THE INTERACTION OF HYDROLYSIS AMMONIATED LIGNIN WITH BROMINE

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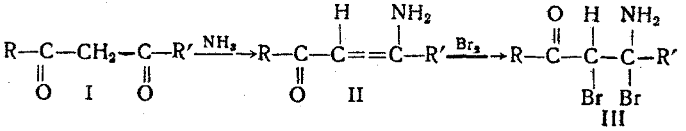
Lignin activity reacts with halogens [1-4] and, in particular, with bromine [5, 6]. Both in bromination [7] and in ammonolysis [8], in addition to specific reactions [1, 9] a number of general reactions are observed as a result of which a lignin macromolecule undergoes certain transformations: demethoxylation, dealkylation, and oxidation, which, in their turn, lead to its activation [10, 11].

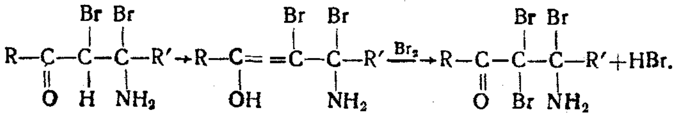
The present paper gives the results of a study of the change in some functional groups in the water-insoluble fraction of hydrolysis ammoniated lignin (HAL) after bromination in an alkaline medium by means of IR spectroscopy and analyses. Bromination was performed on the HAL and, for comparison on hydrolysis lignin (HL) from sunflower husks produced by the Zaporozh'e hydrolysis-yeast factory. The HAL or the HL (1 g with a grain size of 0.14 mm) was brominated (1.5 g of bromine) in 0.1 N aqueous NaOH (100 ml) in sunlight (20-22°C) for 6 h with shaking. The reaction products were washed out with water until bromine ions had disappeared from the wash-waters, and they were dried to constant weight.

In addition to trivial reactions of lignin with bromine [1], the bromination of the HAL probably also takes place through the addition of bromine to the unsaturated keto amines (II) formed from the β-diketone structures (I) after oxidative ammonolysis [8]:



$$R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\underset{\text{I}}{CH_2}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}R' \xrightarrow{NH_3} R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle H}{|}}{C}{=}\overset{\overset{\displaystyle NH_2}{|}}{C}{-}R' \;(\text{II}) \xrightarrow{Br_2} R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}{-}\overset{\overset{\displaystyle NH_2}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}{-}R' \;(\text{III})$$

and also as the result of the enolization [1] in an alkaline medium of compound (III):



$$R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle NH_2}{|}}{C}}{-}R' \rightarrow R{-}\underset{\underset{\displaystyle OH}{|}}{C}{=}\overset{\overset{\displaystyle Br}{|}}{C}{-}\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle NH_2}{|}}{C}}{-}R' \xrightarrow{Br_2} R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}{-}\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle NH_2}{|}}{C}}{-}R' + HBr.$$

The chemical compositions and **contents** of functional groups of the preparations obtained are given below (%)

Content	HAL	Br-HAL	Br-HL
C	57.36	43.14	53.06
H	6.18	3.82	4.25
N	2.71	1.46	—
Br	—	16.73	12.51
	Functional groups		
OCH_3	12.54	2.80	10.07
OH_{tot}	20.96	24.38	18.47
COOH	13.78	16.24	12.38
Amino	0.70	0.76	—
Amido	0.41	—	—

The IR spectra of the Br-HAL showed weak absorption bands of C—Br bonds at 640 cm^{-1}, the presence of which was also confirmed indirectly. The bromine atoms in Br-HAL cause a shift of the characteristic frequencies of the C—H bonds from 810 cm^{-1} in HL to 790 cm^{-1}. In contrast to the spectra of the initial HAL, strong bands appear at 1728 and 1710 cm^{-1} corresponding to the stretching vibrations of —COOH groups and of aromatic β-ketones. The

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absorption bands of $-OCH_3$ groups at 1036-1040 and 2925-2930 cm^{-1} have almost disappeared. The intensity of the absorption band at 3400 cm^{-1} has increased considerably, showing an accumulation of OH groups. As in the chlorination of lignin [11], in the Br-HAL the absorption bands characteristic for a benzene ring at 1505-1515 cm^{-1} have disappeared completely.

Judging from the results of analysis, the functional composition, and the nature of the IR spectra, HAL is considerably more readily brominated than HL, which led to its more complete demethoxylation and oxidation.

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