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THE MECHANISM OF THE FORMATION OF QUINONIC ACIDS IN THE OXIDATION OF THE BARK OF THE SIBERIAN LARCH. II

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The results of a chemical and spectroscopic study of the oxidative degradation of the bark of the Siberian larch have shown that the oxidation of the lignin of the bark to quinonic acids takes place through an intermediate complex with a quinoid system of bonds. This paper presents ideas on the mechanism of the formation of the latter.

The results of a study of the molecular-weight distribution of the samples (Table 1) shows an increase in molecular weight and a fall in the degree of polydispersity of lignin fraction 1 by the end of the third hour of oxidation. This is explained both by a fractionation of the lignin, since its low-molecular-weight fraction (fraction 2) does not precipitate when an alkaline extract is acidified, and also by a polycondensation of the radicals formed. The molecular weights of samples of fraction 1 have been calculated by means of Eq. (1) taking into account the maximum possible increase in them through the effect of fractional dissolution [6]:

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$$M = M_1 W_1 + M_2 W_2, \qquad (1)$$

where M is the molecular weight of the dioxane lignin of larch bark, M_1 and M_2 are the molecular weights of the lignins of lignin fractions 1 and 2, respectively, and W_1 and W_2 are the proportions by weight of the lignins of fractions 1 and 2.

According to the calculations, the molecular weights of the lignins of fraction 1 after oxidation for two and three hours should be 10,500 and 9900, respectively, through fractional dissolution. The values found – 11,300 and 13,800 – are far higher. This indicates that the increase in the molecular weight of the lignin of fraction 1 during oxidation is to a considerable extent due to condensation processes.

Derivatographic investigations have confirmed this conclusion. Thermography enables the heat effects caused by condensation and by the cleavage of the lignin bonds to be detected and studied and, consequently, provides the possibility of following the formation of condensed systems. The differential thermal analysis curves are given in Figs. 1 and 2.

An exothermic effect in the 400–420°C region (see Fig. 1) characterizes the formation of condensed lattices of cyclic polymerized carbon [7]. The nature of the change in the DTA curves shows that with an increase in the time of treatment of the bark the exothermic maximum in this region first appears less distinctly (1st hour) and then disappears completely (2nd and 3rd hours). By comparing this with the nature of the heat stability of the samples (DTG curves) it may be concluded that in the samples subjected to thermography the condensation processes took place before they were tested in the derivatograph. This could be the case only in the initial stages of oxidation under the action of a chemical agent. It is just in the first three hours that intensive demethoxylation of the lignin accompanied by the occurrence of condensation processes takes place. This characteristic has been found not only during a chemical action on bark but also during its pyrolysis [8].

Judging from the DTA curves, the nature of the products obtained after reaction for three hours is quite different from that of the initial lignin. The results obtained are confirmed by a chemical analysis of the alkali lignin. The latter is characterized by a considerable content of carboxy groups, a high "oxidative equivalent," and a large molecular weight. Spectral analysis also showed a change in the nature of the lignin during oxidation: the aromatic system of bonds changes into a cyclohexadienone system.

The temperature range within which the thermal decomposition of the substance takes place definitely characterizes the degree or orderedness and homogeneity of its structure [9]. The zone of active thermal decomposition of lignin oxidized for three hours contracts to 75°C in comparison with the 110°C for the lignin of the initial bark (see Fig. 2), which shows a compaction of the structural units of the latter.

In the second stage of the reaction the intermediate complex begins to decompose. After 4 h, the amount of fraction 1 of the lignin in the solid residue and its molecular weight falls sharply and the degree of polydispersity rises (see Table 1). Furthermore, a considerable amount of acidic products of quinone structure appears in the oxidate [10].

The nature of the derivatographic curves also shows that the degradation is accompanied by a disturbance in the orderedness of the lignin structure: the zone of active thermal decomposition of the samples widens to 120–125°C, and an exothermic maximum again appears in the 400–420°C region which is distinct after the 4th

TABLE 1. Characteristics of the Oxidized Samples of Lignin

Time of oxidation, h	Fraction 1			Fraction 2		
	weight-average molecular wt, $\overline{M}_w$	number-average molecular wt, $\overline{M}_n$	degree of polydispersity γ	weight-average molecular wt, $\overline{M}_w$	number-average molecular wt, $\overline{M}_n$	degree of polydispersity γ
1	8200	5600	1,4	1600	1000	1,7
2	11300	10800	1,1	1900	1100	1,7
3	13800	13000	1,0	1600	1000	1,6
4	8100	5400	1,5	4300	3700	1,2
5	7700	4200	1,8	1800	1200	1,5
6	7300	3400	2,1	1900	1300	1,5
Dioxane lignin of larch bark	9500	3900	2,4			
Phenolic acids of larch bark				1700	1500	1,1

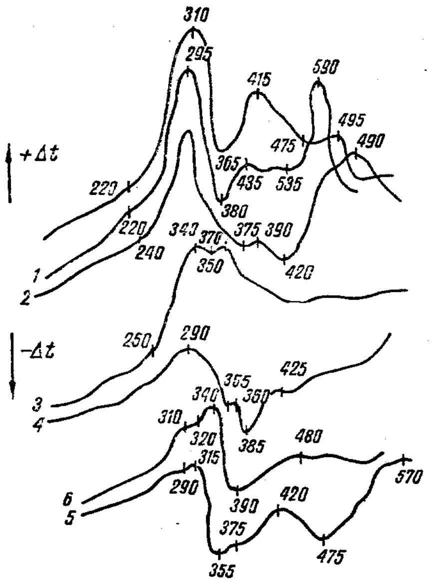

Fig. 1

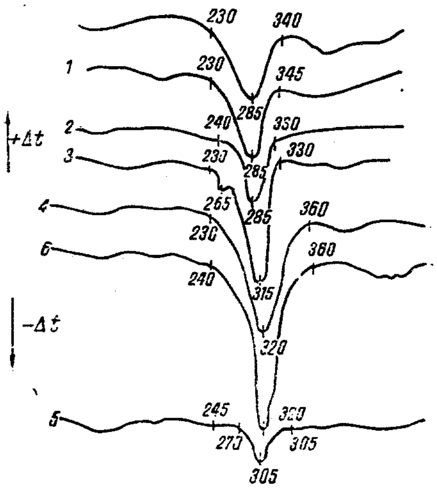

Fig. 2

Fig. 1. DTA curves of samples of oxidized bark (the numbers of the curves correspond to the time of oxidation, h).

Fig. 2. DTG curves of samples of oxidized bark (the numbers of the curves correspond to the time of oxidation, h).

and 5th hours of reaction and is flattened out after the 6th hour. This phenomenon reflects the tendency of the system to adopt a new orderedness of the structural units of the lignin but now with a lower molecular weight.

EXPERIMENTAL

The disappearance of the band at 1515 cm^{-1} in the IR spectra of oxidized lignin and the displacement of the absorption maximum in the long-wave direction in the UV spectra can be explained both by the conversion of the aromatic system of bonds into a cyclohexadienone system and by the occurrence of simultaneous condensation processes [1, 2]. If such processes take place, then in the early stages of oxidation one may expect a considerable increase in the molecular weight of the oxidized lignin. To check this hypothesis we used gel chromatography [3].

Samples of oxidized lignin obtained after reaction for different times (fractions 1 and 2) were passed through a chromatographic column 15 mm in diameter containing a layer of gel (G-75) 270 mm high. For the investigation, 3% solutions of the lignin samples were prepared in dimethyl sulfoxide. The amounts of lignin in the fractions collected were estimated from the optical densities of the solutions, which were determined on a SF-16 spectrophotometer.

Lignin possessing a considerable reactivity cannot be isolated in the native state even from wood, and therefore we used the method of differential thermogravimetry with a compensating standard [4]. This method enables derivatograms of the lignin to be obtained without its isolation from the cell wall, which reduces the possibility of the appearance of side effects connected with the use of chemical reagents. Samples of oxidized bark were investigated in a derivatograph on the Paulik-Paulik-Erdey system. The sensitivity of the DTA recording was 1:10 and of the DTG recording 1:10, the rate of rise of temperature was 6°C/min, and the weight of the sample 0.1 g. As the compensating standard we used a preparation of holocellulose isolated from bark [5] and subjected to a treatment similar to that of the sample investigated. The differential thermal analysis curves are shown in Fig. 1 and 2.

SUMMARY

1. It has been shown by chemical and physicochemical methods of analysis that the oxidation of bark lignin by atmospheric oxygen in nitric acid is accompanied by oxidative-condensation and oxidative-hydrolytic processes.

2. Oxidative condensation leads to the formation of a stable intermediate product with a quinoid system of bonds. This complex fragments under the oxidative-hydrolytic action of the medium. The oligomers obtained undergo oxidative-condensation transformations more readily. Such reactions probably take place successively as far as the formation of relatively simple compounds.

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