TRANSFORMATIONS OF HYDROLYSIS LIGNIN FROM SUNFLOWER HUSKS IN AQUEOUS AMMONIA

B. V. Koval'chuk and Yu. N. Forostyan

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As reported previously [1], the reaction of hydrolysis lignin with 25% aqueous ammonia leads to the addition of nitrogen to the lignin and the formation of two types of "aminated" lignin: water-soluble and water-insoluble.

The present paper gives the results of a study of the changes in the main functional groups in the water-insoluble fraction of the product obtained by means of IR spectroscopy and analysis. The reaction of the lignin with ammonia was performed for 2 h at various temperatures.

The IR spectra of preparations isolated by treating the initial sample at 50°C (III) and 200°C (VI) (Fig. 1b and c, respectively) characterize the individual stages of the transformation most fully.

A comparison of the IR spectra of the initial lignin and the materials mentioned shows their difference. Thus, in a sample of lignin treated with ammonia the intensity of the 1710, 1370, 1160, 1115, and 1060 cm^{-1} bands decreases. The 1710 cm^{-1} band appears when there is an accumulation of β-carbonyl and carboxy groups [2, 7], the carboxy groups forming the bulk. The 1555 and 1405 cm^{-1} bands (Fig. 1b) correspond to the asymmetrical and symmetrical vibrations of COO^- groups [3, 4] formed by the ammonium salts $R-COONH_4$.

In the IR spectra of the material obtained by treating the initial sample with ammonia at 200°C, the bands at 1555 and 1405 cm^{-1} have disappeared almost completely, which is explained by the conversion of the ammonium salts into amides:

$$R-COONH_4 \xrightarrow{\text{heating}} R-CONH_2 + H_2O.$$

The oxidation of hydrolysis lignin in an alkaline medium leads to the appearance of β-diketone structures [7, 8]. The reaction of such structures with ammonia takes place readily and possibly leads to the formation of amines:

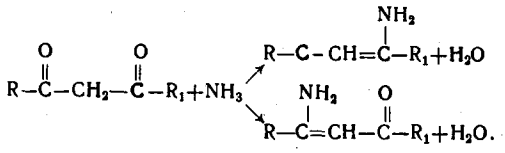

TABLE 1. Content of Functional Groups in the Lignin

Sample No.	Temp. of treatment °C	Content, %					Introduced, %	
		methoxy groups	tot. OH groups	phenolic OH groups	COOH groups	benzyl alcohol groups	amino groups	amide groups
I	Initial	18,70	9,44	4,96	3,95	2,59	—	—
II	20	17,46	10,56	5,18	6,17	3,04	0,22	0,02
III	50	16,12	14,69	5,41	10,62	3,92	0,48	0,13
IV	100	13,14	20,20	5,38	12,79	5,58	0,55	0,21
V	150	11,93	22,18	4,98	13,61	7,45	0,62	0,23
VI	200	12,54	20,96	4,36	13,78	9,51	0,70	0,41
VII	225	13,16	18,78	4,11	14,34	10,84	0,72	0,51

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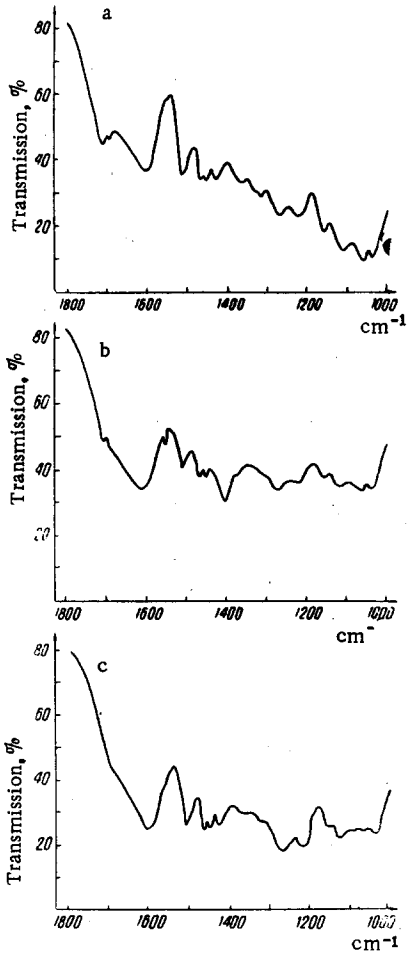

Fig. 1. IR spectra of the initial hydrolysis lignin (a) and of samples treated with ammonia at 50°C (b) and at 200°C (c).

In the region of stretching vibrations, bands are found at 3190 and 3220 cm^{-1} which show the presence of NH groups. The indistinctness of these bands is due to the presence of a broad band in the 3300-3600 cm^{-1} region corresponding to the OH group of lignin and to adsorbed water. The changes mentioned are confirmed by the analysis of the samples. Thus, the total nitrogen content in samples (III) and (IV) was 0.798 and 1.24%, respectively, and after the saponification of the amide groups it was 0.69 and 0.88%.

The 1370 cm^{-1} band corresponds to phenolic OH groups [5]. An increase in its intensity in sample (III) and a decrease in (VI) depend on a change in the number of phenolic hydroxyls. The decrease in the intensities of the 1160, 1115, and 1060 cm^{-1} bands characteristic of methoxy groups [6] is due to a decrease in the number of these groups.

Results of a functional-group analysis of the lignin samples obtained by treating the initial lignin with 25% ammonia at 20, 50, 100, 150, 200, and 225°C are given in Table 1. A comparison of these analyses shows that complex transformations of the hydrolysis lignin take place in aqueous ammonia: oxidation accompanied by an increase in the number of hydroxy and carbonyl groups, demethoxylation, the formation of amines and amides, and other processes.

EXPERIMENTAL

The samples of hydrolysis lignin from sunflower husks were freed with ether from resinous substances and were washed with water to neutrality and to the absence of SO_4^{2-} ions. The samples were treated with 25% ammonia as described previously [1], washed to neutrality, and dried in a vacuum desiccator over P_2O_5 to constant weight. The IR spectra of the samples were measured on a UR-10 spectrophotometer in KBr tablets (3 mg of the substance and 300 mg of KBr). Methoxy groups were determined by the method of Vieböck and Schwappach [9], and the total amount of hydroxy, amino, and amide groups in the samples after their methylation with dimethyl sulfate.

The samples were acetylated by the method of the polymer laboratory of the IKhD of the Academy of Sciences of the Latvian SSR. The amount of groups acetylated was calculated by the method of Zakis and Barzdyn' [12].

The sum of amino and amide groups was determined by the method of Mozheiko et al. [10] from the difference in the content of methoxy groups of the acetylated and dimethyl-sulfate methylated samples. The carboxy groups were determined and calculated from the difference in the amount of methoxy groups after the alkali saponification of the samples methylated with dimethyl sulfate.

The quantitative analysis of the phenolic hydroxyls was performed by potentiometric titration with potassium methoxide in a nonaqueous medium [11].

The content of benzyl alcohol groups in the samples was found after their methylation at 20°C with methanol and HCl [13]. The nitrogen content was determined by the Kjehldahl method, and the content of amide groups was calculated from the decrease in the nitrogen content in the samples saponified with 10% H_3PO_4 at 100°C for 2 h.

The recalculation and reduction to common units of the content of functional groups was performed as described by Zakis and Barzdyn' [12].

SUMMARY

1. In aqueous ammonia, hydrolysis lignin from sunflower husks undergoes transformations connected with oxidation, demethoxylation, and the formation of amide and amino compounds.

2. The oxidation processes are accompanied by an increase in the amounts of aliphatic hydroxyls and carboxy groups.

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