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IR Absorption Spectra of Cellulose Obtained from Ozonated Wood

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Abstract—The kinetic curves of ozone absorption by aspen wood were obtained. Processing of wood with peracetic acid gave cellulose samples. The yields of ozonated wood, water-soluble compounds, and cellulose were determined for the samples corresponding to different consumptions of ozone. The IR absorption spectra of wood and cellulose isolated from ozonated wood were analyzed. The supramolecular structure of cellulose can be changed by varying the conditions of wood ozonation.

Keywords: ozonated wood, cellulose, IR spectra, supramolecular structure.

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INTRODUCTION

The unique physicochemical properties of cellulose, its inexhaustible supply in recyclable plant raw materials, and its biodegradability have attracted the attention of researchers. In recent years, many publications have appeared on the properties of various modifications of cellulose and methods for their synthesis due to the development of innovation materials for medicine, pharmacology, and engineering [1–5]. There has been growth of interest in environmentally clean technologies for biomass processing, in particular, in the oxidation involving oxygen, ozone, and hydrogen peroxide [6–14].

The effect of ozone on aspen and pine wood was studied in [9–14]. It was shown that ozone causes destruction of lignin (LG) and partial oxidation of wood carbohydrates [9, 10]. The authors of [10, 15] showed that the degree of polymerization of cellulose decreases after prolonged ozonation of aspen, pine, and fir wood. The ozone consumption determines the yield of cellulose and the content of residual LG in the cellulose-containing material obtained in the ozonation of aspen wood [10]. The medium degree of polymerization and molecular mass distribution of ozonated wood cellulose was reported to depend on the ozone consumption [10].

The goal of this study was to study the structure of cellulose obtained from ozonated wood by IR spectroscopy and to correlate the transformations of wood under the action of ozone with the structure of cellulose obtained from it.

EXPERIMENTAL

Cellulose was prepared from aspen wood (0.315–0.63-mm fraction) and ozonated wood. Wood with a moisture content (MC) of 65, 80, and 120% was ozonated at a flow rate of the ozone–oxygen mixture of 4 L/h and ozone concentration of 90 mg/L by the procedure of [9]. Cellulose was isolated from ozonated washed wood with a 15% peracetic acid (PAA) solution by the procedure of [16].

The yield of ozonation products (Y_1) was calculated as the ratio of the mass of the absolutely dry ozonated sample to the mass of initial oven dry wood (ODW). To determine the yield of the insoluble products of ozonation (Y_2), we determined the mass of the oven dry sample washed with water. The yield of water-soluble compounds Y_s was calculated as $Y_s = Y_1 - Y_2$. The cellulose content in the wood sample (c_w) was determined as the ratio of the mass of absolutely dry cellulose to the mass of the absolutely dry, preliminarily washed sample of the initial or ozonated wood. The cellulose yield (Y_c) was calculated as the ratio of the mass of absolutely dry cellulose to the mass of ODW. The decrease in the mass of the sample after processing with PAA was $Y_{PAA} = Y_2 - Y_c$. The mass of oven dry samples was determined by the procedure of [17].

The IR spectra were recorded on an Equinox 55/S (Bruker) IR Fourier spectrometer. To determine the absorbance (A) of IR bands, the model base line was subtracted from the experimental spectrum, and the overall complex spectrum was approximated using the individual Gaussian components. To measure the IR spectra of wood and cellulose, we prepared pellets with KBr and 0.3% $K_4Fe(CN)_6$ (external standard). The sample to KBr ratio was 1 : 850 for wood and

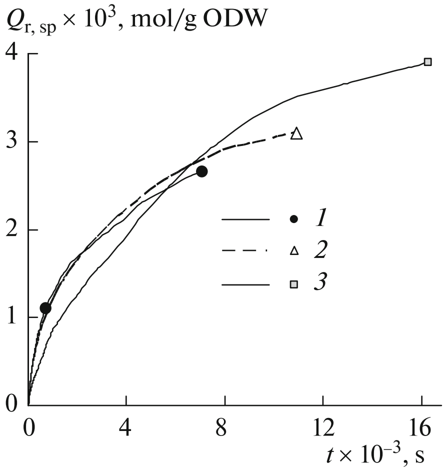

Fig. 1. Kinetic curves of ozone absorption by the aspen wood samples with water contents of (*1*) 65, (*2*) 80, and (*3*) 120%.

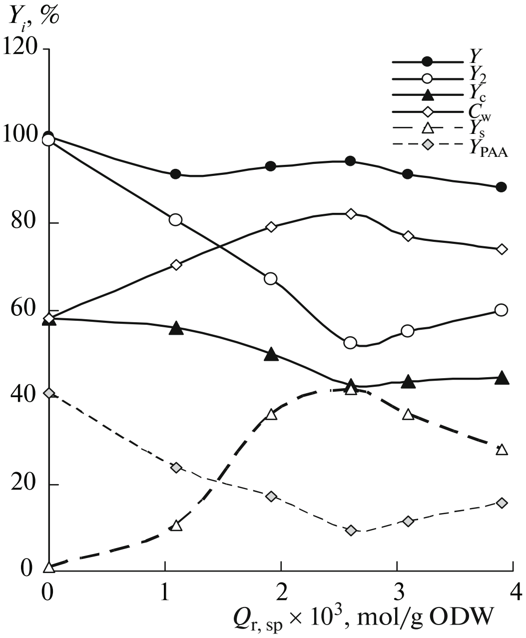

Fig. 2. Dependences of the yields Y_1, Y_2, Y_s, and Y_c; cellulose contents in wood c_w; and decrease in the mass of the sample after treatment with PAA on the ozone consumption during wood ozonation.

1 : 160 for cellulose. The spectrum of KBr with $K_4Fe(CN)_6$ was subtracted from the obtained spectra of wood and cellulose. The relative absorbance of the band (A_ν) was determined as the ratio of the absorbance of the band with a wave number ν to the absorbance of the band $\nu = 2072$ cm^{-1} corresponding to $K_4Fe(CN)_6$. The IR spectra of cellulose were analyzed using the parameters A_{1372}/A_{2899}, A_{1429}/A_{898}, and the half-width of absorption Δ (cm^{-1}).

The hydrogen bond energy was calculated by the equation

$$E_H = (1/K)[(\nu_0 - \nu)/\nu_0],$$

where ν_0 is the standard wave number corresponding to the vibrations of free OH groups (3600 cm^{-1}), ν is the wave number of bound OH groups, and $K = 1.6 \times 10^{-2}$ kcal [18].

RESULTS AND DISCUSSION

Wood Ozonation. Product Yields

Figure 1 shows the kinetic curves of ozone absorption by the aspen wood samples with 65, 80, and 120% water. As MC increases, the ozone absorption rate decreases, and the time of ozonation and the maximum ozone consumption increase. The dots mark the values of ozone consumption corresponding to the ozonated wood samples under study. The end of ozonation corresponds to the w3, w4, and w5 samples. The w2 sample was obtained by ozonation of wood with MC = 65% for 850 s; w1 is the initial wood sample (Table 1).

Figure 2 presents the yields of ozonated wood relative to ODW. The yield Y_1 depends on the composition of the low-molecular products of oxidation and decreases in the range of ozone consumptions corresponding to the formation of formic and glyoxalic acids and other volatile compounds. It increased in the range of consumptions corresponding to the predominant formation of oxalic acid and its salts. These considerations are confirmed by the data on the composi-

Table 1

Sample	MC, %	$Q_{r,sp} \times 10^3$ mol/g ODW	Position of absorption band, cm^{-1}				$\Delta\nu_{OH}$, cm^{-1}
			ν_{arom}	ν_{CH}	ν_{COO}	ν_{OH}	
w1	–	0	1506, 1590, 1425	2921	1739	3429	382
w2	65	1.1	1506, 1590, 1425	2917	1738	3428	386
w3	65	2.6	–	2903	1737	3422	400
w4	80	3.1	–	2902	1738	3410	415
w5	120	3.9	–	2902	1738	3409	418

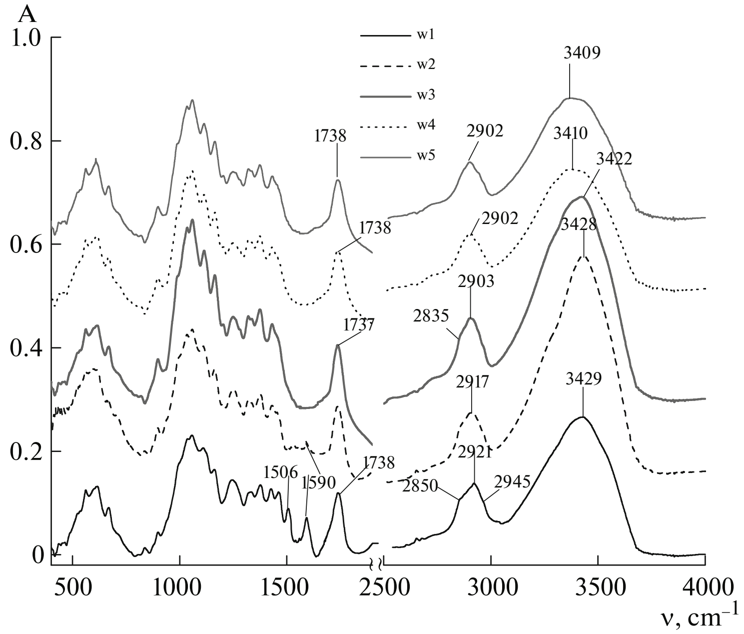

Fig. 3. IR absorption spectra of the ozonated wood samples. The spectral notation corresponds to the samples in Table 1.

tion of the solutions of the low-molecular ozonation products of aspen wood [14]. The mass decreased after washing with water and removing the water-soluble compounds from the surface. The lowest yield Y_2 was observed at a specific ozone consumption of $Q_{\mathrm{r,sp}} = 2.6 \times 10^{-3}$ mol/g ODW (w3), which corresponds to the highest yield of water-soluble nonvolatile products of wood oxidation (Y_s) (Fig. 2).

Figure 2 shows the dependences of the yield of cellulose (Y_c) relative to ODW and the dependence of the cellulose content c_w in the ozonated washed wood samples versus the specific ozone consumption. The mass of the sample decreased by 40% (Fig. 2) after its treatment with a PAA solution, which corresponds to the destruction of lignin and some part of hemicelluloses (HCs). The authors of [17] noted that though cellulose is hydrolyzed with difficulty, any reagent capable of eliminating lignin to a sufficient degree also has a certain destroying effect on cellulose. The data of Fig. 2 show that the w3 sample is characterized by the lowest yield of wood after ozonation relative to other samples ($Y_2 = 52.2\%$), the highest yield of water-soluble compounds ($Y_\mathrm{s} = 41.8\%$), the highest content of cellulose ($c_\mathrm{w} = 82\%$), and the lowest amount of substances that can be removed with an peracetic acid solution ($Y_{\mathrm{PAA}} = 9.4\%$). All the wood samples were subjected to treatment with PAA; therefore, the data of Fig. 2 indicate that preliminary ozonation has the most pronounced effect on LG, HC, and possibly wood cellulose in the case of the w3 sample.

The cellulose content in aspen wood was ~46% [19]; therefore, the higher yields of cellulose obtained for $Q_{\mathrm{r,sp}} \leqslant 1.9 \times 10^{-3}$ mol/g ODW are explained by a considerable hemicellulose impurity, which corresponds to "high-yield cellulose." For the w4 and w5 samples, the yields of cellulose were $Y_\mathrm{c} = 43.5$ and 44.4%, respectively. The lowest value of $Y_\mathrm{c} = 42.8\%$ was obtained for $Q_{\mathrm{r,sp}} = 2.6 \times 10^{-3}$ mol/g ODW. In the ozone consumption range $Q_{\mathrm{r,sp}} = (2.6–3.9) \times 10^{-3}$ mol/g ODW, not only lignin and hemicelluloses, but also some part of cellulose undergo ozone and PAA destruction.

IR Absorption Spectra of Wood

Figure 3 shows the IR absorption spectra of wood. Table 1 lists the positions of the maxima and the half-widths of the absorption bands of the OH stretching vibrations. Figure 4 presents the dependences of the relative optical density of some IR absorption bands of wood on the ozone consumption. The optical densities of the 1590, 1506, and 1425 cm^{-1} bands (C–C vibrations of the aromatic rings) decreased when the ozone consumption increased because of the oxidative destruction of lignin (Figs. 3 and 4). This agrees with the data of [10], which showed that the LG content in ozonated wood was over 10% for $Q_{\mathrm{r,sp}} = 1.0 \times 10^{-3}$ mol/g ODW, 3–4% for $Q_{\mathrm{r,sp}} = 2.5 \times 10^{-3}$ mol/g ODW, and 2–2.5% for $Q_{\mathrm{r,sp}} = 4.0 \times 10^{-3}$ mol/g ODW.

Earlier [9, 14], it was noted that the destruction of the aromatic structures of LG during wood ozonation is accompanied by the formation of low-molecular carboxylic acids. Figures 3 and 4 show that the carboxyl groups of wood fiber are characterized by

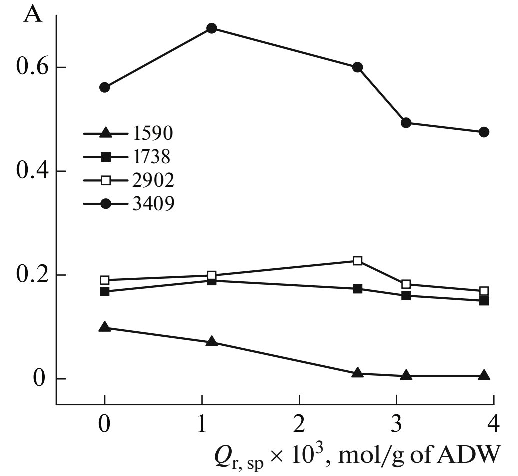

Fig. 4. Dependences of the relative absorbance of wood IR bands on the specific ozone consumption. The marked positions of maxima refer to the w5 sample.

absorption band at 1737–1738 cm^{-1}, and their content is low and decreased at increased ozone consumption.

The absorption band corresponding to the C–H stretching vibrations in the spectrum of the initial wood has a maximum at 2921 cm^{-1}. The band is a superposition of the bands that relate to the C–H vibrations in the methyl and methylene groups of lignin (the shoulders at 2850 and 2945 cm^{-1}) and $\nu_{\text{C–H}}$ in the methylene and methine groups of cellulose (~2900 cm^{-1}) and hemicelluloses (2835 and 2935 cm^{-1}) [20]. As the ozone consumption increases, the maximum of the absorption band shifts to 2902 cm^{-1}, which is explained by a decrease in the LG and HC contents reported in [12] and an increase in the cellulose content in the sample after ozonation. The relative absorbance at the maximum of the band $\nu_{\text{C–H}}$ increased at increased ozone consumption and had its maximum value at $Q_{\text{r,sp}} = 2.6 \times 10^{-3}$ mol/g ODW. This result agrees with the above-mentioned high cellulose content in the w3 sample (Fig. 2).

The highest relative absorbance of OH stretching vibrations at 3428 cm^{-1} was observed for the w2 sample (Fig. 4). This is probably caused by hydrogen bonding between the hydroxyls and the carboxyl groups of ozonated wood. According to Fig. 3 and Table 1, the relative absorbance decreases, the ν_{OH} band shifts toward lower wave numbers, and the halfwidth of the band increases in the spectra of the w3, w4, and w5 samples as the amount of absorbed ozone increases.

Thus, the changes in the IR spectra of wood during ozonation are explained by the removal of lignin and some part of hemicelluloses from wood. The w3, w4, and w5 samples are characterized by an inhomogeneous (in the hydrogen bond energy) structure and formation of stronger hydrogen bonds when the specific ozone consumption increases.

IR Absorption Spectra of Cellulose

Figure 5 presents the IR absorption spectra of cellulose samples isolated from ozonated wood. Table 2

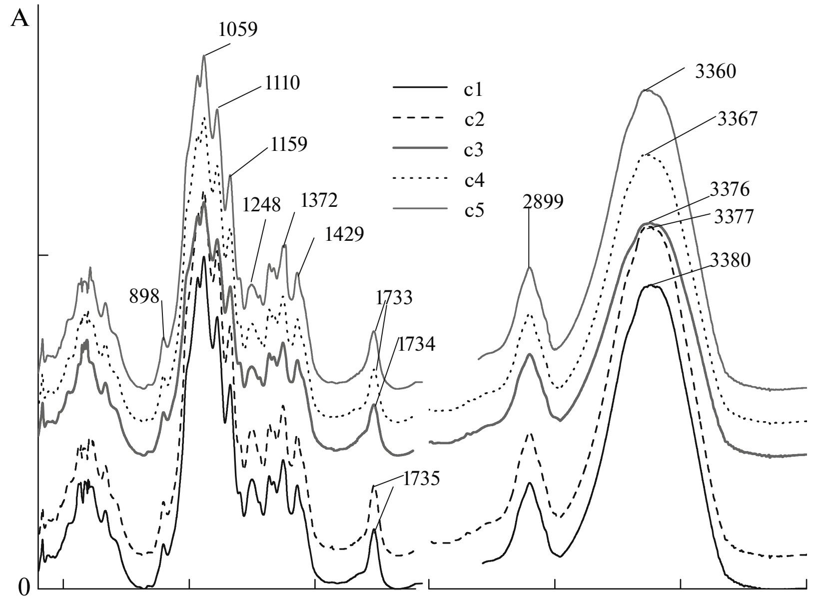

Fig. 5. IR absorption spectra of cellulose samples isolated from ozonated wood. The spectral notation corresponds to the sample in Table 2.

Table 2

Sample	$Q_{r,sp} \times 10^3$, mol/g ODW	ν_{OH}, cm^{-1}	ν_{COO}, cm^{-1}	$\Delta(\nu_{O-H})$, cm^{-1}	A_{1372}/A_{2899}	A_{1429}/A_{898}	E_H, kcal
c1	0	3380	1735	352	1.22	2.31	3.82
c2	1.1	3377	1735	369	1.21	2.25	3.87
c3	2.6	3376	1734	390	1.07	2.18	3.88
c4	3.1	3367	1733	374	1.22	2.23	4.04
c5	3.9	3360	1733	369	1.19	2.29	4.17

lists the positions of the absorption maxima and several parameters of IR spectra. All the spectra are basically identical and are characterized by the 898, 1059, 1110, 1159, 1248, 1372, 1429, and 2899 cm^{-1} bands typical for cellulose [3, 5, 20]. The wide absorption band in the range 3700–3100 cm^{-1} is related to the stretching vibrations of OH groups involved in hydrogen bonding. The range of low wave numbers characterizes the hydroxyl groups involved in stronger (presumably, intramolecular) interactions, and the range of high wave numbers is characteristic for hydroxyls involved in weaker (intermolecular) interactions.

The 2899 cm^{-1} band relates to the stretching C–H vibrations of the methylene and methine groups of cellulose; the absorption bands at 1429 and 898 cm^{-1} are due to the scissor vibrations of the methylene groups and the C1 atom and the vibrations of its four surrounding atoms in the β-glycoside structures [20]. The spectrum of the c1 sample obtained from the starting wood contains signals of HC (the 2835 cm^{-1} shoulder), which agrees with the high yield Y_c for the w1 sample (Fig. 2).

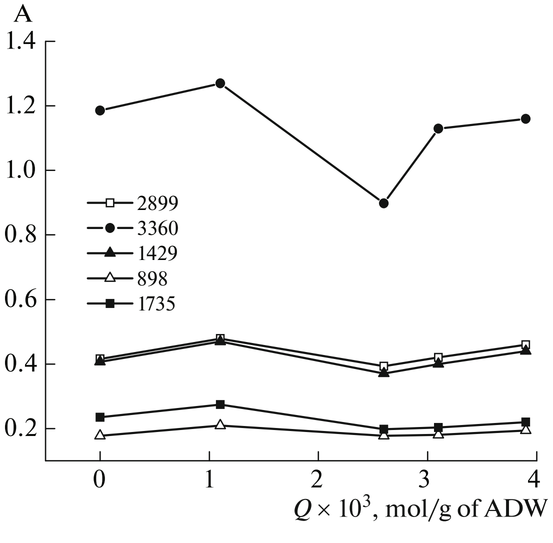

Fig. 6. Dependences of the relative absorbance of the cellulose IR bands on the specific consumption of ozone. The marked positions of maxima refer to the c5 sample.

Figure 6 presents the dependences of the relative absorbance of the cellulose IR bands on the ozone consumption. In the spectrum of the c2 sample ($Q_{r,sp} = 1.1 \times 10^{-3}$ mol/g ODW), A_{1735} (the stretching vibrations of carboxyl groups) increases.

The ratios A_{1372}/A_{2899} and A_{1429}/A_{898} are used for evaluating the crystallinity of cellulose because the 1429 cm^{-1} band is considered the "crystallinity" band, while the 898 cm^{-1} band is the "amorphism" band [3, 5, 20]. The spectrum of c3 is characterized by the lowest A_{1429}/A_{898} and A_{1372}/A_{2899}, which suggests that the amorphous regions of the cellulose sample increase. For c3, A_{2899} and A_{3376} decreased, which was observed during the amorphization of cellulose [5]. The low value of A_{3376} and the high value of the half-width of the ν_{OH} (390 cm^{-1}) band (Table 2) point to the structural nonhomogeneity of the sample.

For the c4 and c5 samples, the relative optical densities of the 2899, 1372, and 1429 cm^{-1} bands and A_{1429}/A_{898} and A_{1372}/A_{2899} increase (Table 2, Fig. 6). The absorption band of the OH stretching vibrations shifts toward shorter wave numbers, which is evidence for the formation of stronger hydrogen bonds in the structure of cellulose. Table 2 lists the hydrogen bond energies, which point to their increased strength at increased ozone consumption; the decreased half-width of the ν_{OH} band suggests that the structural nonhomogeneity of cellulose increased compared with that of the c3 sample. The c5 sample ($Q_{r,sp} = 3.9 \times 10^{-3}$ mol/g ODW) is characterized by the highest degree of ordering.

Thus, "high-yield cellulose" with high HC content and a "loose," but relatively homogeneous structure was obtained from the initial wood. Cellulose c3 with a "loose" and nonhomogeneous structure was obtained from ozonated wood (w3) with a destroyed structure, and the c5 sample with the most homogeneous structure and strongest hydrogen bonds was obtained from the w5 sample with a nonhomogeneous structure and stronger hydrogen bonds. Since the same PAA treatment was performed for all wood samples, the above structural features of cellulose can be explained by addressing the results of the physicochemical study of wood ozonation.

Effect of Wood Ozonation Conditions on the Structure of Cellulose

The physicochemical regularities of wood ozonation were considered in [9–12]. The water content in wood was found to determine the specific ozone consumption corresponding to the end of the reaction and also the composition of the products formed during wood ozonation. The specific ozone consumption was shown to be the main factor governing the degree of wood transformations [9–14]. However, the conditions of ozonation also play an important role during wood transformations under the action of ozone: the water content in wood, gas flow rate, ozone concentration, and ozonation time. It was shown that at water contents above the fiber saturation point (MC = 28%), the transformations of swelled wood involve ozone dissolved in water [9, 10]. It was noted [11] that under the given experimental conditions, the ozone absorption rate is maximum in ozonation of wood with MC = 55–60%, when the thickness of the water layer on the surface of the polymer wood composite is a few nanometers on the average. Ozone reacts with the functional groups of LG, hemicelluloses, and cellulose in amorphous regions accessible for the reagent [11, 12]. At MC = 65%, which is close to the above value, the wood polymer is profoundly destroyed, which corresponds to the low yield of wood after ozonation Y_2, high yield of soluble compounds, and low yield of cellulose Y_c. This agrees with the conclusions about the structural peculiarities of cellulose obtained from the w3 sample. A consequence of deep destruction of wood LG and hemicelluloses during ozonation is high cellulose content c_w in the w3 sample.

The fraction of ozone absorbed in the aqueous phase in reactions with dissolved products of ozonation increased at high MC values. In this case, the ozone concentration on the polymer surface decreased, the reactions involve the most reactive groups (primarily, the aromatic structures of lignin), and carbohydrates are destroyed to a lesser degree. Deep transformations of compounds in solution result in a decrease in the fraction of the soluble products of ozonation and an increase in Y_2 at increased ozone consumption.

Treatment with PAA leads to delignification of cellulose and hydrolysis of carbohydrates (hemicelluloses and, to a lesser degree, cellulose). Ozonation causes an increase in the wood surface area [13], including the surface accessible for the peroxy reagent and thus favors a more effective action of peracetic acid; therefore, deep destruction of wood during treatment with ozone creates conditions for the preparation of cellulose with a disordered structure. The results of the present study show that the conditions of wood ozonation allow variation of the supramolecular structure of cellulose obtained from ozonated wood.

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