Chapter 23

OZONE APPLICATION FOR MODIFICATION OF HUMATES AND LIGNINS

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Abstract

The modifications of lignins and humic substances under ozone action were investigated in this paper. The rate constants and ozone consumption in these reactions were estimated. UV/Vis, IR-, and NMR-spectroscopy methods were used to follow functional groups changes in the course of ozonation. The pathways of lignins and humic substances ozonation were suggested.

1. Introduction

The synthesis of new and environmentally benign complexing agents to heavy metals on a base of humic substances (HS) and lignins attracts great interest. Lignin is irregular aromatic polymer of phenolic nature consisting of phenyl-propane units substituted predominanlty with OCH_3 and OH groups, and linked together via carbon-carbon and ether bonds. HS are also natural irregular polymers of acidic nature consisting of aromatic core highly substituted with carboxylic and hydroxylic groups and bound to it carbohydratic-peptidic peripheral fragments [1]. Both lignin and humic compounds are rich in oxygen-containing functional groups and can be considered as promising resources for production of complexing agents. The latter can be used as detoxifying agents for metal polluted environments or as chelates for production of micronutrients (Fe, Mn, Zn -complexes). To make such complexing agents competitive with the highly specific low molecular weight chelates, the modification of lignin and humic materials should be conducted aimed at an increase of the content of oxygen-containing functions. A use of ozonation technique for this purpose deserves particular consideration while a use of ozone as an oxidant has a whole number of advantages. Among those are high reactivity and selectivity which allow to conduct oxidation under relatively mild conditions facilitating a control over oxidation degree of reactive products. The latter is of particular importance to avoid formation of toxic by-products.

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The literature data concerning the kinetics and mechanism of ozonation of such complicated macromolecular compounds are scarce. Mostly qualitative observations on the kinetics have been published [2-4] based on chromatographic data and numerical simulations. The problem is that the ozonation is multistage process, and a wide variety of intermediates formed is difficult to identify. An additional complication is a strong dependence of the ozonation products on the experimental conditions (pH, temperature, etc.). For example, the ozonation pathways of phenolic compounds depend greatly on pH [5].

It is known that molecular ozone preferably oxidizes electron-rich sites (aromatic carbon-carbon double bond, aromatic alcohols, and non-saturated structures) [6]. As a result, a dramatic decrease in ultraviolet (UV) absorbance at 254/280 nm is observed during ozonation of the aromatic compounds [7]. The application of small doses of ozone was shown to result in polymerisation processes [8].

The major end products of lignin ozonation are reported to be carbonyl compounds, low molecular weight (MW) carboxylic acids, mainly acetic, formic, and oxalic acids, which are stable to ozonation [9, 10]. In spite of many studies on the structure of HS and of their oxidation products, the reaction pathways that HS undergo during ozonation process remain poorly understood. The production of lower MW fulvic acid (FA) using ozone oxidation of higher MW humic acid (HA) has been discussed by several researchers [11-13]. The obtained FA showed a high content of oxygen and carboxylic groups.

It is known that during ozonation in water solutions, hydroxyl radicals (OH•) reactions proceed along with direct ozonation [14, 15]. OH• radicals react relatively unselectively. The radical generation is usually ascribed either to ozone self-decomposition in neutral and basic media, or to substrate-ozone reactions. In its turn, OH• radicals produce organic radicals as a result of their reactions with organic compounds. The reactions with OH• radicals may bring about substantial structural changes in macromolecules including hydroxylation, decarboxylation, and depolymerisation of the initial materials, producing oxidized structures that are less hydrophobic and less aromatic (16).

At present, the advanced oxidation processes (AOPs) are being developed to improve the kinetics of ozone reactions with natural organic matter. A strong and selective oxidation could be brought about by addition of the effective catalysts, e.g. transition metal ions. Some heterogeneous catalysts have also been found to enhance the ozonation efficiency of aquatic HS [17] and lignin-containing materials [18]. The catalysts facilitate the oxidation of less reactive organic compounds in aqueous solutions and diminish the ozone consumption [19]. Some studies illustrate that a use of metal ions in the ozone reactions with aromatic compounds could lead to reactions of hydroxylation, alkyl radicals oxidation, oxidative condensation, etc. [20] without aromatic ring destruction.

To deepen the understanding of the kinetics and mechanism of ozone reactions with lignins and HS, the objectives of this paper were: to estimate the kinetic parameters of ozonation; to study structural changes of lignin and HS brought about by ozonation; to suggest the ozone oxidation pathways for lignin and HS.

2. Materials and methods

Materials. Sulphate lignin (LG) (Germany), sodium ligninsulphonate (LS) (Sloka paper mill, Latvia) and potassium humate (CHP-K) produced from leonardite (Humintech, Germany) were used in this study. Elemental composition and molecular weight of the samples used are given in Table 1.

Table 1. Elemental composition and molecular weight (M_w) of humic and lignin samples used in this study.

Sample	Content of elements, %				M_w, kDa
	C	H	N	Ash	
LG	64.4	5.81	0.26	n.d.	3.0
CHP-K	42.2	3.04	1.02	26.0	3.2

Preparation of solutions. The solutions of LS and CHP-K were prepared in the range of concentrations of 0.5-5.0 g/L. To obtain solutions at pH 8.6, 0.13 M phosphate buffer was used. To attain strongly basic or acidic pH, concentrated NaOH or H_2SO_4, respectively, was used.

Ozonation procedure. Ozonation was carried out in a bubble reactor at 20°C. The latter was a thermostated glass cylinder with a porous filter bottom equipped with an outlet tube and a special valve, to facilitate solution sampling during the reaction. Ozone generated in the air-fed ozonator was bubbled through the liquid or solid sample placed in the reactor. The volume of the reaction mixture was 20 mL. Ozonation was performed at an initial ozone concentration of $1.2\cdot10^{-3}$ M, the volume flow velocity of the gas mixture was 10.0 L/h. The reaction was stopped when inlet and outlet ozone concentrations became equal. After the ozone treatment, the contactor was purged with the air to remove residual ozone. The inlet and outlet ozone concentrations in the ozone-air gas mixture were determined using absorbance measurements at 260 nm. The ozone concentration was calculated from the known molar extinction value of 3300 mole/(L·cm). After ozonation, the reaction mixture was rotor-evaporated to obtain the solid preparations for further structural investigations.

Structural characterization of the samples before and after ozonation. To follow transformations of LS and CHP-K structures, the *UV/Vis absorption spectra* were recorded with Cary 3E UV/Vis spectrometer (Varian, USA). The optical length was 1 cm. Prior to the analysis, the samples collected in the course of the reaction were diluted up to the concentration of 0.1 g/L.

Elemental Analyses (C, H, N) were performed on a Carlo Erba Strumentazione elemental analyser. Ash content was determined manually by dry combustion.

Infrared (IR) spectra were recorded with a Specord 75 IR spectrophotometer in KBr pellets. The optical density was determined using $K_4Fe(CN)_6$ as an external standard. The relative optical density (a_ν) for a frequency ν was determined as a ratio of the optical density for a given band to that of $K_4Fe(CN)_6$ at 2015 cm^{-1}.

^{13}C solution-state NMR spectra of LG and CHP-K samples were measured on solutions of these materials in 0.1M NaOD/D_2O at a concentration of 10 g/L. Measurements were made on a Varian VXR-400 spectrometer operating at 100 MHz ^{13}C observation frequency. Each spectrum was a result of 12000-14000 scans. Sodium trimethylsilylpronanesulphonate was used as an internal standard. The spectra were recorded at a 4-s delay time. These conditions were shown to provide quantitative determination of carbon distribution among the main structural fragments of HS [21].

To quantify the obtained spectra, for HS samples the assignments were made according to [21] (in ppm): 5-50 – aliphatic H and C-substituted C atoms (C_{Alk}), 50-95 – alcoholic and ether groups (C-OH, C-OR), 95-105 – C atoms of -O-C-O- groups; 105-145 – aromatic H and C-substituted atoms (C_{Ar}-H,C), 145-160 – aromatic O-substituted C-atoms (C_{Ar}-O), 160-188 – C atoms of carboxylic and esteric groups (COO), 188-220 – C atoms of quinonic and ketonic groups (C=O). For LG sample, the assignments were made according to [22] and were as follows: 6-54 – aliphatic H and C-substituted C atoms (C_{Alk}), 54-62 – aliphatic O-substituted C atoms (C_{Alk}-O), 62-100 – alcoholic and ether groups (C-OH, C-OR); 100-140 – aromatic H and C-substituted atoms (C_{Ar}-H,C), 140-169 – aromatic O-substituted C-atoms (C_{Ar}-O), 169-190 – C atoms of carboxylic and esteric groups (COO), 190-220 – C atoms of quinonic and ketonic groups (C=O).

3. Results and Discussion

3.1. KINETIC STUDIES ON LIGNIN AND HS OZONATION

The ozonation reactions in solution were studied using lignosulphonate (LS) as a water-soluble representative of lignin compounds, and potassium humate (CHP-K) as a representative of humic compounds. Lignin (LG) was use as a suspension. The solubility of LS is provided by -SO_3H groups introduced into initial lignin backbone during sulphite treatment, while the solubility of CHP-K is provided by its presence in the form of the salt of alkali metal – by the high ionisation degree of acidic groups of HS.

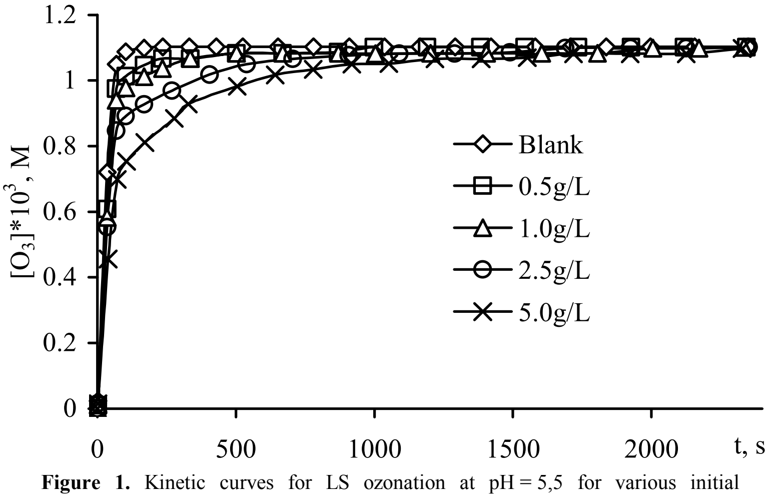

Figure 1. Kinetic curves for LS ozonation at pH = 5,5 for various initial concentrations.

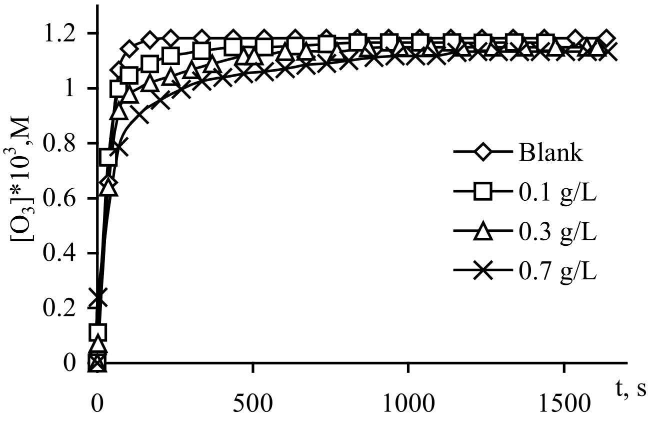

Figure 2. Kinetic curves for CHP-K ozonation at pH=5,5 for various initial concentrations.

The typical ozonation curves obtained for the LS and CHP-K solutions at neutral pH are shown in Figs. 1 and 2, respectively. The data on outlet ozone concentration ($[O_3]$, 10^{-3} M) were further plotted against treatment duration (t, sec). The similar curves were obtained for solutions of these preparations at pH 1.0 (only for LS), 8.6, and 12.0.

To treat the obtained results numerically, the kinetic model for ozone reactions with chemical compounds in a bubble reactor was used [23]. The model assumes that (1) the rate of reaching the equilibrium ozone distribution between the gas and solution phases substantially exceeds the reaction rate, and (2) the dissolved compounds interact with dissolved ozone only.

To calculate the quantitative kinetic parameters – rate constants and ozone consumption – out from the obtained kinetic curves using the above model, the approach developed in our previous papers [24, 25] was used. For the reaction:

$$\mathbf{A + O_3 \xrightarrow{k_{eff}} products} \tag{1}$$

Solution of the corresponding system of differential equations can be written as follows:

$$\mathbf{y}/[\mathbf{A}]_0 = \mathbf{a}\cdot(1 - \exp(-\mathbf{k}_{eff}\cdot\mathbf{K}\cdot\mathbf{x})) \tag{2}$$

where $[\mathbf{A}]_0$ is the concentration of the initial compound with dimensional units (g/L), **a** is the total ozone consumption, $\mathbf{k}_{eff}$ is the effective rate constant ($M^{-1}sec^{-1}$), **K** is the equilibrium constant of ozone distribution between gas phase and solution, **y** and **x** are parameters calculated from the integration of the kinetic curves according to the following expressions:

$$\mathbf{y = W\int_0^t (c_0 - c)dt - Kc(t)} \tag{3}$$

$$\mathbf{x = \int_0^t c\,dt} \tag{4}$$

where **W** is the specific gas flow rate (sec^{-1}), $\mathbf{c_0}$ and **c** are inlet and outlet ozone concentrations, respectively (M), **t** – ozonation time (sec).

As follows from eqs 3 and 4, **y** is the amount of ozone consumed up to the time **t**; **x** is a parameter proportional to the amount of residual ozone. The rate constant $\mathbf{k_{eff}}$ can be calculated by fitting the experimental **y** *versus* **x** relationship using eq 2.

At the start time eq 2 can be rewritten as follows:

$$\mathbf{y/[A]_0 \sim k_{eff}Kx} \qquad (5)$$

In this paper, the initial slope of **y** *versus* **x** relationships was used as a numerical value for the comparison of kinetic data on ozonation of lignin and HS preparations. Ozone consumption (**a**) was calculated from the same curves. The corresponding results are summarized in Table 2.

Table 2. Kinetic parameters of the lignin and humic substances reactions with ozone at various pH.

pH	**a**, g O_3/g			$\mathbf{k_{eff}}$ ($\times 10^2$), $L \cdot g^{-1} \cdot sec^{-1}$		
	LG*	LS	CHP-K	LG	LS	CHP-K
1.0	0.48±0.07	0.34±0.05	–	2.8±0.8	4.7±1.4	–
5.5	3.60±0.54	0.91±0.14	1.82±0.27	9.0±2.7	7.9±2.4	16.2±4.9
8.6	3.00±0.45	1.92±0.29	1.73±0.26	8.0±2.4	19.5±5.9	27.9±8.4
12.0	–	2.26±0.34	1.87±0.28	–	71.0±21.3	71.9±21.6

* LG was used as a suspension – heterogeneous reaction.

Table 2 indicates that the rate constants $\mathbf{k_{eff}}$ for LS and CHP-K oxidation by ozone are on the same order of magnitude, and increase substantially with an increase in pH. Concerning the ozone demand (**a**), it strongly depends on pH in the case of LS ozonation, and, in contrast, it does not change for the CHP-K reaction with ozone. The similar dependence – increase of oxidation rate and ozone demand along with an increase in pH – was observed for the LG suspension.

3.2. STRUCTURAL STUDIES ON THE OZONATED LIGNIN AND HS

To follow the pathways of ozonation reactions, the structural changes in the ozonated lignin samples – LS and LG, and HS were characterized using UV/Vis-, IR- and ^{13}C NMR-spectroscopy.

Figs. 3 and 4 display UV/Vis spectra of LS and CHP-K samples, respectively, in the course of ozonation at pH 5.5. Very similar spectra were observed at pH 1.0 (for LS only), 8.6, and 12.0.

For CHP-K, the UV absorbance at 280 nm started abruptly decreasing even at initial moments of ozonation. For LS, the relationship of the absorbance at 280 nm versus time of ozone consumption, has more complicated character (Fig. 5). Ozone consumption was calculated per mole of LS structural units (M_r = 240).

IR- spectra of ozonated LS samples were treated using the semi-quantitative data treatment technique for determination of the content of functional groups [26]. The results obtained show that ozonation caused oxidation of LS sulpho-groups to sulphate ions. The reduction in intensity of spectral bands corresponding to aromatic carbon along with an increase in the intensity of carbonyl groups suppose opening the rings due to oxidation with follow up formation of additional carboxyls or ketone. The formation of quinones cannot be excluded as well.

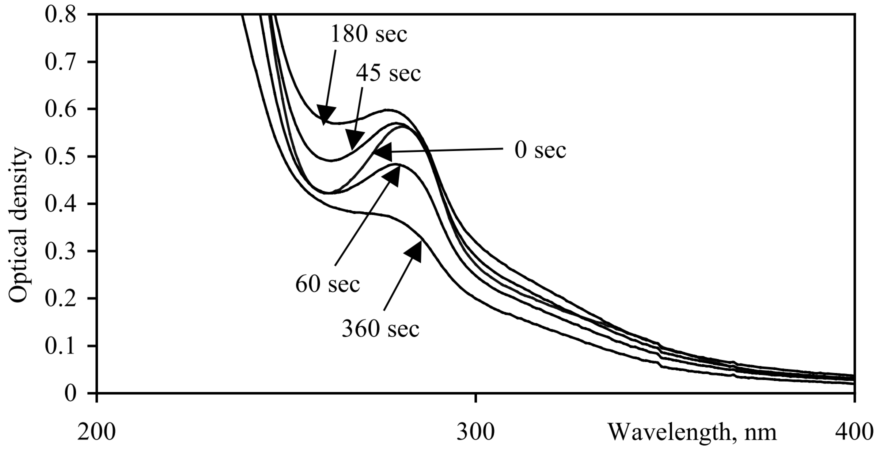

Figure 3. UV/Vis spectra of LS in the course of ozonation (pH = 5.5).

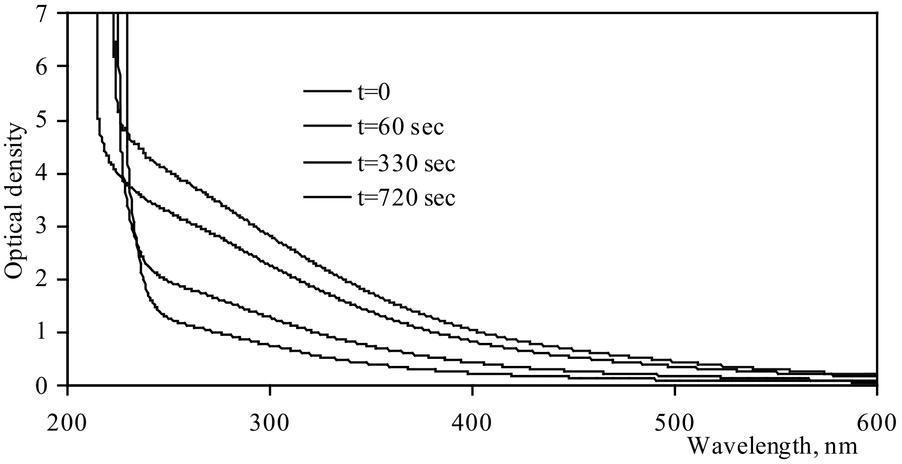

Figure 4. UV/Vis-spectra of CHP-K in the course of ozonation (pH=5.5).

^{13}C NMR spectroscopy requires high sample concentrations and solubility in NaOH. So, LG rather than LS was taken for this analysis. The ^{13}C NMR spectra of initial LG sample and of the samples ozonated in neutral and alkali solution (pH 12.0) are given in Figure 6. As it can be seen, the spectra of ozonated LG samples are characterized with a substantial decrease in spectral intensity in the range of non-substituted aromatic carbons (100-140 ppm) along with an increase in the spectral intensity of O-substituted aromatics (140-169 ppm) and carboxylic carbon (169-190 ppm). The most significant changes in the peak shapes – broadening and substantial overlapping – are observed for the sample ozonated in the alkali solution indicating its higher degradation during the ozone treatment compared to that in neutral solution.

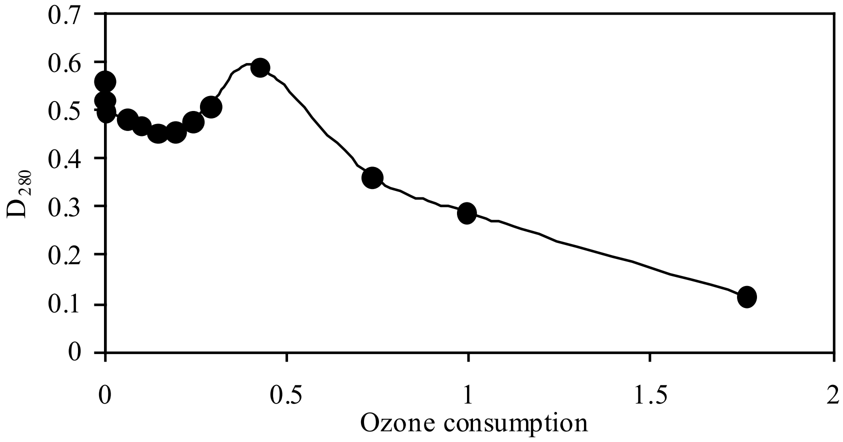

Figure 5. Dependence of UV absorption at 280 nm of LS solution (pH 5.5, c_{LS}=1.0 g/L) on ozone consumption.

To quantify the changes in structural features of the LG samples brought about by ozonation at pH 5.5 under the different levels of ozone consumption, the distribution of carbon between main structural groups was calculated from the given spectra and summarized in Table 3.

Table 3. Distribution of carbon among the structural units in the LG sample before and after ozonation at pH 5.5 at the different level of ozone consumption.

Group	Range of chemical shift, ppm	Content of carbon, % of total C		
		Before ozonation	Sample 1 0.16 g O_3/g LG (m = 195.5 mg)	Sample 2. 0.36 g O_3/g LG (m = 196.4 mg)
-COOH, -COOR	169-190	2.1	9.34	13.3
-C_{Ar}-OH, -C_{Ar}-OR	140-169	20.1	16.21	13.60
C_{Ar}-H,C	100-140	42.2	36.06	25.80
-C-OH, -C-OR	62-100	9.9	9.72	18.80
-OCH_3	54-62	12.8	10.50	8.70
C_{Alk}	6-54	13.0	18.17	19.60

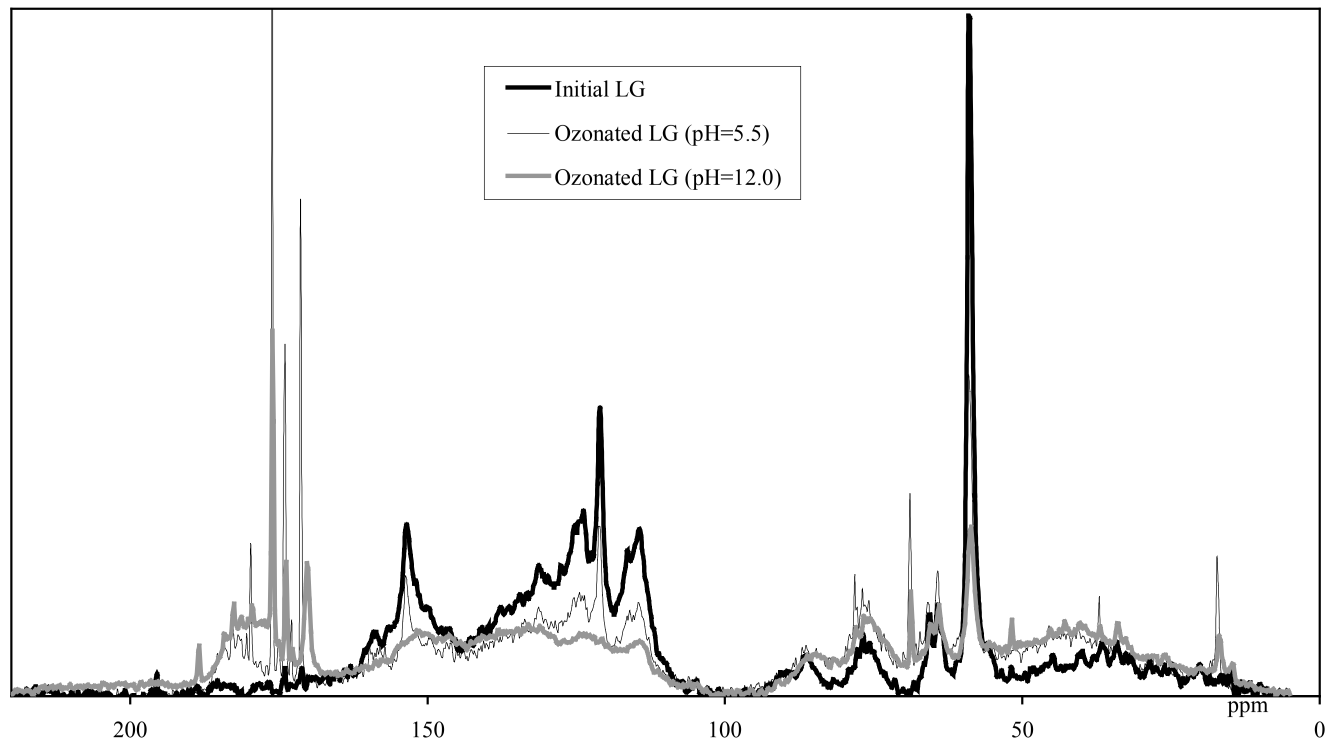

Figure 6. ^{13}C NMR-spectra of LG samples in 0.1 M NaOD/D_2O ozonated at neutral (5.5) and alkali (12.0) pH.

As follows from Table 3, the content of carboxylic, alcoholic, and ether groups in the course of ozonation increases along with a decrease in the content of aromatic structures. The most drastic increase is observed for carboxylic groups – from 2.1 to 13.3%. This allows to suppose that the prevailing pathway during lignin ozonation is splitting of aromatic rings with subsequent formation of carboxylic groups.

3.3. COUPLING THE PHYSICAL-CHEMICAL AND STRUCTURAL DATA ON LIGNIN OZONATION

To surmise on the reaction pathways of lignin ozonation, the values of ozone demand obtained in the kinetic experiments, were compared to an increase in the amount of the oxygen-containing structural groups for LS sample. The ozone demand was calculated from the kinetic curves, and an increase in O-containing functional groups - from the NMR-spectra.

Sample 1:

Kinetic curves: ozone consumption is **0.16 g/g LG**.

From elemental analysis carbon content in LG sample is 64.4%.

^{13}*C-NMR spectra*: carbon content in the sample weight (m_C) was equal to $0.644*m_{LG}$ (m_{LG} = 195.5 mg) or 125.9 mg. An increase in the content of carboxylic groups Δm_{COO} can be estimated from the data in Table 3 as $(9.3 – 2.1)/100*m_C$ = 9.1 mg, that equals to 0.76 mmol C. Changes in alcohol and ether groups content are negligible at this stage. Assuming that one ozone molecule is consumed for formation of one carboxyl group from aromatic C, ozone quantity needed for formation of the additional COO groups is 0.76 mmol*48 g/mol = 36.5 mg. Specific ozone demand in this case would be 36.5 mg/195.50 mg = **0.186 g/g LG**. The calculated value is rather close to the experimentally determined value of 0.16 g/g LG.

Sample 2:

Kinetic curves: ozone consumption is **0.36 g/g LG**.

^{13}*C-NMR spectra*: $m_C = 0.644*m_{LG}$ (m_{LG} = 196.4 mg) = 126.5 mg. An increase in carboxylic groups (from Table 3) content equals to $\Delta m_{COO} = (13.4 – 2.1)/100*m_C$ = 14.3 mg. An increase in alcoholic and ether groups is $\Delta m_{COH,\ COR} = (18.8 – 9.9)/100*m_C$ = 11.3 mg. Given a simultaneous decrease in the content of methoxylic groups by $(12.76 – 8.70)/100*m_C$ = 5.2 mg, the resulting increase in O-containing groups can be calculated as follows: (14.3 + 11.3 – 5.2) = 20.4 mg, or 1.7 mmol C. The ozone quantity needed for such an increase in O-containing groups accounts for 1.7 mmol*48 g/mol = 81.6 mg that corresponds to the specific ozone demand of 81.6 mg/196.4 mg = **0.42 g/g LG**. The calculated value is rather close to the experimentally determined one of 0.36 g/g LG.

The above calculations indicate that under the chosen reaction conditions the ozone consumption calculated from the kinetic curves is in a good agreement with the changes in structural group composition of the ozonated lignin samples.

The conducted investigations using kinetic analysis as well as UV/Vis-, IR-, and NMR-spectroscopy allowed us to suggest the principal transformations of lignin and HS samples during ozonation in solution.

Aromatic rings cleavage is a preferred direction of ozone reactions with lignin and HS in solutions. As a result, unsaturated oxidized compounds are formed. They further transform into aliphatic structures. The literature data show that small ozone doses leads to condensation processes. The decrease of LS absorbance at 280 nm at initial time moments could be due to condensed structures formation or various modifications of LS functional groups (C=O, C–OH).

The experimental data presented allow us to conclude that the variation of operating conditions (pH, ozone dose, etc.) enables regulation of the ozonation process, producing oxidized molecules with desirable contents of O-containing functional groups.

4. Conclusion

The rate constants for LS and CHP-K ozonation in solutions increase substantially with an increase in pH. Total ozone consumption strongly depends on pH for LS ozonation, and, does not change depending on pH media for the CHP-K reaction with ozone. The ozonation in solutions is much deeper than in solid state. The content of O-containing groups (carboxylic, alcoholic, and ether groups) increases in the course of LG, PHF, and CHP-K ozonation along with aromatic ring destruction.

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