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EFFECT OF PARTIAL HYDROLYSIS ON THE

ALKALI SOLUBILITY OF WOOD

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EFFECT OF PARTIAL HYDROLYSIS ON THE  
ALKALI SOLUBILITY OF WOOD<sup>1</sup>

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It has been pointed out by Bray<sup>2</sup> that during the decay of wood by several different fungi the alkali solubility of the residue rapidly increases. When the decay has resulted in a loss in weight of about 30 per cent, the alkali solubility of the residue may amount to as much as 57 per cent. Bray did not determine how much of this alkali solubility was due to lignin or how much to cellulose, but in certain cases, even if the assumption were made that the cellulose and all other constituents than lignin were completely alkali soluble,<sup>3</sup> yet more than half the lignin must have been soluble also. Since the hydrolysis of wood is similar to decay in that cellulose is removed with but little removal of the lignin, it was decided to determine whether hydrolysis increased the alkali solubility and, if so, whether the increase was chiefly due to changes occurring in the cellulose or in the lignin.

The wood chosen for the test was Sitka spruce in the form of 60-80 mesh sawdust. Its composition and its behavior under direct alkali treatment were first determined as a basis for comparing results obtained with hydrolyzed specimens. The analysis of the original wood is given in Table I, and in Table II is shown the composition of the residue left after treatment with 1 per cent caustic soda for 1 hour at the water-bath temperature.

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<sup>1</sup>Published in Ind. Eng. Chem., vol. 19, no. 6, June, 1927, p. 742.

<sup>2</sup>Paper Trade J., 78, no. 1, 58 (1924).

<sup>3</sup>Hawley and Wise, "The Chemistry of Wood," p. 299, The Chemical Catalog Co., Inc., New York, 1926.

Table I.--Analysis of original wood

(Results on basis of weight of original dry wood)

	<u>Per cent</u>
Water soluble.....	4.1
Ether soluble.....	.7
Alkali soluble.....	12.0
Cellulose.....	62.5
Lignin.....	29.3
Methoxyl.....	4.8
Total pentosans.....	9.9
Pentosans not in cellulose.....	6.2

Table II.--Analysis of wood residue after treatment  
with 1 per cent NaOH for 1 hour at  
100° C.

(Results on basis of weight of original dry wood)

	<u>Per cent</u>
Loss on alkali treatment.....	13.7
Cellulose.....	59.2
Lignin.....	27.7
Methoxyl.....	4.3
Total pentosans.....	7.4
Pentosans not in cellulose.....	3.9



In each of the tables there is given a figure unusual in records of wood analysis -- viz., "pentosans not in cellulose." Pentosans are determined on the total sample and then in the crude cellulose and are commonly recorded as "total pentosans" and "pentosans in cellulose." In the interpretation of the analytical data here presented, however, it was found that the value for the pentosans not in the cellulose was used frequently but the pentosans in cellulose not at all. The values for the former were therefore computed and used in the tables.

### Experimental

In studying the alkali solubility of the hydrolyzed wood, the general plan was to subject samples to different degrees of hydrolysis, analyze them, treat them with caustic soda, and analyze the residue. It has frequently been found, however, that on account of the difficulty of obtaining the same conditions throughout the mass, a chemical reaction which takes place with small quantities of wood, such as the sample for analysis, can not be reproduced exactly when larger quantities are used. For this reason it was not attempted to hydrolyze enough wood so that the residue would be sufficient for an analysis, alkali treatment, and the further analysis of the residue. Instead, two samples were hydrolyzed under as nearly as possible the same conditions, one of which was used for intermediate analysis and the other for alkali treatment and final analysis. The analyses are shown in Tables III and IV. The loss in weight on hydrolysis as given in the second columns of these tables shows the relatively slight variation in the results obtained by the duplicate hydrolyses.

### Comparison of Results

In Table III the values headed "calculated loss in weight" are obtained by adding together the losses in cellulose, lignin, and "pentosans not in cellulose" as determined from the analyses of the original wood (Table I) and of the residue after hydrolysis, to which is also added the water soluble in the original wood, on the assumption that this is all removed by hydrolysis. It is immediately noticeable that the calculated loss is always considerably higher than that actually determined. This difference can be explained

Table III.---Analysis of wood residue after treatment for 6 hours with  
HCl at 100° C.

(All results expressed as percentages of weight of original wood)

Acid concen- tration	Loss on hydrolysis	Cellu- lose	Lignin	Methoxyl	Total pentosans	Pentosans not in cellulose
0.05	6.0	55.6	28.9	4.6	7.5	5.1
.25	10.0	55.3	28.7	4.7	6.4	4.2
1.5	17.6	49.0	26.7	4.7	4.4	3.5
8.0	22.9	46.2	26.4	4.2	3.4	2.1
15.0	36.2	32.7	26.3	4.3	.9	.6

Table IV.---Analysis of wood residue after treatment with HCl for 6 hours and subsequent treatment with NaOH for 1 hour at 100° C.

(All results expressed as percentages of weight of original dry wood)

Acid concen- tration	Loss on hydrolysis	Loss on alkali treatment	Total loss	Cellu- lose	Lignin	Methoxyl	Total : Pentosans : pento- : sans : cellulose
0.05	6.1	12.9	19.0	52.4	26.4	4.6	4.9
.25	11.4	18.2	29.6	42.5	26.3	4.1	3.6
1.50	17.2	16.1	33.3	38.1	26.3	3.9	3.3
8.00	26.9	12.8	39.7	33.4	25.2	3.7	2.1
15.00	34.3	17.1	51.4	25.1	23.2	2.7	.8

only on the basis of some constituent being present in the partly hydrolyzed wood which was not isolated or determined as cellulose, lignin, or pentosans. Looking at the figures a little more closely, it is seen that while the sum of the four main constituents of the original sample of wood is 102.1 per cent, the sums of the three main constituents of the partly hydrolyzed samples all lie between 93 and 98 per cent of the weight of the residue. It is not intended to imply that the sum of the main constituents, such as cellulose, lignin, "pentosans not in cellulose," and water soluble, should add up to exactly 100 per cent, but when the original wood totals more than 100 per cent and all the partly hydrolyzed samples to considerably less than 100 per cent, there is good reason to assume the presence of some material in the latter which was not present in the original and which does not show in any of the determinations. Whatever the substance, there is evidence that it is largely removed by the alkali treatment, in that the sums of the three main constituents determined on the alkali-treated wood (Table IV) all come very close to 100 per cent of the actual weight of residue, the extreme variations being between 99.2 and 100.5 per cent.

The figures in Table III, aside from the differences between determined and calculated losses, give little information that has not been available previously. The slight effect of hydrolysis on the amount of lignin and methoxyl and the continuous but not complete removal of the pentosans have been shown in previous work. This set of analyses is furnished mainly for comparison with Table IV in order to show the quantitative effect of the alkali treatment. Table IV gives the loss in weight of the duplicate samples on hydrolysis, their loss in weight on alkali treatment, and then the analysis of the residues after the alkali treatment. The alkali treatment was identical with that used in the analytical determination of the alkali-soluble content of the original wood -- viz., treatment with 1 per cent sodium hydroxide at boiling water temperature for 1 hour.

Despite the small differences in the loss on hydrolysis between the second column of Table IV and the second column of Table III, some conclusions may safely be drawn from a comparison of the analytical determinations as they stand. It will be noticed that in every case the loss in weight due to the alkali treatment is made up of losses in each of the constituents determined, and this is also the case in the alkali treatment of the original wood (compare Table II and Table I). Moreover, in every case the amount of



each constituent is less in Table IV than in the corresponding part of Table III. There is always a decrease in the constituents shown in Table IV as the severity of the hydrolysis increases, with the exception that the lignin during the first three hydrolyses remains practically constant.

The largest variations between the two tables, however, are in the cellulose. Comparing the sixth column of Table IV with the fourth of Table III, it is seen that the alkali solubility of the cellulose becomes very high after the last four hydrolyses, although there is no orderly increase in the alkali solubility with increasing severity of hydrolysis. The lignin, on the other hand, is rendered only slightly soluble by the hydrolysis, and even after the most drastic treatment, with 15 per cent hydrochloric acid, only 3 per cent out of the 26 per cent present after hydrolysis is removed by the subsequent alkali treatment.

The methoxyl is removed by the alkali treatment in increasing amounts as the hydrolysis progresses. Although after the first three hydrolyses the amount of methoxyl decreases while the lignin determination remains stationary, this fact should not be considered an indication that the methoxyl was not a part of the original lignin, since the chemical method by which the lignin was isolated has been shown to result in the loss of a considerable portion of the methoxyl,<sup>4</sup> and it is in this relatively unstable portion that the principal methoxyl loss on alkali treatment may be supposed to occur.

The first mild hydrolysis, while without great influence on the alkali solubility of the cellulose, lignin, and methoxyl, nevertheless has a considerable effect on the alkali solubility of the pentosans. The 7.5 per cent pentosans in the hydrolyzed wood were decreased to 4.9 per cent by the alkali treatment, although in the original wood pentosans to the amount of 7.4 per cent were insoluble in alkali (Table II). This high alkali solubility of the pentosans in the partly hydrolyzed wood was progressive as hydrolysis became more severe.

Unlike the action of decay, a partial hydrolysis of wood does not greatly increase the alkali solubility of the residue. It is noticeable, however, that after hydrolysis the alkali solubility is due to different constituents. In the original wood the alkali solubility (Table II) is due more to the water-soluble constituents (4.1 per cent) than to any other one constituent, with the cellulose next (3.3 per cent

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<sup>4</sup>Ritter, Ind. Eng. Chem. 15, 1264 (1923).



soluble). In partly hydrolyzed wood the most soluble constituent at all stages of hydrolysis is the cellulose, the loss in cellulose reaching 12.8 per cent in two cases. The lignin, on the contrary, is very little affected by the hydrolysis, the lignin of the original wood being almost as soluble in alkali as the lignin in the hydrolyzed residues.

#### Remarks

Although the work here reported was not intended as a study of analytical methods for wood, yet it has been plainly shown that we must not rely too much on the absolute meaning of the accepted "determinations" of various wood components. Here we have a case where there is very evidently present in the partly decomposed wood a substance, probably a degradation product of the cellulose which is neither soluble in water nor isolated nor determined as cellulose, lignin, or pentosans. From the analytical results alone the presence of such a material might not have been suspected, and it was only the statistical data on the loss in weight and the composition of the original wood that threw a real light on the situation. A similarly undetermined material has been previously noted in partly decayed wood, and there again its presence was detected only because the analysis of the original wood was available and the loss in weight and the analyses of the partly decayed wood could be used in comparison. Frequently the loss of cellulose in partly decayed woods is considerably greater than the total loss in weight due to decay.<sup>5</sup>

A further example of the unsatisfactory condition of our analytical methods for wood is the fact that paper pulp prepared by the alkali process, when bleached, shows an increase in the lignin determination, although it is quite evident that the bleaching process can not manufacture lignin from some other constituent of wood pulp.<sup>5</sup> Another instance of a mistaken conclusion which might be made from comparative determinations of cellulose is found in the pulping of wood with neutral sodium sulfite.<sup>6</sup> On cooking aspen wood with sodium sulfite solution at low temperatures, the amount of cellulose based on the weight of the original wood is actually increased, if one is to credit the evidence afforded by the chlorination method of cellulose determination.

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<sup>5</sup>Hawley and Wise, op. cit., p. 259.

<sup>6</sup>Rawling and Staidl, Paper Trade J., 81, no. 8, 49 (1925).

### Summary

1. Although the principal effect of decay on wood, so far as removal of constituents is concerned, is apparently the same as a hydrolysis, yet these two processes differ in their effect on the alkali solubility of the residue.

2. The total alkali solubility of partly decayed wood is much greater than that of wood which has been hydrolyzed to the same extent (as shown by equal loss in weight).

3. The solubility of the lignin in alkali is very slightly increased by partial hydrolysis, whereas decay may render the lignin 50 per cent soluble.

4. The solubility of the residual cellulose is considerably increased by partial hydrolysis, but probably not to the same extent as it is by decay.

5. There is in partially hydrolyzed wood a material, probably a degradation product of the cellulose, which is not determined as cellulose, lignin, or pentosans. This material is soluble in 1 per cent sodium hydroxide.