TRANSFORMATIONS OF HYDROLYSIS LIGNIN FROM CONIFEROUS WOOD UNDER CONDITIONS OF ELECTROLYTIC OXIDATION

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The oxidation of lignin by various methods has been described in fairly great detail [1-3]. In the present paper we give the results of a study of the change in some functional groups in the water-insoluble fraction of hydrolysis lignin after electrolytic oxidation in acid and alkaline media by means of IR spectroscopy.

The choice of the electrolytic method of oxidation was due to the unlimited possibility of varying the conditions: By changing the electric potential and current density and also the metal of the anode and the concentration of solvents it is possible to find conditions permitting the attack of only predetermined functional groups while retaining the basic structure of the unit of the lignin macromolecule.

We investigated hydrolysis lignin from coniferous wood obtained from the Verkhne-Tavdinskii Hydrolysis Plant. The electrooxidation of the lignin was performed at a controlled potential with nonautomatic regulation of the potential [4]. The comparison electrode was a saturated calomel half-cell. The potential was checked by a VK-7 cathode voltmeter. The electrolyzer with a diaphragm having a capacity of 200 ml with an external cooler was fitted with a centrifuge pump in polyfluroethylene resin (100 liters/h)[5]. The cathode ($S = 156\ cm^2$) and the anode ($S = 120\ cm^2$) were made from lead of S 000 grade. The solvent was 20% H_2SO_4 (150 ml; $i = 0.5\ A/cm^2$; $\varphi = 7.5$ V) or 5% KOH (150 ml; $i = 0.4\ A/cm^2$; $\varphi = 7.5$ V).

Differences depending on the conditions of electrooxidation were found in the IR spectra of the samples investigated.

In an acid medium, the lignin underwent no fundamental destructive changes and practically no water-soluble fraction was formed. In this case, some analogy can be seen with the oxidation of lignin by air in an alkaline medium to a degree of oxidation of 50% [3]. Thus, for example, an increase in the intensity of the bands at 1710 and 1610 cm^{-1} corresponding to carbonyl groups is observed, together with displacements of them to 1705 and 1602 cm^{-1}, respectively. The former is due to an increase in the number of carboxy groups and the latter to the appearance of a carbonyl group in the enolic form of a structure of the type of the β-diketones. A substantial broadening of the 3400-cm^{-1} band corresponding to the OH group of the lignin, and of the 1215-cm^{-1} band, characterizing the stretching vibration of the phenolic hydroxyls, took place. At this stage of the investigations, it is difficult to explain the marked increase in the intensity of the 2930-cm^{-1} band due to the asymmetric and symmetric stretching vibrations of methylene groups [6, 7], and also of the band of the stretching vibrations of C–O bonds in methoxy groups at 1272 cm^{-1} [3].

In an alkaline medium the electrooxidation of lignin is accompanied by far-reaching changes as a result of which about 50% of the lignin passes into the water-soluble phase. In a study of IR spectra, attention is drawn to the absence of any bands whatever in the 1800-1600-cm^{-1} region that is most characteristic for lignin. This shows that in the process of oxidative electrolysis the oxidation of the carbonyl groups to carboxy groups took place, and the appearance of very weak bands in the 1550-and 1400-cm^{-1} region corresponding to the asymmetric and symmetric stretching vibrations of COO^- [8] and also the voluminous evolution of CO_2 during the electrolysis process is explained by the fact that in addition to oxidative degradation and the formation of carboxy groups, these groups underwent decarboxylation, i.e., the electrolysis of lignin in an alkaline medium takes place by the Kolbe reaction [9]:

$$2R-COO^- \rightarrow 2CO_2 + R-R.$$

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The considerable decrease in the intensity of the 1275-cm^{-1} band shows a demethyloxylation of the lignin, while the accumulation of phenolic OH groups is confirmed by an increase in the intensity of the band in the 1220-cm^{-1} region. A new band is observed in the 682 cm^{-1}-region the appearance of which can probably be referred to the formation during the electrooxidation of lignin of structures of the type of 1,3,5-trisubstituted aromatic systems [8].

Thus, it may be concluded that the medium (solvent) has a substantial influence on the electrooxidation of lignin.

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A STUDY OF DIOXANE AND HYDROLYSIS LIGNINS FROM THE SEED HULLS OF THE COTTON PLANT

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The seed hulls of the cotton plant are a raw material for the hydrolysis industry. At the present time, investigations are being performed on the use of hydrolysis lignin in the national economy [1].

Natural lignin from the seed hulls of the cotton plant has been little studied chemically [2]. The investigation of this lignin is of interest because its formation takes place without a direct connection with the cambial layer of the plant. The functions that this lignin fulfills – the protection of the seed kernel from mechanical damage and its capacity for swelling during growth – are different from the functions of the lignin in the stems and pods of the cotton plant.

From the comminuted (0.25 mm) seed hulls of the cotton plant of variety 108-F which had previously been extracted with a mixture of ethanol and benzene (1 : 1), we isolated the dioxane lignin (DLA) by a modifidation of Pepper's method [3] with a yield of 3.8% on the initial material (about 17% on the Komarov lignin).

After purification by Björkman's method, the DLA contained 2.8% of carbohydrates and consisted of an amorphous powder soluble in the usual solvents for lignins and readily soluble in water. Its UV spectrum, taken in aqueous dioxane, was typical for cotton lignins: λ_{max} 280 nm and 330 nm (shoulder) ($\log \varepsilon$ 3.5; c $2.675 \cdot 10^{-4}$ M). The IR spectrum (tablets of KBr) had absorption bands at (cm^{-1}) 3400 (OH), 1710 (carbonyls), 1620, 1530 (benzene rings), and 1470 (methoxyls).

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