

## **Influence of environment, temperature and time of the thermal modification of ash wood (*Fraxinus excelsior* L.) on the cellulose weight average degree of polymerization**

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**Abstract:** *Influence of environment, temperature and time of the thermal modification of ash wood (*Fraxinus excelsior* L.) on the cellulose weight average degree of polymerization.* Using the size-exclusion chromatography (HPLC SEC) method, the weight average degree of cellulose polymerization was determined. The polymer was isolated by the Kürschner-Hoffer method from ash wood (*Fraxinus excelsior* L.). The wood was thermally modified in different environments (nitrogen, steam and air) at 190°C and modification times of 2, 6 and 10 hours. Depending on the anaerobic atmosphere used, the highest values of the weight average degree of cellulose polymerization were obtained for the nitrogen environment, followed by steam and air. The effect of modification time on the weight average degree of polymerization was observed. The highest values were obtained for wood modified at 2 hours, then 6 and 10 hours of modification. The native wood showed the highest degree of polymerization. On the basis of the results obtained, it can be concluded that for the material studied the oxidation and degradation reactions occurring depend on the environment and time for a given temperature of wood modification.

**Keywords:** wood, thermal modification, modification environment, cellulose, degree of polymerization, degradation, oxidation

### **INTRODUCTION**

Thermal modification of wood is the process of exposing wood to elevated temperatures in a variety of protective environments for a specified period of time to improve its properties (Hill 2006). This type of modification is used to increase the value of wood of species that are readily available in given regions, but often of low aesthetic or functional value. The modification, depending on the conditions and environment applied, causes, among others, a change in the colour of the wood, improves its dimensional stability and makes it resistant to biotic and abiotic factors (Kamdem et al., 2002, Sailer et al., 2000, Viitaniemi et al., 2001, Mitsui 2006, Szczęśna et al., 2010, Gawron 2012).

High temperature modification also causes numerous changes in the chemical properties of wood. A number of chemical reactions and processes take place, the most important of which are, in the case of cellulose, the degradation of the amorphous part and the increase in crystallinity. At higher temperatures, cellulose decomposes into cyclic furan compounds (Rowell 2002, Yildiz and Gumukaya 2007, Zawadzki 2009).

Currently, several modification technologies based on different modification environments have been developed and used. These can be: steam (Thermowood) (Viitaniemi et al., 2001) nitrogen (Retification) (Kamdem et al., 2000, Chanrion and Schreiber, 2002), oil (Vernois, 2004). These processes differ in the conditions under which the modification is carried out.

Most modification processes take place in environments with an oxygen content reduced to a maximum of 2%. This limits the oxidation process and the far-reaching degradation of the degree of cellulose polymerization, resulting in a severe decrease in wood strength (Gawron 2012).

Depending on the temperature, the decomposition of cellulose is approximately three to six times faster under oxygen than under nitrogen (Rowell 2013). Mitchell (1988) also found that exposure of wood to high temperatures in the presence of atmospheric oxygen further influences the depolymerisation of carbohydrates. Furthermore, in air, the effect of temperature on cellulose accelerates the oxidation reactions of hydroxyl groups to aldehyde, carboxyl and carbonyl groups (Hill 2006).

The aim of this study is to investigate the effect of temperature and modification time of ash wood (*Fraxinus excelsior* L.) in different environments on the degree of cellulose polymerization determined by size-exclusion chromatography (HPLC SEC).

## MATERIAL AND METHODS

Samples made of ash wood (*Fraxinus excelsior* L.) cut from boards obtained from the uncoloured part of heartwood were used in the research. Part of the material was left without the modification process for testing (native samples), while the remaining part underwent thermal modification.

The samples were initially dried and then thermally modified in air, steam and nitrogen at 190°C for 2, 6 and 10 hours, respectively.

### Thermal modification of ash wood in air and steam

The thermal modification of wood in the tested environment was carried out in a laboratory dryer. The modification was preceded by drying the samples to an absolutely dry state. Then the temperature was raised to 130°C at a rate of 1°C/min, maintained at this temperature for a period of 30 minutes and again raised to 190°C at a rate of 1°C/min. After reaching the preset modification temperature in the drying chamber, a countdown of the actual modification time of 2, 6 or 10 hours was started. After the set time, the samples were cooled down to ambient temperature for 60 minutes in the dryer in which the modification took place. The samples were then placed in a desiccator.

### Thermal modification of ash in a nitrogen atmosphere

Thermal modification under nitrogen atmosphere was carried out in a 250 cm<sup>3</sup> three-neck round-bottom flask immersed in an oil bath. The temperature and time program followed the modification in an air and steam atmosphere.

### Procedure for dissolving samples of cellulose for chromatographic analysis (SEC)

Control samples of cellulose from unmodified wood and samples of cellulose from wood after thermal modification in different environments (air, steam, nitrogen) were subjected to size-exclusion chromatographic analysis (SEC). The study was carried out on cellulose isolated from wood by the Kürschner-Hoffer method described by (Krutul, 2002).

The cellulose activation and dissolution process was performed according to the method presented by Dupont (2003), modified by Zawadzki et al. (2009) and Antczak (2010). SEC analysis of cellulose samples was performed on a SHIMADZU liquid chromatograph, consisting of the following main components: a LC20-AD pump, a DGU-20A degasser, a 200 µl dosing loop, a CTO-10A oven, a RID-10A refractometric detector, a CBM-10A control module, a column system: PSS GRAM 10000 and PSS GRAM pre-column.

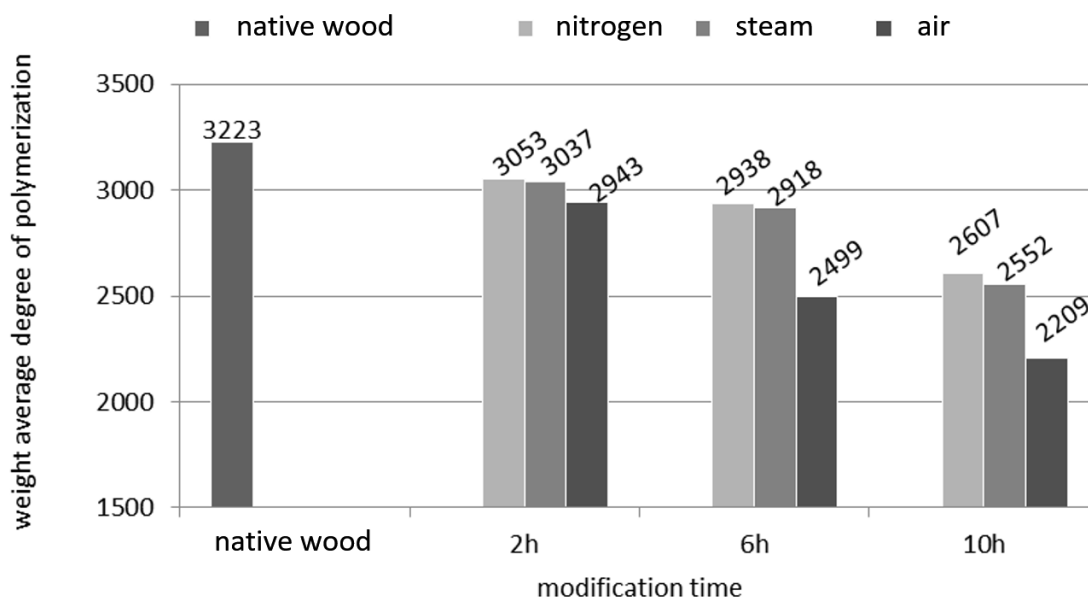
The chromatographic analysis conditions were as follows: eluent - 0.5% (w/v) LiCl solution in DMAc, flow rate 2.0 cm<sup>3</sup>/min, oven temperature 80°C, injection volume: 200 µl.

The column calibration curve was created based on polystyrene standards (Polymer Laboratories). From these, the average molecular weights of cellulose were calculated using the Mark-Houwink universal calibration. The following coefficients were used for calculations:

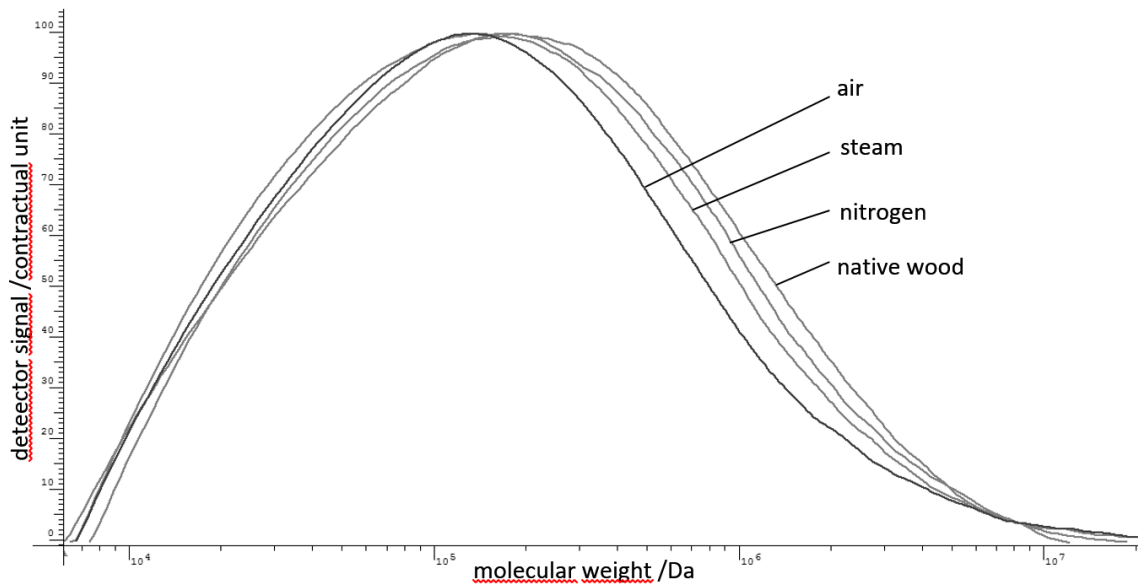
for polystyrene  $K=17.35 \times 10^{-3} \text{ cm}^3/\text{g}$ ,  $\alpha=0.642$  (Timpa 1991), and for cellulose  $K=2.78 \times 10^{-3} \text{ cm}^3/\text{g}$ ,  $\alpha=0.957$  (Bikova and Treimanis 2002).

## RESULTS AND DISCUSSION

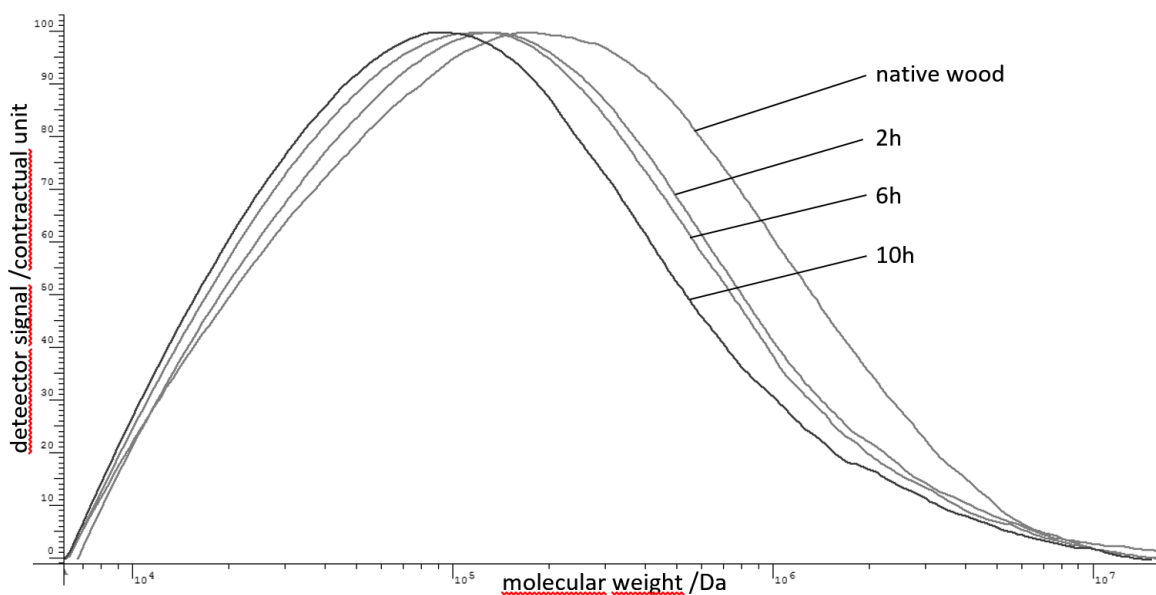
Using the size-exclusion chromatography method, the weight average degree of cellulose polymerization was determined. The polymer was isolated by the Kürschner-Hoffer method from ash wood (*Fraxinus excelsior* L.) unmodified and after thermal modification in different environments (nitrogen, steam and air). The results are presented in Fig. 1. From the results obtained it can be observed that thermal modification at  $190^\circ\text{C}$ , irrespective of the gas atmosphere used, causes a decrease in the degree of cellulose polymerization. In the case of nitrogen and water vapour atmospheres, during two and six hours of the modification process, the decrease is not great. On the other hand, in an air atmosphere, the cellulose degradation is much greater, especially at six and ten hours. An adverse effect of increasing the process time was observed. The results obtained for the degree of cellulose polymerization after 10h of modification are much lower in comparison with the corresponding results after shorter times (2h and 6h) of this process.



**Fig. 1.** Weight-average degree of polymerization of K-H cellulose isolated from ash wood (*Fraxinus excelsior* L.) unmodified and after thermal modification in different environments (nitrogen, steam and air).



**Fig. 2.** Molecular mass distribution of K-H cellulose from ash wood (*Fraxinus excelsior* L.) unmodified and after 2h thermal modification in different environments (nitrogen, steam and air).



**Fig. 3.** Molecular mass distribution of K-H cellulose from ash wood (*Fraxinus excelsior* L.) unmodified and after different times of thermal modification in an air atmosphere.

Examples of the molecular weight distribution of cellulose are shown in Figs. 2 and 3. Comparing different conditions of thermal modification it was confirmed that air atmosphere is the most degrading environment - the highest shift of cellulose molecular weight distribution curve towards lower values (Fig. 2). It can also be concluded that the highest molecular weight fraction of cellulose degrades under high temperature irrespective of the gas atmosphere used. Increasing the time of thermal modification in an air atmosphere to 10h causes an acceleration of the degradation of cellulose chains - an even greater shift of the molecular weight distribution curve to the left (Fig. 3).

Additionally, size-exclusion chromatography was used to investigate the kinetic dependence of cellulose degradation during thermal modification of ash wood (*Fraxinus*

*excelsior* L.). The reaction rate constants of cellulose degradation were determined from Ekenstam's equation, whose form is as follows:

$$\frac{1}{P_{w,t}} = \frac{1}{P_{w,0}} + kt$$

where:

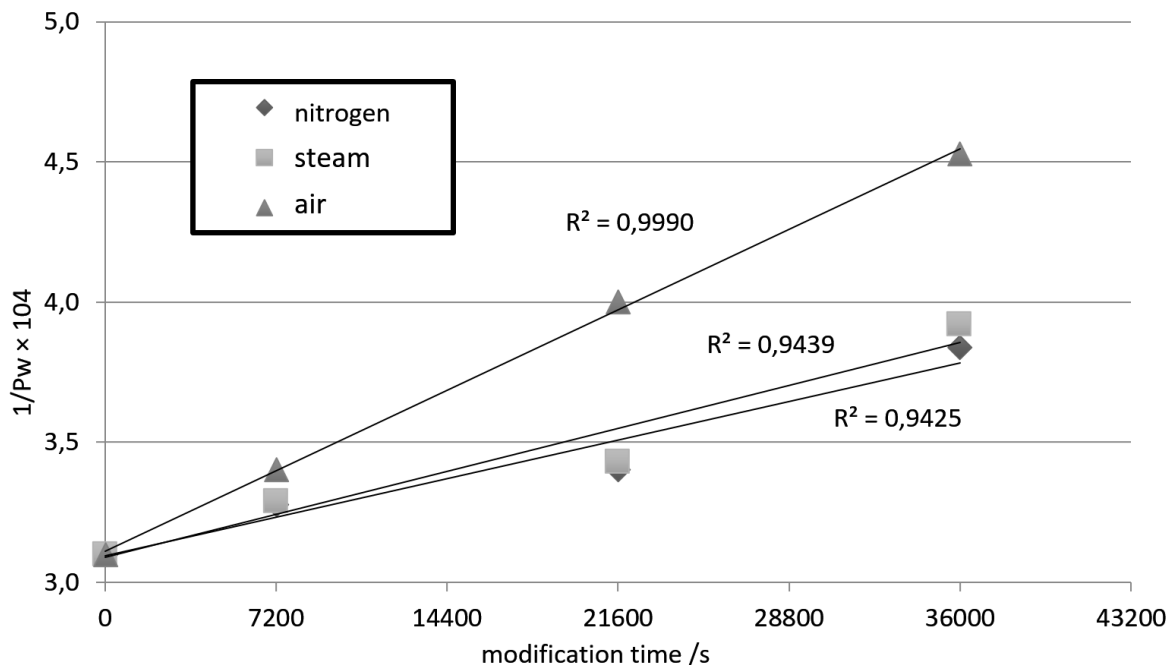
k - degradation reaction rate constant / s<sup>-1</sup>,

t - duration of the degradation reaction / s,

P<sub>w,t</sub> - weight average polymerization degree after time t of the degradation reaction

P<sub>w,0</sub> - weight average initial degree of polymerization

The above equation is a relation very often used to describe thermal degradation of cellulose (Fung 1969, Emsley and Stevens, 1994, Testa et al., 1994, Zou et al., 1996, , Zawadzki, 2009, Antczak, 2010). Fig.4, according to the Ekenstam model, shows the results of the inverse of the weight-average degrees of cellulose polymerization as a function of thermal modification time.



**Fig. 4.** Kinetic dependence of the degradation process of cellulose extracted from ash wood (*Fraxinus excelsior* L.) during thermal modification in different environments (nitrogen, steam and air).

The relationship observed in Fig. 4 is linear, which indicates a random mechanism of the cellulose degradation process under thermal modification. These observations are consistent with the results obtained by Zawadzki (2009). The determined rate constant of the cellulose depolymerization reaction at 190°C in a nitrogen atmosphere was  $k = (1.91 \pm 0.32) \times 10^{-9} \text{ s}^{-1}$ , while in water vapour it was slightly higher and amounted to  $k = (2.12 \pm 0.38) \times 10^{-9} \text{ s}^{-1}$ . On the other hand, in an air atmosphere under similar temperature conditions, an almost twofold increase in the cellulose degradation reaction rate was observed. The determined rate constant was  $k = (3.97 \pm 0.09) \times 10^{-9} \text{ s}^{-1}$ . The presented kinetic relations confirm that the process of thermal modification of ash wood (*Fraxinus excelsior* L.) in an air atmosphere is much more aggressive than the process in an inert gas or water vapour. Thermal modification of wood in an air atmosphere causes a rather rapid decrease in the degree of cellulose polymerization, which may be associated with a deterioration of the strength properties of the obtained wood as a result of oxidation and degradation processes.

## CONCLUSIONS

Thermal modification of ash wood carried out at different times and environments for a given temperature causes changes in the weight-average degree of polymerization of cellulose, which was extracted from the wood. The following values for the weight average degree of polymerization of cellulose are obtained depending on the environment: native wood > nitrogen environment > water vapour environment > air environment; Depending on the modification time used: native wood > 2 hours > 6 hours > 10 hours.

Size-exclusion chromatography (HPLC SEC) was used to investigate the kinetic dependence of the cellulose degradation process during thermal modification of ash wood. The determined reaction rate constants of cellulose depolymerization at 190°C in a nitrogen atmosphere and in water vapour have similar values. On the other hand, in an air atmosphere under analogous temperature conditions, an almost twofold increase in the rate of the cellulose degradation reaction was observed in comparison with the previous ones.

The data obtained allow to predict and monitor the degradation of the polymer as measured by its degree of polymerization depending on the time and environment of thermal modification.

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Streszczenie: *Wpływ środowiska, temperatury i czasu modyfikacji termicznej drewna jesionu wyniosłego (Fraxinus excelsior L.) na wagowo średni stopień polimeryzacji celulozy.* Wykorzystując metodę chromatografii wykluczania przestrzennego (HPLC SEC), wyznaczono wagowo średni stopień polimeryzacji celulozy. Polimer wyodrębniono metodą Kürschnera-Hoffera z drewna jesionu wyniosłego (*Fraxinus excelsior* L.). Drewno poddano modyfikacji termicznej w różnym środowisku (azot, para wodna i powietrze) w temperaturze 190°C i czasach modyfikacji wynoszących 2, 6 i 10 godzin. W zależności od zastosowanej atmosfery beztlenowej uzyskano największe wartości wagowo średniego stopnia polimeryzacji celulozy dla środowiska azotu, następnie pary wodnej i powietrza. Zaobserwowano wpływ czasu modyfikacji na wagowo średni stopień polimeryzacji. Największe jego wartości uzyskano dla drewna modyfikowanego w czasie 2 godzin następnie 6 i 10 godzin modyfikacji. Drewno natywne wykazuje największy stopień polimeryzacji. Na podstawie uzyskanych wyników można stwierdzić, że dla badanego materiału zachodzące reakcje utlenienia i degradacji są zależne od środowiska i czasu dla zadanej temperatury modyfikacji drewna.

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