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International Journal of Current Research
Vol. 8, Issue, 11, pp.41714-41721, November, 2016

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

OZONATION AS PRETREATMENT METHOD OF WOOD FOR CELLULOSE PROCESSING

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ARTICLE INFO

Article History:
Received 07th August, 2016
Received in revised form
22nd September, 2016
Accepted 18th October, 2016
Published online 30th November, 2016

Key words:

Wood,
Ozone delignification,
Cellulose,
Degree of polymerization,
IR absorption spectra.

ABSTRACT

Ozonation of wood is considered as a pretreatment of vegetable raw materials with the aim of a subsequent cellulose processing. The process of ozone consumption by aspen wood of various moisture content (MC) was investigated. The data on wood and cellulose transformations in the course of wood ozonation are presented. Yields of ozonized wood, water-insoluble wood ozonationproduct (WOP), water- soluble ozonation products, and cellulose were found. The lignin and cellulose content in WOP was determined. Both WOP and cellulose samples were investigated by the IR spectroscopy method.The degree of polymerization (DP) of cellulose obtained from ozonized wood is presented. It is shown that the destruction of wood by ozone includes lignin hemicelluloses and, partially, cellulose degradation. The yield, DP and supramolecular structure of cellulose obtained from WOP can be regulated by the variation of the initial MC of the substrate. It was found that the MC of 55% corresponds to the most efficient ozonation with theprominent wood structure transformation. A key role of water in biomass ozonation is emphasized. It is concluded that the ozonation of wood is controlled by diffusion. It is supposed that the wood destruction is caused by reactions of molecular ozone, as well as radical species generated in the course of ozone reactions with water present in the wood structure.

Citation: Mamleeva, N. A., Autlov, S.A., Bazarnova, N. G. and Lunin, V.V. 2016. "Ozonation as pretreatment method of wood for cellulose processing", *International Journal of Current Research*, 8, (11), 41714-41721.

INTRODUCTION

Lignocellulose biomass offers many possibilities for the chemical industry due to its chemical composition, abundant availability and relative low costs. It is an inexhaustible source of new materials for the production of demanded chemicals, materials and biofuels (Garcia-Cubero *et al.*, 2012; Bogolitsyn *et al.*, 2009 and Kuznetsov *et al.*, 2012). Vegetable raw biomass has a complex structure mainly formed by cellulose (40-50%), hemicellulose (25-35%) and lignin (15-35%), and other components such as extractives and several inorganic compoundsLignin (LG) is an amorphous three-dimensional polyphenolic polymer composed by a set of methoxyl-, propyl and hydroxyl groups attached to aromatic groups. Cellulose is a linear polymer formed by glucose units that can form fibrils due to the formation of hydrogen bonds between polymer chains generating recalcitrant structures. Hemicellulose is characterized as an amorphous and branched polymer, composed by pentose and hexose units. LG isboundto carbohydrates chains by C-C and C-O bonds.

Lignin permeates the matrix of cellulose fibers and fills the interspaces between cellulose, hemicellulose, and pectin, acting as a link of these structural blocks of cell walls. Modern technologies demand a sustainable processing of biomass into a number of target products. In recent tendencies of biomass processing the oxidation technologies with oxygen, hydrogen peroxide, and ozone as the most environment friendly oxidants are preferable. For a number of reasons, ozone is an attractive alternative among various oxidants. Firstly, ozone is highly reactive compound. It does not leave toxic residues in the treated material, and it can be decomposed back to oxygen by a simple catalyst bed or by increasing the temperature. Finally, most of ozonation reactions take place at near-ambient temperatures and pressures. Being an oxidant of aromatic compounds (Bailey, 1982; Razumovsky & Zaikov, 1984), ozone has found a wide application as a bleaching agent in the oxidation of residual ligninin paper pulp process (Brochier *et al.*, 2006; Dontsov, 2001; Roncero *et al.*, 2003; Rounsaville & Rice, 1997; Simoes & Castro, 1999). Ozonation was used as a pretreatment method of biomass for intensifying the subsequent process of enzymatic hydrolysis to sugars and ethanol. Ozone is considered asa reagent of wood pretreatmentwith the aim of consequent cellulose processing (Mamleeva *et al.*, 2009; Mamleeva *et al.*, 2015; Mamleeva &

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Lunin, 2016 and Schuerch, 1963). Direct ozone impact upon the poplar, aspen, pine, spruce, sugar-cane, wheat and rye straw, corn stalk and a number of other plant substrates was studied in (Ben'ko *et al*., 2013; Euphrosine-Moy *et al*., 1991; Garcia-Cubero *et al*., 2012, Lee *et al*., 2010; Li *et al*., 2015; Mamleeva *et al*., 2009; Mamleeva *et al*., 2015; Mamleeva & Lunin, 2016; Quesada *et al*., 1998; Schuerch, 1963; Souza-Corrêa *et al*., 2013; Sugimoto *et al*., 2009; Travaini *et al*., 2016 and Yu *et al*., 2011).

It was found lignin destruction under ozone impact onbiomass (Euphrosine-Moy *et al*., 1991; Garcia-Cubero *et al*., 2012; Lee *et al*., 2010; Mamleeva *et al*., 2009; Schuerch, 1963; Souza-Corrêa *et al*., 2013; Travaini *et al*., 2016; Yu *et al*., 2011). Ozone treatment of biomass reveals in the formation of a number of carbon acids (oxalic, tartaric, glyoxyic, malonic, malic, succinic, glycolic, formic, muconic, acetic, and *et al*.) (Ben'ko *et al*., 2013; Euphrosine-Moy *et al*., 1991; Quesada *et al*., 1998; Travaini *et al*., 2016). It was found carbonyl- and carboxyl- containing aromatic productsformed in the process of aspen woodozonation (Mamleeva *et al*., 2009).Ozonation of lignocellulose biomass causesboth lignin and hemicelluloses degradation. It was noted that lignin destructs first of all, followed by hemicelluloses and finally by cellulose degradation. Some authors suppose that cellulose destruction is negligible (Ben'ko *et al*., 2013; Sugimoto *et al*., 2009). Unlike, it was found that cellulose obtained from ozonized spruce and aspen is significantly transformed by ozone (Mamleeva *et al*., 2016; Schuerch, 1963). It was investigated ozone treatment of a number of biomass types containing water of various amounts. Moisture content of biomass was found to be a significant factor of ozone consumption process, as well as a vegetable substrate transformation (Ben'ko *et al*., 2013; Garcia-Cubero *et al*., 2012; Lee *et al*., 2010; Li *et al*., 2015; Mamleeva *et al*., 2006; Mamleeva *et al*., 2013; Mamleeva *et al*., 2016; Schuerch, 1963; Souza-Corrêa *et al*., 2013; Travaini *et al*., 2016 and Yu, 2011). However, so far, a role of water content in biomass ozonationappears to benot clearly understood. In presentresearch, the ozonation of aspen wood samples containing various water amounts is investigated.The aim of the paper is to study a transformation of wood and cellulose obtained from ozonized wood, and to establishthe principal factor controlling the ozonation process, as well asthe substrate conversion under ozone impact. The data on wood degradation by ozone are discussed below in context of the problem of optimization the biomass ozonation process, later.

MATERIALS AND METHODS

Materials

The sawdust of aspen wood (*Populustremula*) with a particle size of 0.315 – 0.63 mmwas the substrate of the research. Contents of cellulose (46%), hemicelluloses (26%) and lignin (25%) in the wood were determinedby methods described in (Obolenskaya *et al*., 1991). Wood samplesof a moisture content (MC) range of 8% - 160% relatively to the mass of oven-dry wood (ODW)were prepared by means of the penetration of air –dry sawdust (of 8% MC) by water according to the procedure (Mamleeva *et al*., 2009).

$MC = (m_{H2O}/m_{o.d.w.}) \times 100\%$.

Ozonation experiment

Ozonation of wood samples (1.3-2.1 g) was carried out using ozone generator Medozone 03/05 (Russia). The experimentwas conducted in a flow system with a temperature-controlled (t=20°C) fixed bed reactor. The ozone - oxygen mixture of90 mg/Lozone concentration was passed through the reactor at a flow rate of 4.4 L/h. At the experiment completion ozone generation was stopped, the system was purged with oxygen. Unreacted ozone was decomposed at the outlet of the system by the catalyst (Tkachenko *et al*., 2012). Ozone concentration was measured usingMedozone-254/5 photometer (Russia). The accuracy of measurements was about 3%.Coincidence of ozone concentration at the inlet and the outlet of the reactor was a criterion of the completion of the reaction.A current value of the ozone consumption $Q_{abs}(t)$ was computed via a graphic integration of kinetic curves of Fig 1A, corresponding to Eq.(1).

$$Q_{abs}(t) = U\int_0^t (C_t^* - C_t)\,dt \qquad \text{Eq. (1)}$$

$U$is the gas flow rate (L/s),$C_t$and C_t^* are the current ozone concentration (mol/L) at the outlet and inlet of the reactor containing the investigated sample, respectively.

The ozone consumption degree $\alpha(t)$ was calculated using Eqs. 2 and 3.

$$\alpha(t) = \frac{Q_{abs}(t)}{Q_0(t)} \times 100\%, \qquad \text{Eq. (2)},$$

$$Q_0(t) = U\int_0^t C_t^*\,dt \text{Eq. (3)}.$$

The $Q_{abs}(t)$ is a current ozone amount absorbed by the sample,and$Q_o(t)$is a current value of ozone amount at the inlet of the reactor. A current value of the specific ozone consumption ($Q_r(t)$) was calculated, using Eq.4.

$$Q_r(t) = \frac{Q_{abs}(t)}{m_{o.d.w.}} \text{Eq. (4)}$$

$m_{o.d.w.}$ is the mass of oven-dried wood.

Experimental runs of ozone consumption by the wood samples of the same MC were four times repeated.

Yields of ozonation products

The yield Y1 of ozonized wood (OW) was defined as a ratio of the mass of oven dry ozonized sample to the mass of the original ODW. To obtain water-insoluble wood ozonation product (WOP), the samples of OW were washed with water to remove soluble compounds, and then were dried. The yield Y2 of the WOP was determined as a ratio of the mass under consideration to the mass of original ODW. Water-soluble compounds yield was calculated as (Y1-Y2). The yield Y3 of cellulose was calculated as a ratio of the mass of the oven-dry cellulose to that of the original ODW. The lignin content in the original wood and WOP samples of wood was determined as Klason lignin following to the standard procedure (Obolenskaya *et al*., 1991). The wood sample (1 g in terms of ODW.) was treated with 15 ml of 72% H_2SO_4 at room temperature for 2.5 hours. Then the acid concentration was reduced by dilution by water to 8% and was boiled in a flask with a fluid-cooling condenser during 1 h. After cooling, the precipitate was filtered, washed by water until neutral pH and dried at 103± 2°C to a constant weight. Cellulose was obtained from holocellulose (HC). HC was obtained from wood and WOP samples (1g) treatment by the 10% peracetic acid solution (50 ml) for 5-7 min at room temperature. Then the flask was incubated inbath for 20 minutes at a temperature of 75°C with periodic mixing. The content was diluted with 50 ml of distilled water (50°C), then HC was filtered, washed with distilled water (50°C) until a negative reaction with titanylsulphate, and then washed using acetone-ethanol (1:1) mixture at 20°C. The HC sample was air-dried, with subsequent determination of MC of air-dried HC (Obolenskaya *et al*. 1991). Cellulose was obtained by hydrolysis of HC (1g) by the 2 % aqueous HCl solution (40 ml) upon boiling (3 h). The precipitate at the filter was washed with hot water (50°C) and air-dried followed by MC determination of air-dry cellulose (Obolenskaya *et al*., 1991).

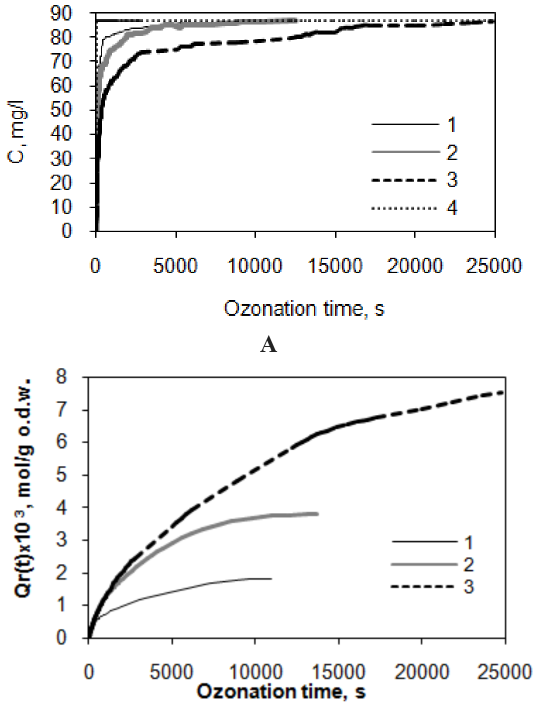
Viscometer and IR spectra measurement

A degree of polymerization of cellulose solutions in cadoxene was defined by the capillary viscometer VPG-3 (Russia). The IR absorption spectra of wood and cellulose were registered by Equinox 55/S (Bruker) in the range of 400-4000 cм$^{-1}$. KBr pellets of 0.1% sample (wood, WOP) and of 0.3% sample (cellulose) with 0.3% $K_4Fe(CN)_6$ as an external standardwere prepared.

RESULTS AND DISCUSSION

Ozonation of wood

The kinetic curves of the ozone concentration at the outlet of the reactor containing aspen wood samples are presented in Fig.1A (curves 1-3). The kinetic curve of the inlet ozone concentration is presented as curve 4 in Fig.1A.



A

B

Fig.1. Kinetic curves of the outlet ozone concentration (A),specific ozone consumption (B) for wood samples ofMC, %: 30 (1), 55 (2), 160 (3). Ozone concentration at the reactor inlet (Fig.1A, curve 4)

The $Q_r(t)$ kinetic curves of aspen wood containing different moisture content are presented in Fig.1B. Ozone treatment is carried out in a flow system, so the moisture content of a sample decreases as the ozonation time increases (Mamleeva *et al*., 2009). It is seen from Fig.1B that an increase of MC allows achieving higher values of $Q_r$bythe long-time ozone treatment of the wood sample. As a result, the specific ozone consumption corresponding to a completion of ozone exposure (Q_r) increases following to the sequence $Q_{r1} < Q_{r2} < Q_{r3}$ for the samples of Fig 1B. Kinetic dependences of ozone consumption degree α (t) of the samples of various MC are presented in Fig.2 A. It is seen that α(t) of the samples decreases from 100% to 11-20% during ozonation.

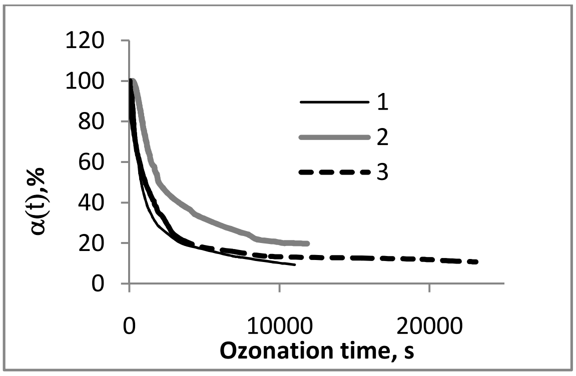


Fig.2A. Kinetic curves of ozone consumption degree of wood samples of MC, %: 30 (1), 55 (2), 160 (3)

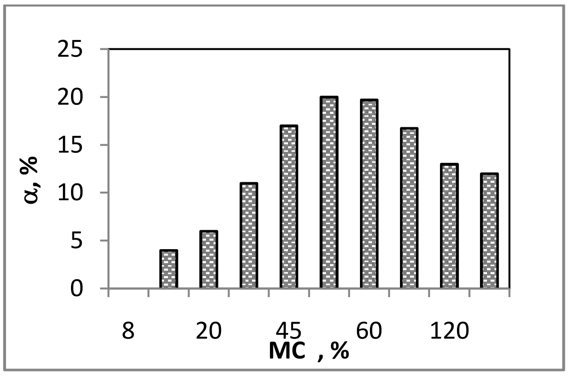


Fig.2B. Ozone conversion degree (2) *vs* initial moisture content of aspen wood

A decrease of α with ozonation time is due to ozone reactions with less active groups of the sample. The dependence of ozone conversion degree (α), corresponding to the complication of ozonation process is presented in Fig. 2B. The terminate ozone consumption degree corresponding to the completion of ozonation process depends on the MC of the sample.It is seen from Fig 2B.that the α value of 55% MC sample is equal to 20%, and this value is the largest one. The data show that the ozone consumption process by wood of 55% MC is characterized by the best efficiency.

Role of water in wood ozonation

Water presence has an effect on wood structure. It is well known that wood swells in water vapor. Swelling is due to formation of hydrogen bonds between water and hydrophilic groupsof wood cell walls. Water, absorbed by cell walls, is named “the bound water”, and the water amount corresponding to the complete saturation of cell walls is called the “fiber saturation point” (FSP). Cell cavities of wood of MC above FSP are filled with water. Water filling the wood cavities is named "the free water" (Stone & Scallan, 1967). Wood swelling results in many times increasing the wood surface, and for this reason, a number of the substrate reactive groups available to reagent also arise. Therefore, ozone consumption increasing, as well as the initial ozone consumption rate increasing with MC, as it is presented in Fig.1, 2, is obvious.

Table 1. The yield of the ozonized wood (Y1), the water-insoluble wood ozonation product (WOP) (Y2), cellulose (Y3) and the content of residual lignin (LG) and cellulose (Cell) in WOP depending on the specific ozone consumption for the samples of various moisture content (MC) in wood

Sample No	MC, %	Qr, ×10 ^{3}mol/g $_{\text{o.d.w.}}$	Y1,%	Y2,%	Y3, %	Cell, %	LG,%
1	8	0	100	98 ±1	42±1	44±1	25.3
2	8	0.8	99±1	97±1	43±1	44±1	21.5
3	30	1.8	98±1	83±1	43±1	52±1	6.1
4	55	3.8	102±1	63±1	41±1	65±1	3.8
5	160	7.6	106±1	66±1	46±1	70±1	1.7

Our data show that the most favorable for ozonation process is MC of 55% that exceeds the aspen wood FSP corresponding to 28% MC. The need for some excess water relatively to FSP of the substrate to achieve a noticeable effect of ozone was emphasized by a number of authors (Ben'ko *et al*., 2013; Lee *et al.*, 2010; Li *et al*., 2015; Mamleeva*et al*, 2009; Mamleeva*et al*, 2016; Schuerch, 1963; Travaini*et al*, 2016).A number of surface reactive groups achievesmaximum for the sample of 28% MC, and it keeps unchanged for MC above FSP.For this reason, it should be other explanation forthe higher ozonationefficiencyof wood samples of MC above FSP thanthat of 28% MC sample.The marked peculiarity may be attributed to the structure of the bound water. It was shown that the bound water consists of three monolayersof water molecules tightly bound each other (Zografi&Konthny1986).

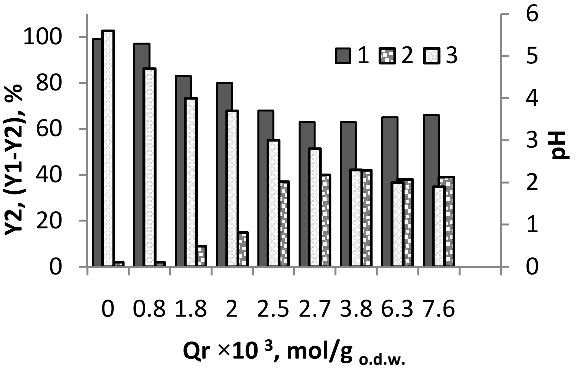
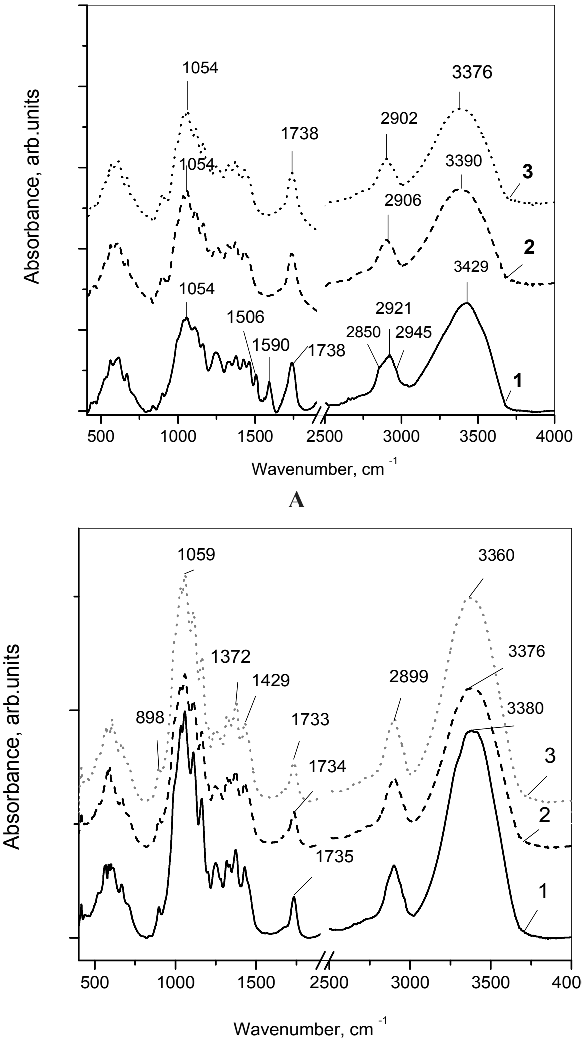


Fig. 3. The WOP yield (1), water-soluble products of ozonation (2), and pH of contact solutions (3)*vs* specific ozone consumption

Thus, the layer achievesa thickness of about 1nm. Bound wateris characterized by higher density, low molecular mobility;it differs in other physical properties, as compared to the bulk water (Schnieder *et al*, 1991; Zografi & Konthny1986). It is evident that the structured water layer restricts an inclusion of reagent molecules into the layer. A transfer of ozone molecule of 0.4 nm in diameter into the bound water layer involves problems of a steric character, in addition. For this reason, the ozone concentration in bound water decreases and, consequently, the ozonation efficiency decreases, too. In the presence of a water exceed above FSP ozone first of all transfer from gas to free water volume. Thermal movement and diffusion result in transfer of water molecules from free to bound water and conversely. These processes provide a transfer of ozone dissolved in free water to the bound water layer. This explanation is consistent with the necessity of water exceed above FSP. It also shows that diffusion play a governing role in the ozone consumption process by the wood. Therefore, it is seen that the ozone absorption is controlled by both an availability of surface groups and the reagent concentration in bound water, where reactions take place. Apart from reactions in bound water, the ozone is partially demanded in the free water.



A

B

Qr×10^{3} mol/g $_{\text{o.d.w.}}$: 0 (1), 3.8 (2), 7.6 (3).

Fig.4. IR absorption spectra of the original wood and WOP samples (A) and cellulose (B)

First of all it comes from the lignocelluloseozonation byproducts dissolved in water. Since the water phase arises at high MC, a contribution of water phase reactions of ozone with byproducts increases. So, in the MC region above 55%, the ozone consumption process is complicated noticeably by reactions of ozone with compounds dissolved in water phase. The rate constants of short-chain acids known as byproducts of lignocellulose destruction by ozone are much lower than that of aromatic and other lignocellulose surface functional groups (Bailey, 1982; Ragnar *et al*., 1999; Razumovsky & Zaikov, 1984). With this context the data on ozone conversion degree of Fig.2 appears to be rather transparent. Thus, the water content governs a number of available reactive groups of lignocellulose and an amount of byproducts dissolved in water. Being a medium for the reagent and byproducts transport water plays a key role in wood ozonation. We believe that the principal regularities of water effect on wood structure should be useful in other researches of plant raw materials.

Woodtransformation

Wood transformationswere considered both as a whole material and by analysis the transformations of its main structural blocks (for example, LG, cellulose). The valuesof the yield of ozonated wood (Y1), WOP (Y2), and cellulose (Y3) and the content of residual lignin (LG) in the WOP obtained from the samples of various moisture contents are shown in the Table 1. The mass of samples after ozonation increases to 106 % as Qr increases to 7.6×10^{-3} mol/g $_{\text{o.d.w.}}$. The increase in mass is due to oxidation of functional groups of wood under ozone impact, and to adsorption of low molecular products on wood surface (samples No 4 and No 5). After washing of OW sample the yield of WOP (Y2) achieves 63-66% (samples No 4 and No 5). The yield of water-soluble products of wood ozonation is presented in Fig.3. In the Qr range of $(2.5 \div 7.6)\times10^{-3}$ mol/g$_{\text{o.d.w.}}$(0.05 ÷ 0.16 mg/g$_{\text{o.d.w}}$.) the yields of soluble compounds correspond to 39 - 40% with notable decreasing at low Qr values (Fig. 3). A composition of water-soluble products is characterized by various acids (pH of the contact solution changes from 5.6 of the original wood sample to 1.9). A formation of formic, glyoxalic, oxalic and acetic acids in the course of ozonation of aspen wood was observed in (Ben'ko *et al*., 2013). The yields of cellulose are varied within the range of 41 - 46% (Table 1). These values are close to the cellulose content in the original wood. The data of Table 1 show that the sample No. 4 obtained by ozonation of wood sample of 55% MC, is characterized by the lowest cellulose yield (Y4=41%).

Figure 4 presents the IR absorption spectra of the original wood and WOP samples. The absorbance of the 1590, 1506, and 1425 cm^{-1} band (the skeletal C–C vibrations of the aromatic rings) decreases because of the oxidative destruction of ligninby ozone. Carboxyl groups are characterized by absorption at 1738 cm^{-1}, and the intensity of this band changes slightly asQ_r increases.The absorption band corresponding to the stretching C–H vibrations in the spectrum of the original wood is characterized by a maximum at 2921 cm^{-1}. The band is a superposition of the bands relating to the C–H vibrations in the methyl and methylene groups of lignin (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}) (Bazarnova *et al*., 2002). The band of the stretching C–H vibrations of the sample No 5 shifts to 2902 cm^{-1}due to the cellulose content increasing in WOP sample. According to Fig. 4A, the absorbance band of $\nu_{\text{O-H}}$ shifts from 3429 cm^{-1} (the original woodsample) toward lower wavenumbers, and the half-width of the band increases in the spectra 2 and 3 (samples No 4 and 5) as the amount of absorbed ozone increases. Thus, the changes in the IR spectra are explained by a removal of lignin from wood, and cellulose content increasing in WOP samples. This result is confirmed by the data on cellulose and lignin content of WOP samples presented in Table 1. The IR absorption spectra of cellulose are shown in Figure 4B. All these spectra are identical, and are characterized by the bands of 898, 1059, 1110, 1159, 1248, 1372, 1429, 2899cm^{-1}, that is typical for cellulose (Bazarnova *et al*., 2002; Ciolacu *et al*., 2011). A broad absorption maximum in the region of 3700-3100cm^{-1} is relatedtothestretching vibrations of OH - groups involved in hydrogen bonding. The band at 2899cm^{-1} is attributed to C-H stretching vibrations, bands at 1429cm^{-1} and 898cm^{-1} are assigned,respectively, to the scissor vibrations of the methylene groups and theC^{1} atom and the vibrations of the four surrounding atoms in β – glycoside structures, respectively (Bazarnova *et al*., 2002; Ciolacu *et al*., 2011). The absorbance ratio of the bands at1372 cm^{-1} and 2899 cm^{-1} (A_{1372} /A_{2899}) was proposed for determining the crystalline index of cellulose material (Bazarnova *et al*., 2002; Ciolacu *et al*., 2011). The A_{1372}/A_{2899} values are 1.21, and 1.07 and 1.31 for spectra 1, 2 and 3 in Fig.4B, respectively. Spectrum 2 is characterized by the lowest A_{1372}/A_{2899}. One may assume that this is due toincreasing amorphous areas of this cellulose sample. The intensity of the band at 3376cm^{-1} decreases, the band widens, giving evidence toamorphization of cellulose (Bazarnova *et al*., 2002; Ciolacu *et al*., 2011). These data point out to the structural heterogeneity of the cellulose sample obtained from wood sample of 55% MC (No 4 in Table 1).

The average degree of polymerization (DP) of cellulose obtained from the initial wood is of 700. As one can see from Fig. 5, the DP decreases when the ozone consumption increases. Cellulose of DP 280 corresponds to Qr3.8 10^{-3}mol/g$_{\text{o.d.w.}}$. Cellulose from ozonized wood of 160% MC is characterized by the DP of 220. So, the cellulose structure is transformed when the wood ozonation. As it is seen from Fig. 1 and 5, the degradation of cellulose is observed at high ozone consumption values achieved by long-time ozonation. These results are consistent with the cellulose de-polymerization during ozonation of hardwood (Schuerch, 1963). The dependence of LG content on the ozone consumption is also presented in Fig.5. As compared to cellulose, the lignin destruction occurs at much lower ozone consumption. Moreover, at the low specific ozone consumption values the LG destruction is a dominant process. It was shown that apart from LG hemicelluloses are also destructed in the course of aspen wood ozonation (Mamleeva *et al*. 2016). It was noted above thatthe ozonation of 55% MC wood causes a decrease of WOP yields, and a decrease of cellulose yield. Evidently, that cellulose can be decomposed by ozone only in its amorphous regions with increasing their area in wood ozonation. It is of primary importance that in this case the lignin isnot destructed completely. (LG content is of 3.8% (Table 1)). It is seen that in spite of the well-known fact that the ozone oxidation rate of lignin is several orders more in magnitude than that of carbohydrates(Olkkonen *et al*., 2000), cellulose begins to destruct when LG is not completely destroyed. Therefore, the substrate oxidation by ozone is controlled by an availability of the substrate structural blocks. This data show that diffusion is a governing factor of wood transformation under ozone impact.

Ozone reactions with wood

Wood oxidation by ozone is due to ozone dissolved in water presented in the cell structure of the swelled wood. Ozone dissolution in water is a complex process, that is, a number of ozone molecules are presented in a molecular form (O_3), but some of them react with water accompanying by generation of reactive radical moieties, which, in turn, can react with the substrate. Molecular ozone reacts with aromatic structures by ionic cyclo - addition, and subsequent cleavage of double and aromatic bonds by Criegee'smechanism (Bailey, 1982; Olkkonen *et al*., 2000; Razumovsky & Zaikov, 1984)

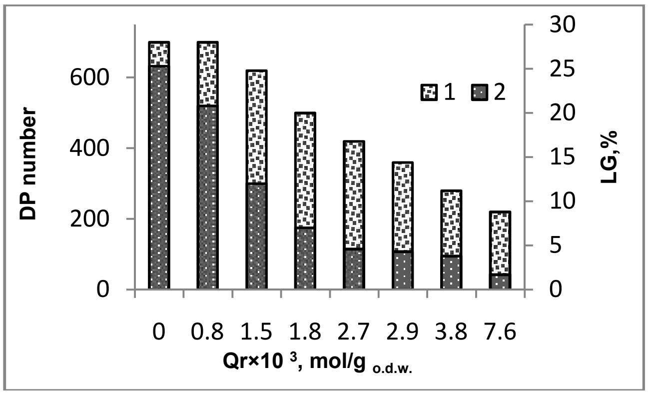


Fig.5.Cellulose degree of polymerization (1), and lignin content in WOP (2) *vs* specific ozone consumption

This mode has been claimed to be the major reaction pathway for lignin model compounds (Sugimoto *et al*, 2009) This mechanism seems to be acceptable for wood lignin reactions. Lignin β-O-4 bonds can be oxidized by molecular ozone through electrophilic addition mechanism (Bertaud *et al*., 2001; Sarkanen *et al*., 2002). Other reactions, such as the hydroxylation of the coniferic or paracoumarylic structures of lignin or the oxidative cleavage of methoxy- groups are also possible (Bailey, 1982). It is knownanother pathway, namely a generation of phenoxyl- radicals with the subsequent disclosure of aromatic ring and formation of unsaturated acids, aldehydes, and peroxide compounds (Razumovsky&Zaikov, 1984). Ozone decomposition in water is accompanied by a formation of OH° and $O_2^{\circ -}$ radicals. Hydroxyl radicals are easily transformed into superoxide and *vice versa* (Staehelin., Hoigné 1982; Erikson & Gierer, 1985; Ragnar *et al*., 1999*)*. According to (Ragnar *et al*., 1999), the first radical formed is a superoxide anion radical ($O_2^{\circ -}$) that then reacts with ozone and give rise to chain reaction that generates OH°- radicals. It is supposed that being short-lived species, hydroxyl radicals (Roncero *et al*., 2003) donot diffuse because of their high reactivity. In contrast, long lived superoxide-radicals diffuse into fiber, then $O_2^{\circ -}$ increases the generation of OH°- radicals, and furthermore $O_2^{\circ -}$ serves as a vehicle for transfer of the OH°radicals into fibers, where they can react with cellulose (Roncero *et al*., 2003).The effect ofO_3 and OH°- radicals on carbohydrates consists in glycoside bonds cleavage and oxidation of alcohol groups (Brochier *et al*., 2006; Demin *et al*., 1999; Lemeune *et al*., 2004; Olkkonen *et al*., 2000; Simoes&Castro; 1999). As a result, a decrease of cellulose degree of polymerization as well as a formation of carbonyl and carboxyl compounds takes place. It has been noted (Dontsov, 2001), that lignin degradation can occur by OH°- radicals.A proportion betweenmolecular ozone and radical moieties depends on various factors, primary on pH value (Staehelin&, Hoigné, 1982; Erikson & Gierer,1985; Ragnar *et al*., 1999). It was noted (Ragnar *et al*., 1999), that the yield of OH°- radicals generation increases above pH 3 of solutions. With this data, one may suppose that OH°- radicals can be generated at the initial stages of wood ozonationbecause of pH of the initial contact water solution is of 5.6. Since the wood ozonation results in pH decrease, the radical yield could decrease, and reactions of molecular ozone could dominate.

Apart from the mentioned pathways, lignin and cellulose degradation could be performed as processes connected to each other.Carbohydrates destruction could be induced by intermediate products of aromatic systems oxidation (phenoxyl- radicals, OH°-radicals, ozonides). This proposal was discussed by (Dontsov, 2001; Olkkonen *et al*., 2000), and it seems to be a suited way of aspen wood destruction with ozone.So, there is a great dealof the wood degradation pathways that will allow an understanding the observed transformation of lignin and cellulose during ozone impact on the wood. The interaction of ozone with wood occurs in the amorphous regions of lignin-carbohydrate complex (LCC) contained hemicelluloses and lignin (Bogolitsyn *et al*., 2009). Being the most readily oxidized structure of LCC organization, lignin available to the reagent is destroyed first of all. Deconstruction of LG matrix induces fragmentation of lignocellulose arrangement, and this process inevitably leads to the transformation of carbohydrates since they are covalently - linked with lignin. Our data show that cellulose, characterized by the most resistance structure, is also subject to decomposition.

Conclusion

The process of ozone consumption by aspen wood of various moisture amountswas investigated in the research. Ozonation of wood results in oxidative destruction of lignin and carbohydrates. Wood degradation enhances as the specific ozone consumption increases. The moisture content of 55% corresponds to the most effective ozonation process accompanied by the most prominent wood structure transformation. The yield of cellulose, average degree of polymerization, and supramolecular structure depend on initial MC of wood. The variation of MC allows controlling the properties of the cellulose obtained from the wood treated with ozone. It was concluded that diffusion is a governing factor of ozone consumption as well as of a depth of wood structural blocks. Water isconsidered as a component of the system providing an availability of the biomass surface groups to the reagent and an amount of byproducts dissolved in water. Being a medium for the reagent and byproducts transport water playsa governing role in wood ozonation.It is supposed that the wood degradation is due to reactions of molecular ozone as well as radical species generated by ozone reactions with water existing in the sample.

Funding

The work was supported by Russian Science Foundation (Grant No 16-08-00876).

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