EFFECT OF VARIOUS PRE-EXTRACTIONS ON THE LIGNIN DETERMINATION OF WOOD

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EFFECT OF VARIOUS PRE-EXTRACTIONS ON THE LIGNIN DETERMINATION OF WOOD[1]

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The present methods for the determination of lignin in wood are subject to criticism because they cannot be applied alike to all types of material. The sulfuric acid method, which is favored by most analysts because it is simpler to perform and gives, under controlled conditions, more uniform results than other methods, is subject to the same criticism: Certain carbohydrates are converted into a water-insoluble material, which appears in the lignin residue if allowed to stand in contact with the sulfuric acid too long a time or at too high a temperature (6, 7, 10, 11). To overcome this objection and to make control of temperature unnecessary, several investigators (5, 8) have suggested that these unstable carbohydrates be removed by a preliminary extraction with hot dilute acid. They assumed that the easily hydrolyzable carbohydrates as determined by Hawley and Fleck (4) were the same as those which were responsible for the formation of the insoluble ligninlike residue. Campbell and Bamford (1) contend that preliminary treatment causes a polymerization of some carbohydrate substance with an increase in lignin yield.

Work on this aspect of the analysis of lignin has been in progress at the Forest Products Laboratory at Madison, Wis., for several years. Preliminary extraction with organic solvents, cold water, hot water, dilute sodium hydroxide, barium hydroxide, sodium carbonate, sodium sulfite, and dilute hydrochloric, dilute sulfuric, and 3 per cent oxalic acid have been tried and, in addition, various concentrations of dilute sulfuric acid under pressure. The work with sodium hydroxide on sugar maple sawdust was reported by Harris (3), various treatments with hot and cold water and organic solvents by Ritter and Barbour (9), and some of the work showing the effect of 3 per cent sulfuric acid on sugar maple sawdust by Cohen and Harris (2).

This report contains, in table form, the results of further work with sulfuric acid and of various other pretreatments on wood.

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EXPERIMENTAL PROCEDURE

Sawdust obtained from sawing selected air-dried wood free from bark, knots, and compression wood, was cut to pass a 40-mesh screen in a Wiley mill and extracted successively with cold water, hot 95 per cent alcohol, hot alcohol-benzene mixture, followed by alcohol and then water, and finally dried in the air to 5.5 per cent moisture content.

Table I gives the data for the effect of successive treatments on a boiling water bath with 3 per cent sulfuric and oxalic acid, and also other individual treatments with sulfuric acid on spruce and maple sawdust. Table II shows the effect of various other materials at the temperature of the water bath. The furfural determination was omitted because, as shown by Cohen and Harris (2), practically all the furfural-forming material was destroyed by contact with acid. Five hundred cubic centimeters of the acid solution were used for the extraction of each 2 grams of wood. All extractions were carried out in groups of six for each series of extractions and the average of these was taken. The acid extract was filtered from the sawdust while hot, since cooling caused a precipitation of some of the dissolved material.

Table III gives the lignin and cellulose analytical values obtained upon maple wood after treatment at 8.436, 9.49, and 10.545 kg. per sq. cm. (120, 135, and 150 pounds per square inch) steam pressure in sulfuric acid at concentrations from 1 to 7 per cent, in water, and in 3 per cent oxalic acid.

DISCUSSION

Examination of Tables I and II shows that pretreatment of either softwood or hardwood with dilute sulfuric or oxalic acid removed lignin as well as carbohydrate material. Spruce wood, which had been extracted by six 3-hour treatments with 3 per cent sulfuric acid, lost 16.8 per cent of its lignin. (No record was made of the loss at the end of the fifth 3-hour treatment.) Three treatments with 3 per cent oxalic acid removed 13.9 per cent of the lignin from spruce. Filtrates from the extractions of spruce wood gave a precipitate that was soluble in glacial acetic acid, alcohol, and chloroform. The glacial acetic acid solution of this material was poured into a large volume of water, which caused the material to precipitate again. This material contained 16.8 per cent of methoxyl and had properties that indicated that it was lignin.

Maple wood lost 22.5 per cent of the lignin when heated 4 hours with 3 per cent sulfuric acid. When the heating was continued for 6 hours, some of the lignin was again converted into an insoluble compound, since the loss is slightly less than with a 4-hour treatment. Oxalic acid, during six 3-hour treatments, removed 25.5 per cent of the lignin, which was more than that removed by the action of sulfuric acid (2). Material precipitated from the sulfuric and oxalic acid solutions on standing or on increasing the acid concentration was dissolved in glacial acetic and reprecipitated by pouring into water. This material had the same methoxyl content (20.6 per cent) and other properties which indicated that it was lignin.

Treatment with ammonium oxalate had about the same effect on the lignin content as did extraction with water (see Table II). There was a slight loss of lignin.

Sodium sulfite solution also removed lignin from wood. This may be accounted for by the alkalinity of the solution. Barium hydroxide removed less because the barium derivative of lignin is insoluble.

Fifteen per cent sulfuric acid dissolved less lignin from wood than did 3 per cent, perhaps because the higher concentration depressed the solubility of the lignin.

Hydrochloric acid also had the property of removing lignin; the lignin content was lowered almost 15 per cent by treatment with 2 per cent acid for 3 hours at 90° C.

When the hydrolysis took place under pressure, as shown in Table III, a loss of lignin was observed at the lower concentrations of acid and lower pressures. Increase in acid and increase in pressure caused a reprecipitation of some of the lignin and also the conversion of some of the carbohydrates into a ligninlike residue that was isolated with the lignin and, consequently, gave a residue with a low methoxyl content.

This work shows lignin to be soluble in dilute acid solutions. It may be precipated by long heating, heating under pressure, or increasing the acid concentration. Extraction of lignin-containing material with 3 per cent acid, sodium sulfite, and other salts or bases removes lignin and should be avoided if an accurate determination of the lignin content of a sample of wood is desired.

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TABLE I. EFFECT OF ACID PRE-EXTRACTION ON SPRUCE AND MAPLE WOOD

	Wood Treatment	Total Time of Treatment	Alcohol-Benzene-Water Extractives[a]	Loss by Treatment[a]	Lignin Content[a]	MeO in Wood[a]	MeO in Lignin[b]	Calculated Loss of Lignin[a,c]
		Hours	%	%	%	%	%	%
1.	Spruce extracted with alcohol-benzene and cold water	..	4.3	..	27.47	..	16.6	...
2.	No. 1 + 3 hours on boiling water bath with 3% sulfuric acid	3	..	24.0	26.4	6.46	16.5	3.65
3.	No. 2 + 3 hours with 3% sulfuric acid	6	..	28.0	25.5	6.25	16.4	6.95
4.	No. 3 + 3 hours with 3% sulfuric acid	9	..	30.2	24.9	5.87	15.1	9.5
5.	No. 4 + 3 hours with 3% sulfuric acid	12	..	33.9	23.7	5.34	15.0	13.9
6.	No. 5 + 6 hours with 3% sulfuric acid	18	..	37.0	22.9	4.95	14.8	16.8
7.	Spruce + 3 hours with 3% oxalic acid	3	..	16.65	26.1	..	16.5	4.7
8.	No. 7 spruce + 3 hours with 3% oxalic acid	6	..	24.2	24.0	..	16.4	11.5
9.	No. 8 + 3 hours with 3% oxalic acid	9	..	28.4	23.7	..	16.4	13.9
10.	No. 9 + 3 hours with 3% oxalic acid	12	..	28.7	23.7	..	16.0	...
11.	No. 10 + 6 hours with 3% oxalic acid	18	..	29.0	23.7	..	15.9	...
12.	Maple extracted with alcohol-benzene and water	..	4.07	4.07	22.75	..	20.4	...
13.	No. 12 + 4 hours' boiling with 1% sulfuric acid	4	..	23.0	19.85	..	20.5	12.2
14.	No. 12 + 1 hour's boiling with 3% sulfuric acid	1	..	26.7	19.10	..	20.3	16.0
15.	No. 12 + 4 hours' boiling with 3% sulfuric acid	4	..	36.4	17.6	..	20.2	22.5
16.	No. 12 + 6 hours' boiling with 3% sulfuric acid	6	..	34.8	17.75	..	20.0	22.0
17.	No. 12 + 3 hours' boiling with 3% oxalic acid	3	..	25.5	20.3	6.60	20.3	10.5
18.	No. 17 + 3 hours' boiling with 3% oxalic acid	6	..	31.5	18.5	5.95	20.4	18.5
19.	No. 18 + 3 hours' boiling with 3% oxalic acid	9	..	32.6	18.3	5.48	20.3	19.5
20.	No. 19 + 3 hours' boiling with 3% oxalic acid	12	..	36.0	17.4	5.40	20.5	23.5
21.	No. 20 + 6 hours' boiling with 3% oxalic acid	18	..	38.0	16.9	5.40	20.0	25.5

[a] Percentages are calculated from unextracted oven-dried wood.
[b] Percentages based on isolated lignin.
[c] $\frac{\text{Loss of lignin (due to treatment)}}{\text{Original lignin (after alcohol-benzene extraction)}}$

TABLE II. EFFECT OF PRE-EXTRACTION WITH ACID, SALTS, AND ALKALI ON LIGNIN DETERMINATION OF MAPLE WOOD

(On boiling water bath)

Treatment	Time	Loss by Solvent Extraction	Loss by Treatment	Lignin Based on Original Wood	MeO in Lignin
	Hours	%	%	%	%
Alcohol-benzene extraction	...	4.07	4.07	22.7	20.4
1% ammonium oxalate	4	..	2.4	22.5	20.5
2% ammonium oxalate	7	..	12.1	21.0	20.4
2% sodium sulfite	3	..	11.8	20.7	20.4
0.5% barium hydroxide	6	..	10.8	21.2	20.4
15% sulfuric acid	3	..	25.9	21.2	20.5
2% hydrochloric acid	3	..	24.3	19.4	20.3

TABLE III. EFFECT OF HYDROLYSIS ON LIGNIN AND CELLULOSE VALUES IN MAPLE WOOD

Treatment	120 Pounds' Pressure, 30 Minutes						135 Pounds' Pressure, 30 Minutes						150 Pounds' Pressure, 30 Minutes					
	Experiment No.	Hydrolyzed wood	Cellulose[a]	Lignin[a]	Lignin[b]	Methoxyl in lignin	Experiment No.	Hydrolyzed wood	Cellulose[a]	Lignin[a]	Lignin[b]	Methoxyl in lignin	Experiment No.	Hydrolyzed wood	Cellulose[a]	Lignin[a]	Lignin[b]	Methoxyl in lignin
		%	%	%	%	%		%	%	%	%	%		%	%	%	%	%
1% sulfuric acid hydrolysis	473	64.95	63.4	32.5	21.1	20.6	485	63.70	66.0	33.3	21.2	20.5	492	62.87	64.6	35.0	22.0	20.2
2% acid	474	62.30	61.9	36.2	22.5	20.3	486	61.83	63.0	37.1	22.9	20.2	493	60.52	61.6	38.5	23.3	..
3% acid	475	60.10	59.6	37.6	22.6	20.3	487	59.81	61.0	39.0	23.3	20.0	494	58.24	58.5	41.5	24.3	19.8
4% acid	476	58.95	57.1	39.8	23.4	20.0	488	58.74	58.5	41.1	24.1	19.5	495	57.20	55.4	44.6	25.6	..
5% acid	477	56.90	55.6	41.8	23.8	19.7	489	56.80	55.0	45.0	25.5	19.2	496	56.55	52.5	47.2	26.2	18.5
6% acid	...	...	...	...	...	...	490	55.72	54.4	45.4	25.6	18.9	497	54.03	49.4	50.0	27.3	..
7% acid	484	54.18	52.0	46.6	25.4	18.4	491	54.00	49.9	50.2	27.3	17.5	498	52.00	43.0	57.0	29.6	15.9
Water	500	82.50	62.5	27.95	22.9	20.7	...	...	..	..	..	..	...	...	..	..	..	..
3% oxalic acid	499	68.37	63.0	33.6	22.9	20.7	...	...	..	..	..	..	...	...	..	..	..	..

[a] Per cent cellulose and lignin yields based on oven-dry residue after hydrolysis.
[b] Per cent lignin based on weight of original wood.