

Delignification of softwood by ozonation*

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Abstract: Ozonation of aspen sawdust of various moisture content (MC) values was investigated. Ozone consumption corresponding to the completion of the ozonation process was shown to be governed by the wood MC. Cellulose-containing material of a low (1–3 %) residual lignin content (LC) was produced under ozonation. It is proposed that ozone dissolved in water is responsible for delignification. The conversion of lignin during softwood ozonation was investigated by UV and Fourier transform-infrared (FT-IR) spectroscopy. The pathways of lignin transformations are influenced by wood MC value.

Keywords: FT-IR spectra of wood; lignin UV second derivative spectra; softwood delignification; softwood lignin conversions; wood ozonation.

INTRODUCTION

Wood polymer fiber consists of carbohydrates (cellulose, hemicellulose) and lignin. The structural subunits of cellulose and hemicellulose comprise monosaccharide monomers, whereas lignin is irregular polymer constituted by phenylpropane monomers linked through 11 types of covalent bonds [1,2]. These complex combinations of structure with different functions provide scope for a variety of oxidative degradation pathways. Ozone is a powerful oxidant and generally reacts with organic substrates by ionic cycloaddition and subsequent cleavage of olefinic and aromatic bonds [3–5]. This has been reported to be the major reaction pathway for lignin model compounds [3].

Reactions of ozone with lignin and its derivative, lignin-sulfonate, have been studied for several years [6–10], and the kinetics of lignin oxidation by ozone in acidic and basic solutions has received attention [7–9]. Lignin oxidation by ozone in acid media is accompanied by destruction of aromatic rings and formation of a number of aliphatic carbon acids. Oxidation of the powder lignin results in condensation processes and formation polyaromatic structures [7].

The action of ozone on lignocellulosic materials (LCMs) has also been investigated [10–17]. Ozonation of lignin-rich cellulosic materials was carried out with particular attention to the evolution of water-soluble reaction products during oxidation [10–13]. For example, ozonation of corn stalks results in formation of various carbon acids (glycolic, oxalic, malonic, glyoxilic, malic) and aldehydes (hydroxybenzaldehyde, vanillin) [12]. The range of ozonation products is influenced by the nature of the substrate as well as the sample moisture content (MC) [10–12].

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With the high-molecular LCM component, cellulose fiber, there are a lot of investigations devoted to an influence of ozone on its properties: ozone moderately increases delignification degree, content of carboxylic acid groups of cellulose from pulp, and decreases polymerization degree of cellulose fiber. That is why the viscosity of solutions, strength and elasticity of the fiber, absorption activity, and chemical properties of ozonated cellulose change considerably [14,17,18]. Various factors (MC of the pulp, pH value, pulp consistency, presence of additives, ozone consumption value) were found to influence the degree of LCM delignification as well as the strength and brightness of the resultant cellulose product [14–18].

Nowadays, ozone is used in pulp plants in America and Europe in the stage of paper pulp bleaching in combination with other bleaching agents [18]. Ozone is rather selective toward lignin oxidation. There exists a critical level of lignin removal from the pulp. If it is exceeded, carbohydrates begin to destruct. It is marked [18] that this level is due to the accessibility of lignin and transport of ozone to lignin. Free radicals from the decomposition of ozone or its intermediates frequently are blamed for poor selectivity of the pulp bleaching [14,18].

It can, therefore, be reasoned that experience based upon direct ozonation of LCMs should offer more general scope to convert vegetable raw materials into cellulose and various low-molecular-weight, water-soluble compounds. As the only by-product of ozone conversion is oxygen, it can also be argued that ozonation offers an environment friendly pathway for processing of vegetable raw materials.

This paper is the first part of an investigation devoted to transformations of the principle wood components during direct wood ozonation. The main goal of this work is to study how the MC of wood influences the delignification of aspen wood (*Populus tremula*) during ozonation, to clarify the role of water in the delignification process, and to investigate lignin conversions under action of ozone in situ. Wood transformations by ozone were studied with the aid of Fourier transform-infrared (FT-IR) spectroscopy. Lignin conversions during ozonation of the softwood were investigated by UV and FT-IR spectroscopy.

EXPERIMENTAL

Materials and methods

Ozonation of aspen sawdust samples (particle size 0.31–0.61 mm) of varying MC was investigated. The MC value is defined as water mass divided by the mass of oven-dry wood (m_{odw}), $m_{\text{odw}} = (m_0 - m_{\text{H}_2\text{O}})$, where m_0 and $m_{\text{H}_2\text{O}}$ are the mass of the sample and water present there.

$$\text{MC (\%)} = (m_{\text{H}_2\text{O}}/m_{\text{odw}}) \times 100$$

To obtain wood samples of different MC, an amount of water corresponding to $\text{MC} \approx 160\%$ was added to the air-dried sawdust. Then the sample was pressurized for 170 h at 25 °C inside a closed chamber. To obtain the samples of the $\text{MC} < 160\%$, the initial swelled wood sample was dried in air and pressurized for 170 h in a desiccator at 25 °C. Water content was controlled by gravimetric measurements. To determine m_{odw} of the sample, the sawdust was dried at (105 ± 2) °C, then cooled in the desiccator with P_2O_5 and weighed. The procedure was continued until the sample mass became constant.

The effect of ozone on sawdust samples within the MC range of $8 \div 160\%$ was studied. Ozonation of samples was carried out in a flow unit equipped by the reactor with a transit layer at $t = 25$ °C. Ozone was synthesized from oxygen using a “Medozon-03/8” ozonizer. Ozone consumption was controlled by ozone concentration measurements in the reactor inlet and outlet. Ozone concentration was determined by means of a “Medozon 254/3” ozone analyzer. Ozone concentration in the reactor inlet was 80–90 mg/l. The gas mixture flow rate was equal to 4 l/h, and the sample mass was 1.5–1.6 g. The reaction was thought to be complete if ozone concentration in the outlet of the reactor with an investigated sample coincided with the final ozone concentration of the idle experiment. In the idle ex-

periment, the sawdust oxidized earlier by ozone was used as the substrate. The bulk density of this substrate should be identical to that of the investigating sample.

Residual lignin content (LC) in initial and ozonated samples was determined as the acid-undissolved LC. Five ml of 72 % H_2SO_4 solution was added to the sample sawdust (0.3 g) and kept for 2.5 h under mixing. Then the lignin and H_2SO_4 mixture was transported into a 250-ml vessel, and lignin was washed with water (60 ml). The mixture was boiled for 1 h. Lignin was filtered off and washed thoroughly with water until the filtrate was neutral. The filtered lignin was dried in air at 25 °C for 24 h, and was kept in the desiccator with NaOH.

To obtain dioxan lignin (DL), the wood sample was boiled for 1 h in dioxan in the presence of catalytic HCl amounts.

Spectroscopic measurements

UV spectra of aqueous DL solutions were recorded with Cary 3E (Varian) using signal accumulation conditions. Accumulation time was 1 s, scan interval was 0.5 nm, and scan rate was 30 nm/min. Five spectra were measured for each solution. The second derivative spectrum computation followed averaging-out and smoothing of the signal under standard procedures.

FT-IR spectra of wood sawdust and DL were recorded by spectrometer Equinox 55/C (Bruker) with the 4 cm^{-1} resolution. KBr pellets containing wood sawdust (0.1 %) or DL (1 %) were prepared.

RESULTS AND DISCUSSION

Ozone absorption by wood samples

Ozonation kinetic curves of the wood samples of various MC values are shown in Fig. 1a. The kinetic curve of ozone concentration in the idle experiment in the reactor outlet is also shown in Fig. 1a. As seen from Fig. 1a, an increase in water content accompanies noticeable changes of the kinetic curves.

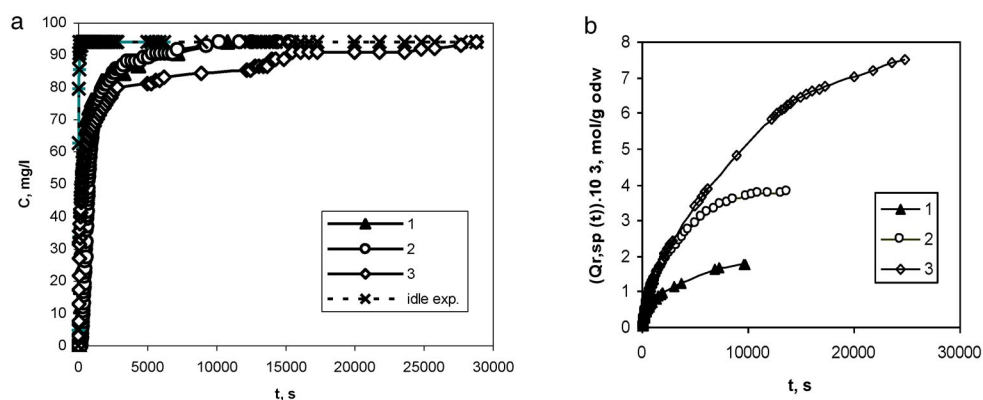


Fig. 1 (a) Kinetic curves of the reactor outlet ozone concentration of wood samples: MC, %: 28 (1), 56 (2), 160 (3). (b) Kinetic curves of the specific ozone consumption of wood samples: MC, %: 28 (1), 56 (2), 160 (3).

Current-specific ozone consumption $[Q_{r,sp}(t)]$ ($\text{mol/g}_{\text{odw}}$) was computed by graphic integration using eq. 1.

In eq. 1, U is the gas mixture flow rate (l/s), c_t and c_t^* are the current ozone concentration (mol/l) in the outlet of the reactor containing the investigated sample and in the idle experiment, respectively.

$$Q_{r,sp}(t) = \frac{U}{m_{odw}} \int_0^t (c_t^* - c_t) dt \quad (1)$$

As seen, $Q_{r,sp}(t)$ is the quantity of ozone consumption during reactions with the substrate at t time and attributed to 1 g of oven-dried wood. It is defined as the difference between the two areas: the area under the c_t^* curve and t -axis and the area under c_t curve 3 (e.g., or curves 1 or 2, instead) and t -axis at t time in Fig. 1.

Using the data of Fig. 1a and eq. 1, the kinetic curves of the specific ozone consumption (Fig. 1b) were calculated. Duration of the sample ozonation as well as the value of the specific ozone consumption increases with the growth of the sample MC. Ozone consumption value corresponding to the ozonation process complication ($Q_{r,sp}$) depends on the initial sample MC (Fig. 2). As shown in Fig. 2, $Q_{r,sp}$ increases 10-fold with the increase of the sample MC from 8 to 160 %.

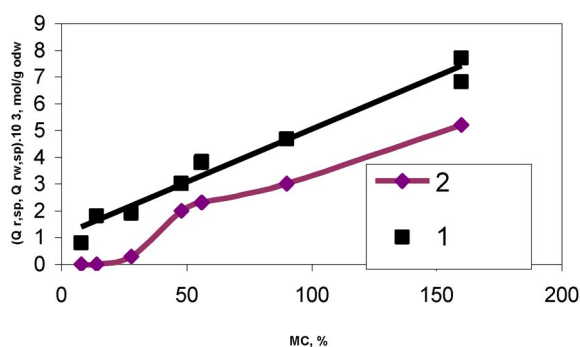


Fig. 2 Dependences of the specific ozone consumption ($Q_{r,sp}$) (1), and of the specific consumption of ozone dissolved in water ($Q_{rw,sp}$) (2) on the samples MC.

As can be seen in Fig. 2, the initial sample MC is the controlling factor in $Q_{r,sp}$ value. The relationship between $Q_{r,sp}$ and MC is explained by the process of water absorption with wood polymer composite fiber.

The kinetics of water absorption by aspen sawdust was studied. We determined the MC value corresponding to the equilibrium moisture content (EMC) in wood at 100 % relative humidity of the atmosphere. It is equal to 28 % at $t = 25$ °C. This EMC is typical for aspen wood [19].

It is well known that wood swells in the presence of water vapor. Swelling is due to hydrogen bonds between water molecules and carboxylic acid and hydroxy groups of the polymer composite that constitute the substance of cell walls. As a result, the distances between carbohydrate fibers increase, and the pores filled with adsorbed and capillary condensed water appear [19,20].

Total fiber saturation is achieved at EMC. Therefore, the internal surface of the substrate there-with increases multiply. At MC above EMC, cell cavities are filled with water. Liquid filling the wood cell cavities is named “free water”. Liquid or vapor chemically bound by hydrogen bonding to the cellulose of wood cell walls is named “bound water” [19,21]. As wood dries, the free water in the cell cavities is drawn away first. Once the free water is removed the bound water is gradually released from the cell walls. The MC at which all of the free water is removed—the cell cavities are empty—but the cell walls are still completely saturated is called the “fiber saturation point” (FSP). It is supposed that the FSP value is close to the EMC.

On evidence derived from [20], carbohydrate carrier substantially affects only about 40 ÷ 60 % of the bound water. The rest of the bound water (~50 % on average) is condensed in wood capillaries. So it may be characterized by thermodynamic parameters of the bulk water. Due to diffusion processes, a continuous exchange of water molecules in walls and cavities takes place. So it has been emphasized in [19,20] that the distinction between free and bound water is arbitrary.

The sample MC smoothly decreases under gas flow action. Ozonation time dependences of the average MC values (\overline{MC}) were found. The data obtained are in agreement with the empiric $\overline{MC} = f(t)$ functions. For example, $\overline{MC}(t) = 56.57 - 0.00215 t - 1.26 \times 10^{-8} t^2$, $\overline{MC}(t) = 162.72 - 0.0045 t - 4.67 \times 10^{-8} t^2$ of the 56 % and 160 % MC samples, respectively.

According to the data above, water presence is one of the conditions necessary for ozone to react with wood. Having it in mind, one can suggest that the reaction zone volume is limited by water volume present in the sample.

$$V = V_{\text{free w.}} + V_{\text{bound w.}} \quad (2)$$

As 50 % of the bound water of the sample of $MC = EMC$ presents as the bulk water, thus the volume of water dissolving ozone can be written as

$$V(t) = m_{\text{odw}} [MC(t) - 0.5 EMC] / \rho \quad (3)$$

$V(t)$ values at the t time were obtained from the data on MC value measurements using the following relationships: $V(t) = m(t) / \rho$; $\rho = 1.0 \text{ g/ml}$.

$$m_0 = (1 + MC) m_{\text{odw}} \quad (4)$$

$$m_{\text{bound w.}} = EMC m_{\text{odw}} \quad (5)$$

$$m_{\text{free w.}} = m_{\text{odw}} (MC - EMC) \quad (6)$$

In the equations above $m_{\text{free w.}}$, $m_{\text{bound w.}}$ is the mass of free and bound water, respectively. $V(t)$ time dependences of various initial MC samples are shown in Fig. 3. The curves in Fig. 3 are vivid examples of water volume decrease during ozonation. Figure 3 also shows the real values of the bulk water volumes.

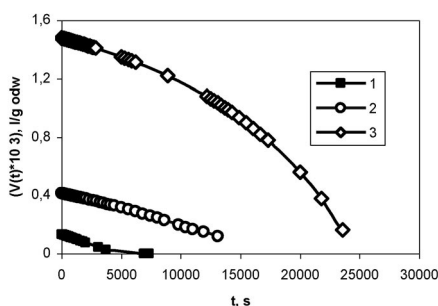


Fig. 3 Time dependences of the bulk water volume during wood samples ozonation. MC, %: 28 (1), 56 (2), 160 (3).

We used $V(t)$ dependences to compute $Q_{\text{rw,sp}}(t)$ values with eq. 7.

$$Q_{\text{rw,sp}}(t) = \frac{U}{Vm_{\text{odw}}} \int_0^t V(t)(c_t^* - c_t) dt \quad (7)$$

$Q_{rw,sp}(t)$ is a current value of the specific absorption of ozone dissolved in the bulk water of wood sample at t time. As seen in eq. 7, the amount of dissolved ozone demand is in a direct proportion to the fraction of the reaction zone volume defined as a volume filled with the bulk water: $\int_0^t \frac{V(t)}{V} dt$.

The kinetic curves of the ozone consumption $[Q_{r,sp}(t)]$ as well as the values of the dissolved ozone consumption $[Q_{rw,sp}(t)]$ during ozonation of wood are presented in Fig. 4. At the beginning of the experiment about 90 % of ozone consumption is due to ozone dissolved in water. When the ozonation is over, this value approaches 70 %. As for the 56 % MC sample, the $Q_{rw,sp}$ consumption fractions are 75 and 62 % at the beginning and end of the experiment, respectively. So, at the initial stages of samples ozonation, ozone absorption is due to the consumption of ozone dissolved in water. The consumption fraction of ozone dissolved in water decreases during the substrate ozonation. Gaseous ozone consumption increases with the samples ozonation.

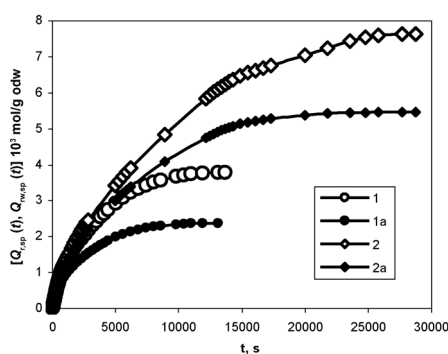


Fig. 4 Kinetic curves of the specific ozone consumption $Q_{r,sp}(t)$ (1,2), and the specific consumption of ozone dissolved in water $Q_{rw,sp}(t)$ (1a,2a) of wood samples. MC, %: 56 (1,1a), 160 (2,2a).

Wood MC dependence of $Q_{rw,sp}$ is shown in Fig. 2 (curve 2). As seen in Fig. 2, this dependence distinguishes noticeably from the monotonic dependence of $Q_{r,sp}$ (curve 1 in Fig. 2). $Q_{rw,sp}$ growth is most pronounced in the MC range from 28 to 56 %. $Q_{rw,sp}$ increases slightly with the sample MC increase from 56 to 160 %. Indeed, $Q_{rw,sp}$ depends on an effective MC value of the sample. This value is above FSP because of water evaporation during wood ozonation.

The wood samples of MC ≥ 50 % are bleaching under ozone action. The bleaching is markedly observed at the initial stages of the ozonation process. Dependence of aspen wood residual LC on the specific ozone consumption is presented in Fig. 5.

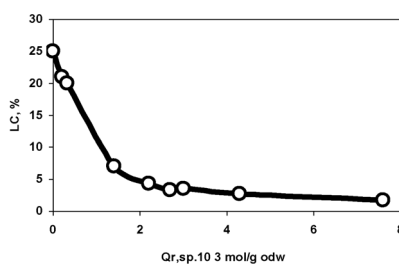


Fig. 5 Dependence of LC on the specific ozone consumption.

LC decreases from 25.3 to 3.5 % with $Q_{r,sp}$ increase up to 3.0×10^{-3} mol/g_{odw}. On the basis of this $Q_{r,sp}$ value, the ozone amount (**a**) absorbed by 1 mol of phenylpropane structural unit (psu) ($M = 170$ g/mol) was calculated. Starting from this $Q_{r,sp}$ value, **a** was found to be on average ~ 2.3 mol O_3 /mol_{psu}. According to the scheme proposed by Ph. Bailey [4], one molecule of ozone is necessary to destruct phenol aromatic ring to muconic acid, two molecules are necessary to generate unsaturated ketones and further degraded carboxylic acids. From this calculation at $Q_{r,sp} = 3.0 \times 10^{-3}$ mol/g_{odw}, lignin aromatic rings would be expected to destruct to carbonyl- and carboxyl-containing compounds. Some of them might contain C=C bond.

As $Q_{r,sp}$ increases up to $(4-5) \times 10^{-3}$ mol/g_{odw}, LC decreases down to 2.4–2.0 %. At $Q_{r,sp} = 7.6 \times 10^{-3}$ mol/g_{odw}, LC is equal to 1.7 %. This value corresponds to the 93.3 % delignification degree. The same delignification degree was found if the treatment of aspen wood was carried out under hard conditions (acetic acid at $t = 140$ °C in the presence of hydrogen peroxide and H_2SO_4 as a catalyst) [23].

Probably, at this ozonation stage, apart from lignin oxidation, ozone reacts with products of lignin initial oxidation. This assumption is supported by the values of **a** that reaches 5.5 at $Q_{r,sp} = 7.6 \times 10^{-3}$ mol/g_{odw} (MC = 160 %). According to the scheme [4], this result suggests that aromatic rings destruct to aliphatic carbon acids. In fact, the pH value of water extracts of ozonated wood samples is varied from 5.5 (for the initial sample) to 1.9 with ozone demand increase.

It is also possible that under ozonation conditions chosen ozone is consumed by carbohydrates of softwood. Carbohydrates can be oxidized by OH^\bullet radicals generated as a result of ozone decomposition in aqueous solutions. Base medium is favorable for OH^\bullet generation [14]. As for acid media, it was shown [23] that almost no OH^\bullet radicals were formed when ozone reacted with lignin model compounds in the pH range 1.3–4.5. Therefore, as acids are formed during wood samples ozonation, the OH^\bullet generation process is probably minimized. Comparison of Figs. 2 and 5 gives evidence that the most pronounced delignification takes place in the MC range of 50–70 %. One would expect that in this case the carbohydrate destruction is a minor process.

Lignin conversion

Lignin conversion during ozonation was studied by UV spectroscopy. It is not possible to extract any information about lignin conversion from integral UV spectra. We use the second derivative UV spectra (the second spectra) of DL to find out the principle ways of aspen wood lignin transformations. The second spectra of DL corresponding to different values of ozone consumption are presented in Fig. 6. To assign the bands of DL extracted from the initial and ozonated wood, the second spectra of lignin-like compounds presented by [24] were used. Spectrum 1 in Fig. 6 corresponds to lignin of the initial sample. The main absorption bands correspond to the $\pi-\pi^*$ transitions of guaiacol (2-methoxyphenol) with the bands at 253, 272, and 280 nm, syringol (2,6-dimethoxyphenol) with the bands at 265, 273, and 280 nm, guaiacylthane (250, 276, and 284 nm), guaiacylethanol (272, 275, and 283 nm). Besides, slight bands of C=O containing aromatic structures are observed. It follows that lignin from initial wood is characterized by guaiacyl (G)- and syringyl (S)-type structures and G-type structures with alkyl-aryl bonds. G- and veratryl-type carbonyl and carboxyl compounds are also present in small amounts. Bands in the region of 285–288 and 310–320 nm prove the presence of aromatic structures with $\alpha-C=C$ bonds [24].

As seen in spectrum 2 in Fig. 6, the aromatic S- and G-structure content decreases with ozonation just as C=C bonds do. The spectrum contains intense bands characteristic of acetoguaiacon (the bands at 259, 267, 270, and 302 nm) and acetoveratron (267, 296, and 301 nm) and other carbonyl-containing compounds. Compared with the initial sample, the contents of vanillic (the bands of 265, 284, and 296 nm) and carboxyvanillic (277, 293, 315, and 324 nm) acids also increase.

Relative content of carbonyl- and carboxyl-containing compounds increases with ozone consumption increase. The second spectrum of the sample of $Q_{r,sp} = 2.2 \times 10^{-3}$ mol/g_{odw} shows that the

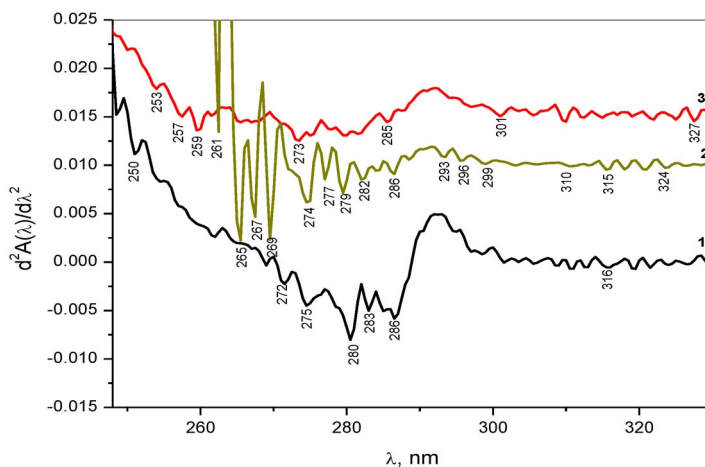


Fig. 6 Second derivative spectra of DL extracted from wood samples: $Q_{r,sp} \times 10^3 \text{ mol/g}_{odw}$: 0 (1), 1.2 (2), 2.2 (3). Spectrum 3 is a fivefold magnification of the experimental spectrum.

content of aromatic acids and ketones in the sample is small (spectrum 3, Fig. 6). UV spectra show that destruction of aromatic rings occurs first of all, and a cleavage of olefinic side-chains may be a result of new ring-conjugated structures (aldehydes, ketones). As the latter are relatively resistant toward ozone, so these structures are observed in the DL second spectra of the ozonated sample. The results in Figs. 5 and 6 indicate that a part of the softwood lignin is not subjected to ozone action.

Destruction of aromatic rings and formation of acids during ozonation of wood is supported by FT-IR spectra of DL (Fig. 7a). The bands of C–C skeleton vibrations of aromatic ring (1507 , 1594 cm^{-1}) decrease, and the band at 1730 cm^{-1} increases with ozonation of wood (spectra 1, 2 in Fig. 7a). This band can be assigned to carbon acids containing keto- and aldehyde C=O group [6,7,25]. As noted above, these structures could be formed as a result of lignin aromatic structures oxidation by molecular ozone.

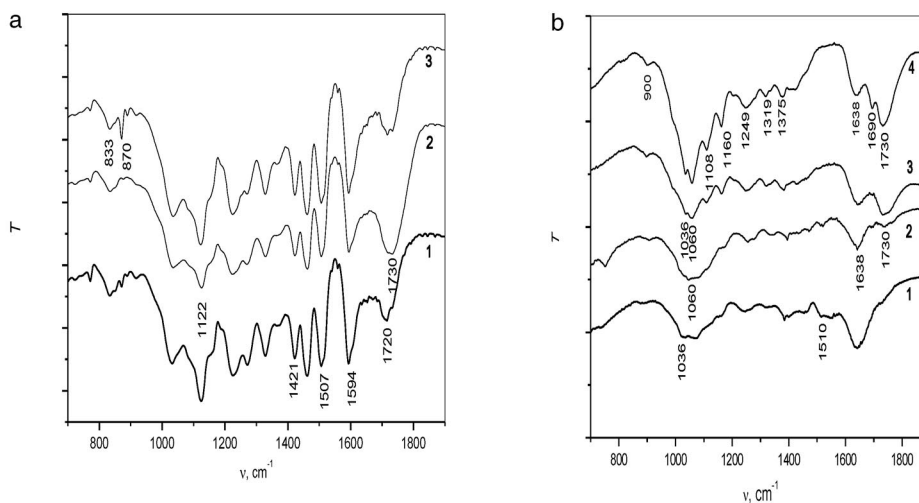


Fig. 7 (a) FT-IR spectra of DL extracted from the sawdust treated with ozone: $Q_{r,sp} \times 10^3 \text{ mol/g}_{odw}$: 0 (1), 0.8 (2), 4.7 (3). MC, %: 90 (2), 8 (3). (b) FT-IR spectra of aspen wood treated with ozone: $Q_{r,sp} \times 10^3 \text{ mol/g}_{odw}$: 0 (1), 0.3 (2), 2.2 (3), 3.0 (4). MC, %: 8 (2), 56 (3), 90 (4).

When the MC value is below FSP of the wood, DL conversions differ drastically from the above. As seen in Fig. 7a, the bands at 1594, 1507 cm^{-1} decrease, the bands of C–H deformation vibrations of aromatic rings at 833, 870 cm^{-1} arise when ozonation of the 8 % MC sample (spectrum 3) occurs. These data show that in this case the condensation of lignin aromatic rings occurs during the softwood ozonation just as in ozonation of the powder lignin [7].

FT-IR spectra of wood give further information about the substrate conversions by means of ozone (Fig. 7b). Ozone consumption increase results in $\nu(\text{C}=\text{O})$ growth of carbonyl and carboxyl groups (1730 cm^{-1}) [25]. Apart from the band at 1730 cm^{-1} , the band at 1690 cm^{-1} is present in the spectrum of aspen wood treated with ozone ($Q_{r,sp} = 3.0 \times 10^{-3} \text{ mol/g}_{\text{odw}}$). The band can be assigned to C=O stretching vibrations of unsaturated acids and ketones [25]. Compounds identical to those were found in IR spectra of lignin-sulfonate oxidized by ozone [7,9]. So, in this case the 1690 cm^{-1} band is assigned to the products of lignin conversion. The presence of this band is well correlated with a value of ozone amount.

As for the other part of the spectra in Fig. 7b, ozonation does not bring about new bands. The band at 1638 cm^{-1} attributed to adsorbed water is present in each spectrum in Fig. 7b [25,26]. Wood ozonation is accompanied with an increase of the bands at 1375, 1319, 1249, 1160, 1108, 1060, 1036, and 900 cm^{-1} . These bands are typical of wood cellulose IR spectrum [26,27].

It is supposed that in wood polymer fiber lignin is mostly bound to hemicellulose [1], so hemicellulose oxidation could also take place. This assumption is supported by the data on LCM ozonation which have shown that lignin is the most severely affected polymer, followed by hemicellulose and finally by cellulose [12,13].

In the process of wood ozonation, carbonyl compounds with the band at 1730 cm^{-1} are formed. This band can be also assigned to the products of hemicellulose oxidation. With the exception of the band extinction and a slight band displacement, IR spectra of hemicellulose are closely related to that of cellulose [25–27]. As is seen in Fig. 7b, the spectrum becomes well defined with the ozone consumption increase. We suppose that it is a result of lignin and partial hemicellulose oxidation. Spectrum 4 in Fig. 7b is similar to that of cellulose [26,27]. Thus, according to FT-IR spectra, ozonation of the sawdust samples of *P. tremula* results in wood delignification and does not have a severe impact on cellulose structure.

As ozone consumption increases, cellulose could also be destructed. To answer this question, cellulose properties of ozonated sawdust samples have to be studied directly.

Softwood ozonation process

On the data of the research, the ozonation process of the softwood could be explained as follows. As FSP = 28 %, at MC \geq 50 % water molecules cover wood particles, incorporate into pores of cell walls, and then water fills cell cavities. As that takes place, a medium dissolving gaseous ozone forms. As ozone solubility in water at 25 °C is 0.0011 mol/kg bar, so its concentration in water can reach $0.6 \times 10^{-3} \text{ mol/l}$. Diffusion processes allow dissolved ozone to penetrate to the internal surface of the substrate. Ozone molecules pass through several water monolayers adsorbed on the surface of carbohydrates. Then, it interacts to the polymer molecule functional groups.

The volume of water phase is limited so the concentrations of the reagents are high, and that favors high rates of the reaction. Wood has three principle components, that is, cellulose, hemicellulose, and lignin. The last of them is characterized by the lowest redox potential, respectively. Therefore, lignin is subjected to ozone oxidation first.

Lignin is covalently bound to carbohydrates of wood cells. It can be oxidized by ozone, and complex polymer composites containing lignin fragments can be formed. These compounds remain inside the pores and are therefore isolated from the oxidative medium. For this reason, they can be observed in the reaction mixture after ozonation completion. At high ozone consumption values, low-weight

products might exist. Dissolution of these compounds in water is limited because of the decrease of the bulk water volume that accompanies the ozonation process.

Therefore, a more extended retention of water phase is favorable to deeper substrate oxidation. The process takes place because of the increase in the swelled wood surface available to ozone. Apart from the above, it occurs as a result of partial removal of oxidation products.

During ozonation, part of the water vaporizes in the gas flow and leaves the reaction zone. The dissolved ozone consumption fraction decreases, in contrast, the gaseous ozone consumption fraction increases. Whereas the samples of MC \geq 50 % ozonation, reactions of gaseous ozone with the substrate practically follow the oxidation of reactive functional groups with ozone dissolved in water. Oxidation of alcohol hydroxyls, ether bonds, and C=O groups slowly reacting with ozone occurs in the course of the whole experiment. Hence, as water evaporates these groups are oxidized mostly by the gaseous ozone. The gaseous ozone reacts with hemicelluloses and products of lignin oxidation. It is obvious that the greater the initial MC is, the higher is the soluble ozone fraction in the oxidation process mentioned above.

The value of 28 % MC corresponds to FSP. In this case, the surface available to the dissolved ozone is limited by small values of capillary-condensed water. That is why ozone consumption is small at this value of MC (Fig. 2). As for the sample of 8 % MC, the substrate reacts with gaseous ozone. Ozone consumption is negligible because of a low content of reactive functional groups on small surface of wood that has not swelled.

It is evident that water presence is of a major importance to wood ozonation. Water induces wood swelling and consequently provides an access for the reagent to functional groups in internal surface of wood cells. It is also a solvent of ozone and some oxidation products.

It was shown that ozonation of aspen wood allows formation of oxyaromatics—products of lignin oxidation by ozone. Besides, aliphatic carbon acids are obtained as a result of both lignin and partial hemicellulose oxidative destruction. Water content influences the products of wood ozonation.

The data obtained show that it is possible to produce a cellulose-containing product of above 90 % delignification degree during direct ozonation of softwood. To decrease ozone demand and to reach a deep delignification, one might use different ways, e.g., to modify the pretreatment stage using acidic aqueous solutions for impregnation of the wood sample. This results in a decrease of the role of radical reactions in wood delignification and thus, the selectivity of the ozonation process might increase. Another way is connected to improving the ozonation process by stages of dissolution of ozonation products with a following evacuation from the reactor.

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