession with cold alcohol-benzene (1 to 2), cold alcohol, cold water, and water at 98° C. The alcohol-benzene and alcohol extractions were made in a continuous, percolating extractor (each for 24 hours' duration), and the water treatments were applied in a glass-lined mayonnaise mixer, the former for 24 hours and the latter in two periods of 3 hours each. The wood was finally washed on a suction filter until the hot wash water remained colorless. Corresponding quantitative treatments, using glass apparatus, indicated that the total loss by extraction amounted to 4.3 percent. The wood was then extracted continuously for 50 hours with water at 98° C. in an apparatus which emptied through a siphon tube once every hour. A similar quantitative treatment in glass showed a further loss of 6.3 percent, making a total loss by extraction and, possibly, by mild hydrolysis of 10.6 percent.

Preparatory to subsequent treatments the wood was dried at room temperature (20° to 25° C.), and then ground in an attrition mill until all of it passed through a No. 80 sieve.

Separate portions of the prepared wood were then boiled under reflux with a 3 percent solution of sulfuric acid (50 ml. per gram of wood) for periods of 2, 4, 8, 16, and 30 hours. Another portion was mixed in a filter crucible with a boiling 5 percent solution of sulfuric acid (10 ml. per gram of wood) for 4 minutes and the acid solution was then withdrawn by suction and renewed. This procedure was continued until the wood had received 10 such treatments.

Following each of the foregoing treatments, the acid was removed by suction and the wood washed free of acid by means of hot water. All samples were subsequently dried at room temperature.

Corresponding treatments, using weighed samples and under identical conditions, furnished data relative to the losses caused by acid hydrolysis.

Determinations of lignin, using the U. S. Forest Products Laboratory's modified procedure, and of furfural yield, using the Tollens method with phloroglucinol as precipitant, were made on all samples.

Additional samples of lignin were prepared and dried at room temperature preparatory to the determination of methoxyl content.

The data, corrected to the basis of unextracted, moisture-free wood, are presented in Table 1.

Discussion

While the furfural yield was only slightly decreased by water treatments, acid hydrolysis caused a rapid decrease which continued steadily with time of hydrolysis until finally, after 30 hours' treatment, only about 1 percent of furfural was obtained. Lignin values showed significant decreases when the wood was heated with hot water, but the losses were not of the same order as that caused subsequently by boiling 3 percent sulfuric acid. The latter, in 2 hours, decreased the lignin value to 17.7 percent which seemed to be the limit, because longer periods of boiling, up to 30 hours, caused no significant losses of lignin. The results (Table 1, D to H) suggested a solubility relationship, the acid solution (a) having become saturated with the slightly soluble lignin in the first 2 hours, (b) having reached a condition of equilibrium between dissolution of lignin and its deposition as a less soluble polymerized material, or (c) having dissolved all the soluble lignin during that period.

The methoxyl content of the isolated lignin remained uniform throughout and, therefore, demonstrated that lignin, rather than carbohydrate substances which might polymerize to an insoluble residue, was being removed. This was verified when the lignin methoxyl contents were calculated as percentages of wood.

It was evident that lignin is soluble in hot dilute acid and an examination of the various filtrates supported this contention. These filtrates were chlorinated and, on the addition of sodium sulfite in excess of that required to react with the acid present, a wine-red color, characteristic of chlorinated lignin dissolved in sodium sulfite, developed. Furthermore, after standing at room temperature for a few days, a brown flocculent substance resembling lignin separated out from the filtrates. Some of this was collected and chlorinated. It brightened in color to orange yellow and dissolved in sodium sulfite to a wine-red solution which changed to a brown color on heating. The methoxyl content of this substance was found to be 20.3 percent.

Apparently the dissolved lignin polymerized to a less soluble form when left in contact with the dilute sulfuric acid for several days. Campbell and Bamford (1) postulated such a reaction involving carbohydrate substances when they recommended the short successive treatments to which reference has already been made (Table 1, I). It is conceivable that the phenomena are identical and that the substance which Campbell and Bamford found to be redeposited was really lignin. Although their method, when

Table 1.--Effect of boiling dilute sulfuric acid on the lignin value of maple wood

Reference	Pretreatment	Loss by:			Loss by:			Lignin:	Methoxyl in
		solvent:	hot-	acid:	solvent:	hot-	acid:		
		extrac-	treat-	hydrol-	extrac-	treat-	hydrol-	con-	lignin
		tion	ment	ysis	tion	ment	ysis	tent	
		(a)	(a)	(a)	(a)	(a)	(a)	(a)	(b)
		Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
A	Extraction with alcohol- benzene, alcohol, and cold water.....	3.2	12.8	23.2	20.2	4.69	
B	Extraction with alcohol- benzene, alcohol, cold water and hot water.....	4.3	12.5	21.5	20.5	4.40	
C	Same as B, plus 50 hours' treatment with hot water as described.....	4.3	6.3	12.1	20.2	20.6	4.16	
D	Same as C, plus hydrolysis for 2 hours with boiling 3% H ₂ SO ₄ aq.....	4.3	6.3	24.8	3.6	17.7	20.4	3.61	
E	Same as C, plus hydrolysis for 4 hours with boiling 3% H ₂ SO ₄ aq.....	4.3	6.3	29.0	2.3	17.3	20.7	3.58	

(a) Expressed as percentages of unextracted, moisture-free wood.

(b) Expressed as percentage of lignin.

(Continued)

Table 1.--Effect of boiling dilute sulfuric acid on the lignin value of maple wood (Continued)

Reference	Pretreatment	Loss by solvent extraction				Loss by hot-water treatment				Loss by acid hydrolysis				Furfural yield				Lignin content				Methoxyl in lignin			
		(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(b)	(b)	(b)	(b)
		Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
F	Same as C, plus hydrolysis for 8 hours with boiling 3% H ₂ SO ₄ aq.....	4.3	6.3	31.3	1.6	17.6	20.3	3.58																	
G	Same as C, plus hydrolysis for 16 hours with boiling 3% H ₂ SO ₄ aq.....	4.3	6.3	32.2	1.3	17.5	20.5	3.59																	
H	Same as C, plus hydrolysis for 30 hours with boiling 3% H ₂ SO ₄ aq.....	4.3	6.3	35.4	0.9	17.3	20.6	3.56																	
I	Same as C, plus 10 treatments with boiling 5% H ₂ SO ₄ aq. (10 ml. per gm.) each for 4 minutes...	4.3	6.3	13.7	10.8	19.7	20.7	4.08																	

(a) Expressed as percentages of unextracted, moisture-free wood.

(b) Expressed as percentage of lignin.

used in this study, did not decrease the lignin yield as much as did the other acid treatments, the filtrate gave a definite color reaction for lignin. Probably continued treatment by their method would eventually have decreased the lignin yield to about 17.7 percent.

The results obtained with dilute acid naturally directed attention to the possibility of similar effects resulting from milder forms of hydrolysis, such as extractions with hot water which had been used in preparing the wood. The lignin content had been appreciably decreased by the prolonged extraction (Table 1, C) and the effluent from the extractor gave a slight color reaction for lignin with chlorine and sodium sulfite. This reaction, although slight as compared with that obtained with the acid filtrates, was very significant because about 40 liters were used in the course of the extraction and, as the effluent was run to waste rather than concentrated, the lignin concentration was consequently small. Digestion with water at 98° C. for shorter periods such as 3 hours also resulted in some dissolution of lignin (Table 1, B) because the filtrate from this treatment gave a very definite color reaction for lignin.

The action of boiling dilute sulfuric acid on wood is comparable with that of methanol-hydrochloric acid when it is used in the extraction of soluble lignin. In both instances, there is an acidic condition which enhances hydrolysis of some carbohydrate substances. These are apparently associated chemically with the soluble lignin and their removal sets it free to dissolve in water on one hand, or in methanol on the other. In fact, the difference between the lignin yields (1) from wood which has been subjected only to alcohol-benzene, alcohol, and cold water (Table 1, A), and (2) from wood which, in addition, has been treated with hot water and dilute sulfuric acid (Table 1, D), is approximately 6 percent -- that is, of the same order as the yield of soluble lignin by the methanol-hydrochloric acid process (3).

The influence of mild hydrolysis in releasing soluble lignin to a solvent was demonstrated by one of the authors (2) when describing the effects of alkaline extraction on the lignin yield. Sodium hydroxide (0.5 percent) was found to have a much greater solvent action on lignin if the wood was first subjected to an extended extraction, amounting to mild hydrolysis, with hot water.

The polymerization of the dissolved lignin to a less soluble aggregate under the influence of cold dilute sulfuric acid may be regarded as a milder form of the action of the 72 percent sulfuric acid employed in the lignin determination. It is significant that the filtrate from a lignin determination does not give any form of color reaction with chlorine and sodium sulfite.

Although this investigation was limited to maple wood, similar results, indicating that in addition to maple some spruce lignin was dissolved by dilute sulfuric acid, have been recorded in an unpublished report of the U. S. Forest Products Laboratory by R. L. Mitchell.

It is concluded that any form of pretreatment involving hydrolysis will cause significant errors in lignin determinations and may even result in the complete loss of that portion of lignin which is known as soluble lignin. It is believed that all forms of pretreatment using hot dilute acids are not only unnecessary for the purpose of removing carbohydrate material, but that they should be avoided, and that, if water must be used to remove interfering extraneous matter, cold extraction should preferably be employed.

Literature Cited

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