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Chemical studies of ozone impact on pinewood (*Pinus sylvestris* L.) degradation

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Abstract: *Chemical studies of ozone impact on pinewood (Pinus sylvestris* L.*) degradation*. The purpose of these studies was verification the impact of ozone on wood degradation. Study the degree of wood degradation was carried out using classical chemical methods – content determination of substances soluble in 1% NaOH, extractives and cellulose isolated by Seifert method. Also, in this work modern analytical SEC method was used to determine the polymerization degree of the main wood structural component – cellulose. On the basis of these results, it was observed, that ozone increases of the content of substances soluble in 1% NaOH and extractives. This indicates, that the wood structural substances are decomposed: the part of lignin and polysaccharides (hemicelluloses, cellulose) - especially with a low degree of polymerization. On the basis of chromatographic analysis (SEC), it appears that the cellulose of the highest molar mass is also prone to depolymerization. Although the percentage content of the cellulose does not change, but under the influence of ozone comes to qualitative change of cellulose - decrease of polymerization degree.

Keywords: ozone, wood degradation, cellulose degradation, SEC, 1% NaOH, cellulose, extractives

INTRODUCTION

In recent years the interest in ozone as oxidizing substance has grown up. Ozone, for example, is used in pulp bleaching processes. Its bigger interest is related with the introduction of environmental policy, under the influence of which bleaching methods have been developed without the use of elemental chlorine - ECF (Elemental Chlorine Free) and the methods totally free of any chlorine compounds - TCF (totally chlorine free). According to the TCF technology classical chlorine agents are replaced by oxygen bleaching agents: oxygen (O_2), hydrogen peroxide (H_2O_2) and ozone (O_3). However, the use of ozone in the bleaching processes is not entirely beneficial. It is associated with poor selectivity and heterogeneity of the strong oxidant, which in turn causes degradation not only lignin, but also polysaccharides - even cellulose [Chirat and Lachenal 1994, Simoes and Castro 2001].

Another recently popular direction in wood protection is the use of ozone as a disinfectant agent. Ozone treatments are performed in order to eliminate the biological factors of wood degradation. Ozone eliminates the insects, mites and even mold fungi spores. This method can be used to disinfect the entire building including all its internal objects. Negative side of the ozone application is its impact on the degradation of wood. However, the degree of degradation caused by the use of ozone is incomparable lower than the degree of degradation caused by wood insect and fungi. To a large extent the cause of significant resistance of wood to the oxidizing agent (ozone) is the presence of natural antioxidants (extractives and lignin). Much faster degradation under the influence of ozone occurs for directly exposed cellulose [Antczak 2010]. An additional serious problem associated with ozonization of historic wooden objects could be a risk of irreversible destruction of very valuable ornaments (polychrome), occurring both inside and outside the building.

Study the degree of wood degradation can be carried out using classical chemical methods, or by using more complex but more accurate instrumental methods. To the former can include the content determination of substances soluble in 1% aqueous solution of sodium hydroxide (NaOH). It is known, that in dilute solutions of alkali polysaccharides with a low

degree of polymerization (hemicelluloses and part of cellulose) are particularly susceptible to dissolution. Moreover partially degraded lignin also can be soluble. The increase of content of substances soluble in 1% NaOH, may be evidence of wood degradation process [Fengel and Wegener 2003]. Another chemical method to study the degradation degree of wood is instrumental modern technique - the size exclusion chromatography (SEC). Using the SEC method you can monitor the degree of degradation of structural wood substances such as cellulose, hemicelluloses or lignin. This method gives information about the weight average molar mass (M_w), the number average molar mass (M_n) and also, what is the most important, the molar mass distribution (MMD) of polymeric sample. Moreover, the degree of polymerization (DP) can be obtained.

The aim of these studies was verification the impact of ozone on wood degradation. In this work modern analytical SEC method was used to determination the degree degradation of the main wood structural component – cellulose.

MATERIALS AND METHODS

In these studies material from hardwood zone of about 90-year-old pine (*Pinus sylvestris* L.) was used. Average density of wood used for the study was 0.515 g/cm^3. To aging tests with ozone, rectangular samples were used, cut along fibers with dimensions (2 x 2 x 3 cm). Ozone treatment was carried out at room temperature (25°C), about 40% relative humidity, in closed vessel (desiccator) and in the flow system (continuous gas supply - air). To obtain the ozone, generator of A2Z Ozone Systems company was used. During the ozone treatment the gas supply flow (air / O_3) was 1dm^3/min. Iodometry method was used to determine the percentage content of generated ozone in the air, which was 0.4%$_w$. Aging time of wood samples in the ozone atmosphere was 7 and 14 days. In the presented time intervals samples were collected to examine the degree of wood degradation.

To examine the degree of wood degradation by chemical methods, the samples were ground using a laboratory mill SM100 (Retsch company). Sawdust fraction passing the sieve with 1.02 mm and remaining on 0.49 mm mesh sieve was used. The following tests were performed to investigate the degradation of wood under the influence of ozone:

- determination of low-molecular substances content soluble in organic solvents (chloroform – ethanol mixture: 93-7 %$_w$) [Antczak et al. 2006]
- determination of substances content soluble in 1% NaOH [Krutul 2002]
- determination of cellulose content according to Seifert method [Krutul 2002]
- determination of polymerization degree of cellulose by SEC analysis

SEC analysis

Preparation of cellulose samples to analysis

In order to study cellulose degradation in aged wood, cellulose was isolated by Seifert method. Then dried at 105°C cellulose samples were submitted to activation and dissolution procedure. The procedure was carried out in vacuum Baker system SPE-12G and was as follows:

- cellulose samples (15 mg) were placed in test-tubes (6 ml), poured distilled water (3 ml) and allowed to swell overnight;
- next day the samples were carried to capillary tubes and subsequently washed with methanol, filtered and poured the next portion of methanol and left for 1 hour; this procedure with methanol was repeated twice;

- after that, the samples were washed with N,N-dimethylacetamide (DMAc), filtered and poured the next portion of DMAc and left for 1 hour; this procedure was repeated and cellulose with DMAc was left untill the next day;
- next day, the samples were filtered and poured 8% lithium chloride (LiCl) in DMAc (4 ml);
- cellulose dissolution in 8% LiCl/DMAc was realised using mixer (RM-2M, Elmi company);
- after 1-2 days of dissolution, part of the sample (0.2 ml) was diluted to 0.5% LiCl concentration with pure DMAc (3 ml);
- finally, prepared samples were submitted to SEC analysis.

Conditions of SEC analysis

SEC analysis of cellulose samples was carried out with using HPLC (High Performance Liquid Chromatography) system (LC-20AD, Shimadzu company), which was equipped with differential refractive detector (RID 10A, Shimadzu), pump (LC-20AD, Shimadzu) and oven (CTO-20A, Shimadzu). SEC analysis conditions were as follows:
- 0.5% LiCl/DMAc as eluent
- column – crosslinked polystyrene-divinylbenzene gel (PSS GRAM 10000, 10µ, 8×300 mm) connected with guard column (PSS GRAM 10µ)
- oven temperature: 80°C
- flow rate: 2ml/min
- injection volume: 200µl

The chromatographic data were processed with PSS WinGPC scientific 2.74 software. Twelve narrow molecular weight polystyrene standards (Polymer Laboratories) were used to calibrate the column. The polystyrene standards were prepared as mixed standards in four separate solutions in DMAc. The first standard solution contained polystyrene of the following peak molecular mass: 6 850 000, 565 000 and 11 300 Da, the second contained: 3 950 000, 170 600 and 2 960 Da, the third contained: 3 150 000, 66 000 and 1 700 Da, and the fourth contained: 1 290 000, 28 500 and 580 Da. This polystyrene standards were used to calculate molecular mass of cellulose according to Mark-Houwink universal calibration: $[\eta]=K\times M^{\alpha}$, where K and α are parameters, which depend on polymer type, solvent and temperature. For our chromatographic conditions, that parameters are the following: for polystyrene $K=17.35\times10^{-3}$ cm^3/g and $\alpha=0.642$ [Timpa 1991] and for cellulose $K=2.78\times10^{-3}$ cm^3/g and $\alpha=0.957$ [Bikova and Treimanis 2002].

RESULTS AND DISCUSSION

In Fig. 1, 2 and 3 the impact of ozone on the percentage content of substances occurring in pinewood was presented. On the basis of results can be observed degrading effect of ozone on the wood. Strongly oxidative gas atmosphere (0.4% of ozone in air) initiates the degradation of structural wood components (especially substances with the low degree of polymerization). Evidence of this is increase of the content of substances soluble in dilute alkali (Fig. 1). The increase is the greatest at the beginning of ozonization (within the first week). In relation to the control sample, after one week of ozonization, the content of substances soluble in 1% NaOH is 2.5 times greater. Prolongation of ozonization to two weeks does not cause a significant increase in this parameter. Certainly, at the beginning depolymerization reaction of the wood structural components occurs in the most easily accessible areas for ozone (amorphous regions). Subsequently, less accessible areas are

attacked, which is associated with a slower course of degradation reaction and a lesser increase of substances soluble in dilute alkali.

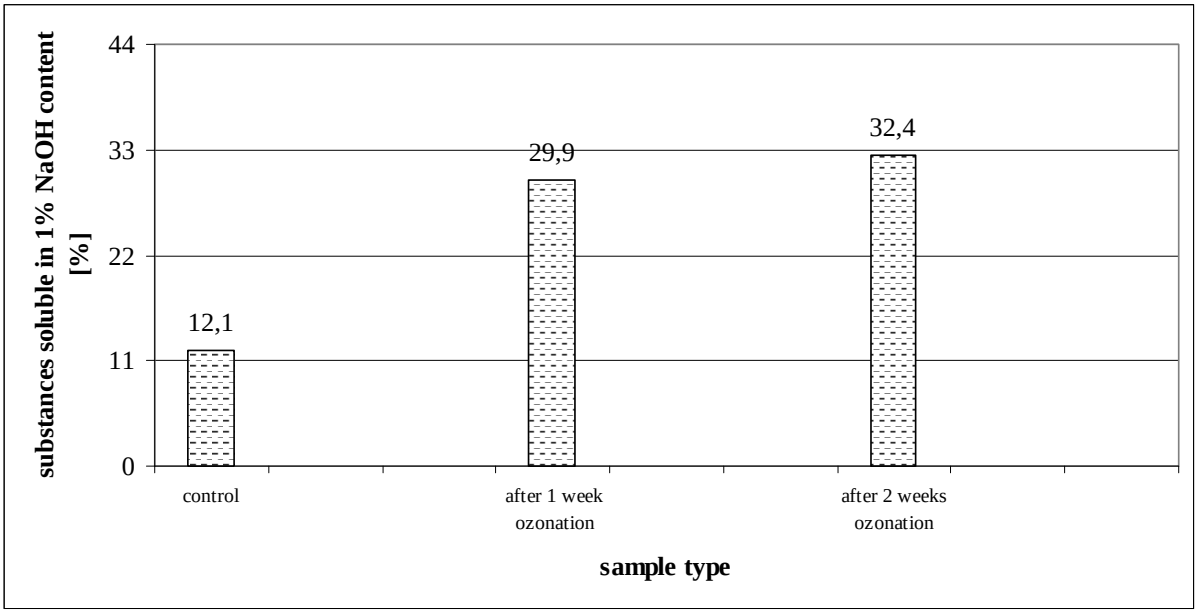

Fig. 1. Ozone influence on the content of substances soluble in 1% NaOH from pinewood (*Pinus sylvestris* L.)

The unfavourable effect of ozone on the wood is also reflected in the increasing content of low molecular soluble substances in a mixture of organic solvents (chloroform - ethanol: 93 - 7%). Fig. 2 shows percentage content of wood extractives in pinewood (*Pinus sylvestris* L.), which has been subjected to ozone. Two-week ozonization (0.4% of ozone in air) causes an increase in low molecular substances content. This demonstrates the gradual disintegration of the structural substances: lignin and polysaccharides (hemicelluloses, cellulose) - probably with a low degree of polymerization from amorphous regions.

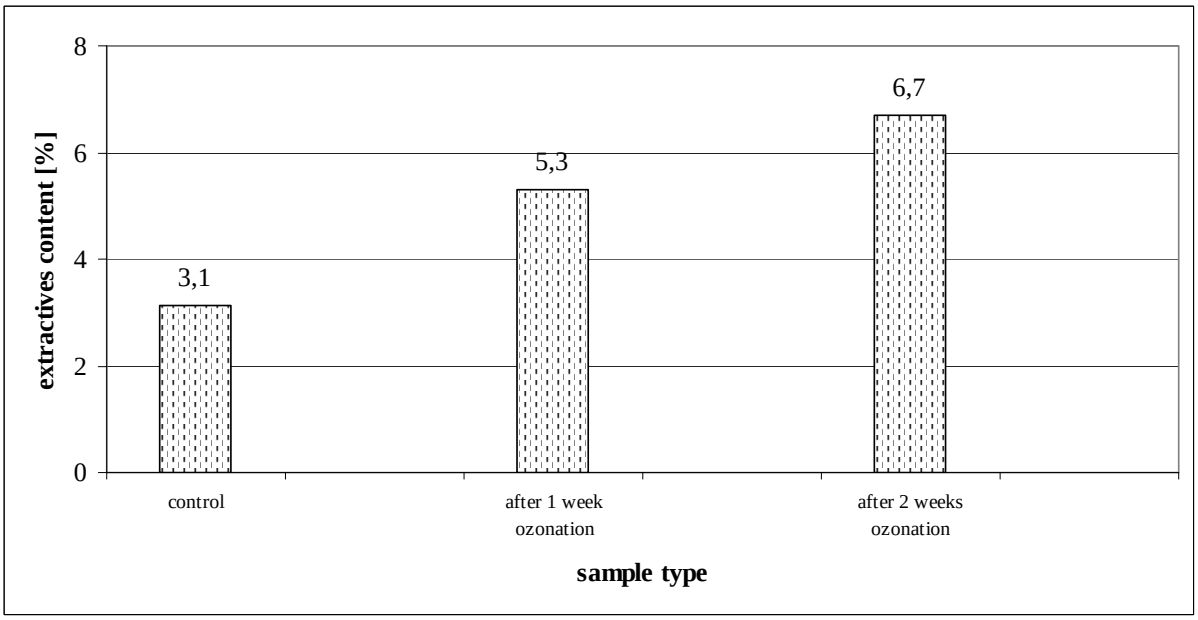

Fig. 2. Ozone influence on the content of extractives from pinewood (*Pinus sylvestris* L.)

Fig. 3 shows percentage content of cellulose separated by Seifert method from pine wood. Cellulose separated by Seifert method represents a polysaccharides fraction from wood

with the highest degree of polymerization. Two-week ozonization (0.4% of ozone in air) practically does not change the percentage content of cellulose.

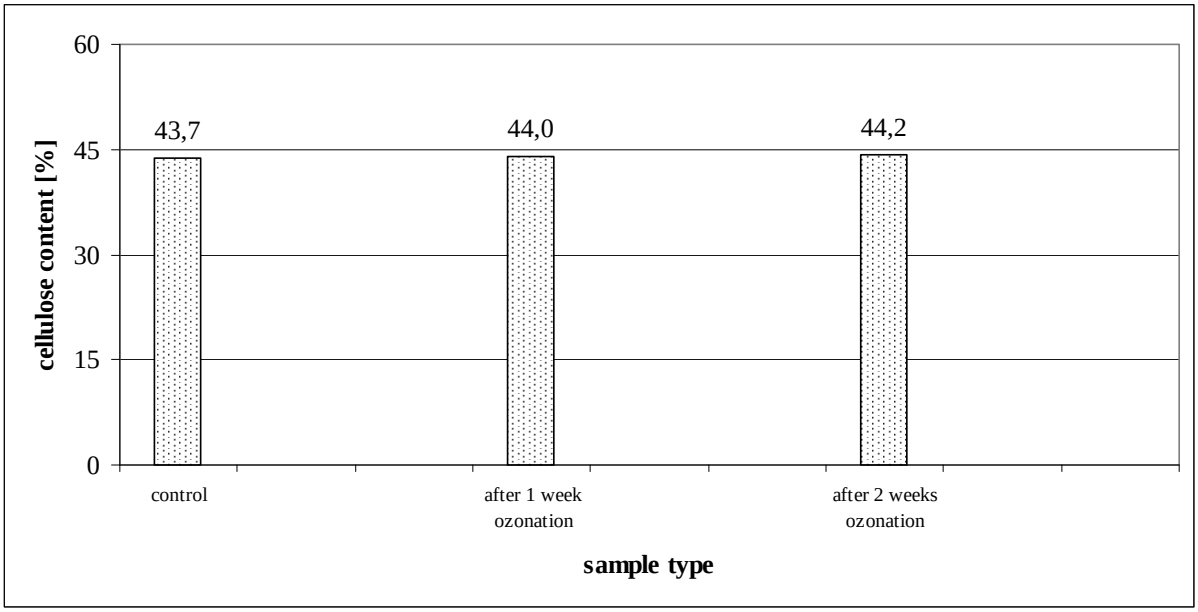

Fig. 3. Ozone influence on the content of cellulose from pinewood (*Pinus sylvestris* L.)

Interesting results were obtained in the SEC method. The weight average molar mass and polymerization degree of cellulose isolated from pinewood by Seifert method were determined (Fig. 4).

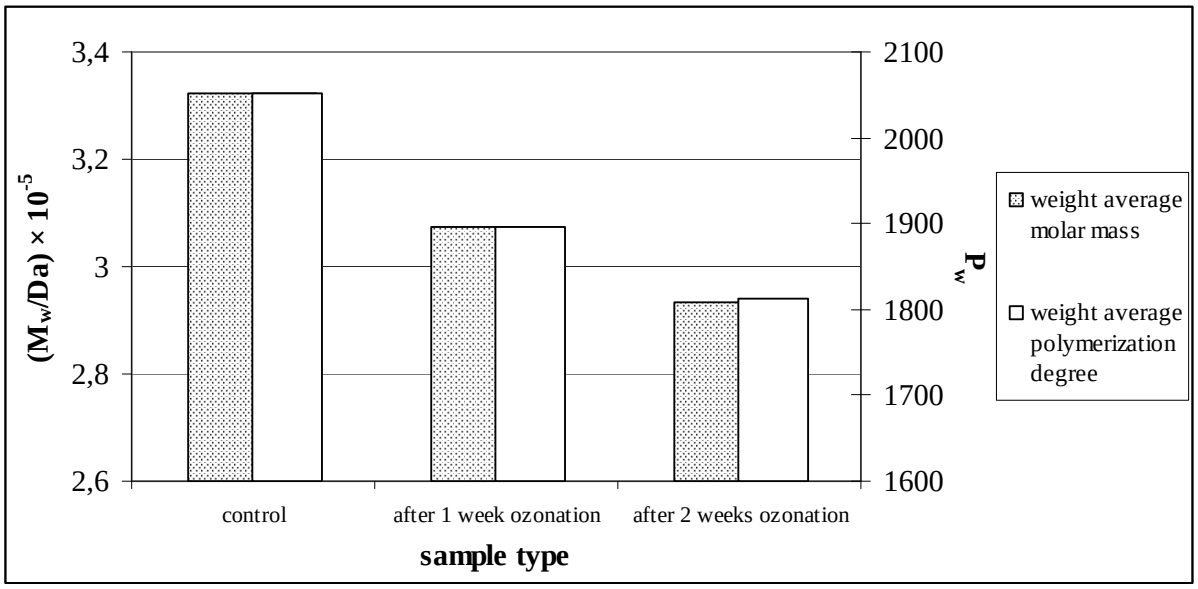

Fig. 4. Ozone influence on the weight average molar mass and polymerization degree of cellulose isolated from pinewood (*Pinus sylvestris* L.) by Seifert method

Based on chromatographic results presented in Fig. 4, it can be concluded that under the influence of ozone occurs to initiate a degradation process of cellulose. Using the molar mass distribution curves (Fig. 5), it appears that the initial depolymerization process may undergo even a cellulose fraction of the highest molar mass. In Fig. 5 it can be observed a gradual decrease in the content of cellulose fraction of the highest molar mass (range 10^6 - 10^7 Da).

On the other hand there is a gradual increase in the content of cellulose fraction of lower molar mass (range 10^5 - 10^6 Da).

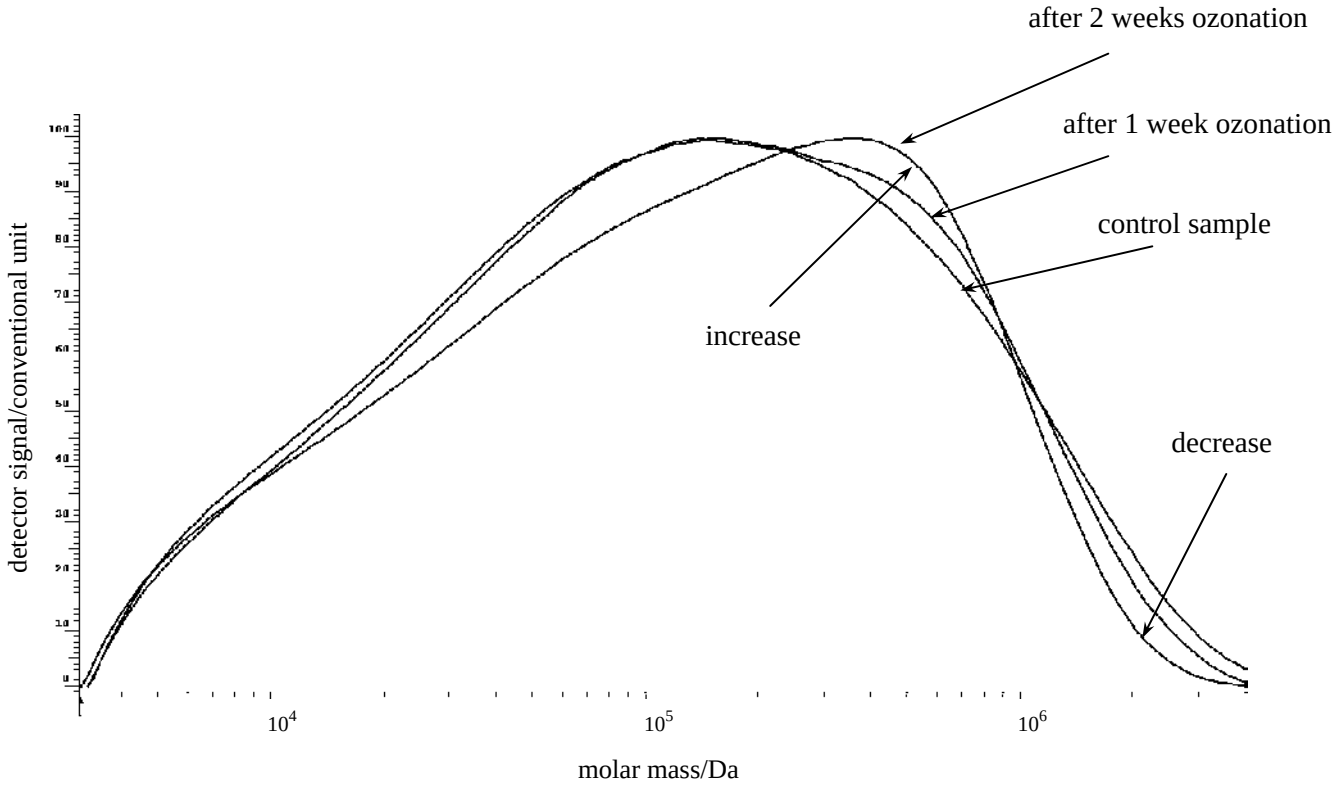

Fig. 5. Molar mass distributions of ozonated cellulose isolated from pinewood (*Pinus sylvestris* L.) by Seifert method

Such a course of cellulose degradation process under the influence of ozone explains the lack of change in the percentage content of cellulose with the highest degree of polymerization presented earlier in Fig. 3. Published literature information confirms, that as a result of ozonization, begins to cleavage of the glycosidic bond in the cellulose chain [Simoes and Castro 2001, Lemeune et al. 2004]. The consequence of this is a decrease of the polymerization degree of cellulose. Lowering the cellulose molar mass is very undesirable phenomenon because it is associated with a decrease in wood strength. This may eventually lead to total destruction of a wooden object.

SUMMARY AND CONCLUSIONS

Ozone as a substance with a very high oxidizing potential causes gradual degradation of pine wood. Under the influence of ozone increases the content of substances soluble in 1% NaOH and extractives. This indicates, that the wood structural substances are decomposed: the part of lignin and polysaccharides (hemicelluloses, cellulose) - especially with a low degree of polymerization. On the basis of chromatographic analysis (SEC), it appears that the cellulose of the highest molar mass is also prone to depolymerization. Although, the percentage content of the cellulose does not change (quantitative composition before and after ozonization practically the same), but under the influence of ozone comes to qualitative change of cellulose (decrease of polymerization degree).

In summary, the use of ozone in the context of cellulose and wood is always associated with degradation process. Poor selectivity and strong oxidizing properties of this substance may contribute to the total destruction of the cellulosic material or wood. This phenomenon is particularly undesirable when dealing with objects of high historical value. Thus, the use of

ozone to the pulp and wood materials should be done only in justified extreme cases, and in the shortest possible time.

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Streszczenie: *Badania chemiczne wpływu ozonu na degradację drewna sosny* (*Pinus sylvestris* L.). Celem badań była weryfikacja wpływu ozonu na degradację drewna. Badanie stopnia degradacji drewna zostało przeprowadzone przy użyciu klasycznych metod chemicznych – oznaczanie zawartości substancji rozpuszczalnych w 1% NaOH, substancji ekstrakcyjnych i celulozy wyodrębnionej metodą Seiferta. Ponadto, w tej pracy do wyznaczenia stopnia polimeryzacji głównego składnika drewna – celulozy wykorzystano nowoczesną technikę analityczną (SEC). Na podstawie wyników zaobserwowano, że pod wpływem ozonu dochodzi do wzrostu zawartości substancji rozpuszczalnych w 1% NaOH i substancji ekstrakcyjnych (małocząsteczkowych). Wskazuje to na rozpad substancji strukturalnych drewna: część ligniny i polisacharydów (hemiceluloz, celulozy) – szczególnie o niskim stopniu polimeryzacji. Na podstawie analizy chromatograficznej (SEC) okazuje się, że również celuloza o najwyższej masie cząsteczkowej jest podatna na depolimeryzację. Pomimo, że procentowa zawartość celulozy nie ulega zmianie, to pod wpływem ozonu dochodzi do jakościowej zmiany celulozy – spadku stopnia polimeryzacji.

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