

It has been shown that under the action of electrochemically activated water a change in the functional composition of the macromolecule of hydrolysis lignin and of lignin sulfonate takes place and, in addition, the latter is desulfurated.

Electrochemically activated water (EAW) has recently become widely used in a whole series of technological processes [1]. Alkaline (catholyte) and acid (anolyte) EAWs are distinguished. The catholyte is capable of giving up electrons, i.e., it possesses reducing properties, containing high concentrations of Na and K in comparison with the initial water. NMR spectroscopy indicates the high energy of this water.

The catholyte is being used successfully in the oil and gas industry for preparing drilling mud both in water and on a hydrocarbon basis. With the aid of EAW it is possible to obtain aqueous solutions of tannin, nitrolignin, brown cola, and other substances without using sodium hydroxide. The catholyte accelerates biological processes, while the anolyte possesses pronounced oxidizing and bactericidal properties [2].

It was of interest to study the influence of EAW on technical lignins — hydrolysis lignin (HL) and lignosulfate (LS) — in connection with the great possibilities of using technical lignins in various branches of industry and their processing into valuable new chemical products [3, 4].

The IR-spectroscopic method is widely used for identifying the most diverse preparations of lignin [5-7], and it was therefore used to evaluate the degree of change in the functional composition of the lignin macromolecule under the action of EAW. The change in the intensity of the absorption bands was found by evaluating the relative optical density (ROD). The baseline was drawn by the fourth method of those described in [8]. The absorption bands at 2845 and 1505 cm^{-1} were taken as an internal standard. The ROD values are given in Table 1.

The absorption band of the stretching vibrations of OH groups at 2940 cm^{-1} had decreased for the modified HL and the modified LS, which is apparently due to the assignment of some of the CH groups to OCH_3 , the amount of which had likewise decreased, and an appreciable fall in the intensity of the 1275 cm^{-1} band due to methoxy groups was also observed.

The intensity of the C=O stretching vibrations of carboxy groups at 1720 cm^{-1} changed both for the HL and for the HS. The reason for this is the reducing action of the EAW, as a result of which some of the C=O groups were reduced to alcoholic OH groups. The intensity of the absorption band at 1720 cm^{-1} decreased, since in this region the absorption bands of carbonyl groups of ketones, aldehydes, quinones, and carboxylic acids are usually superposed [8].

Changes were also observed in the region characteristic for lignosulfonates — 700-500 cm^{-1} , due to the sulfo groups. In the initial LS, four absorption bands, at 735, 655, 615, and 530 cm^{-1} , could be clearly distinguished. The RODs (see Table 1) decreased under the action of the EAW on the LS. It can be stated that under these conditions desulfuration took place the degree of which depended on the structural environment of the sulfo groups in the LS.

No visual changes whatever took place under the action of EAW (catholyte) on the HL and the LS, i.e., the color of the solution did not change to brown, as under the action of a solution of NaOH on lignin, and the solid part of the substance did not dissolve.

TABLE 1. Relative Efficiencies of the Bands of the IR Spectra of Lignin and Lignosulfate Hydrolysis in the Initial State (1) and after Treatment with Electrochemically Activated Water (2)

Wave number, cm^{-1}	Band of the internal standard							
	2845 cm^{-1}				1505 cm^{-1}			
	HL		LS		HL		LS	
	I	II	I	II	I	II	I	II
2940	1,34	1,18	1,34	1,18	1,13	1,0	1,13	1,0
1720	0,8	0,62	0,8	0,62	0,64	0,52	0,64	0,52
1275	1,69	1,45	1,69	1,45	1,36	1,22	1,36	1,22
735	—	—	0,19	0,15	—	—	0,16	0,13
655	—	—	0,37	0,33	—	—	0,3	0,27
615	—	—	0,45	0,38	—	—	0,36	0,32
530	—	—	0,38	0,28	—	—	0,31	0,23

EXPERIMENTAL

Lignin from the processing of sunflower husks containing about 0.5% of unbound sulfuric acid from the Zaporozh'e hydrolysis-yeast factory and birchwood lignosulfate (KBZh TV [Technical Specification] 61-04-225-79) from the Kamo pulp and paper combine were used.

Electrochemically activated water was obtained by the electrolysis of drinking water in an electrolyzer with a diaphragm using stainless steel electrodes at a controlled potential. Electrolysis was carried out until a catholyte with pH 11 had been obtained.

The IR spectra of the samples were measured in a UR-10 spectrophotometer in tablets. The samples of lignin were molded with KBr at a pressure of 5000 kgf/cm^2 (4 mg of substance and 300 mg of KBr). The HL and LS in amounts of 10 g were kept in the EAW at a ratio of 1:0 for 24 h at 20°C, after which they were filtered and dried in a vacuum desiccator over P_2O_5 .

SUMMARY

Under the action of electrochemically activated water a change takes place in the functional composition of the macromolecule of hydrolysis lignin and of lignosulfate and, in addition, the latter is desulfurated.

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