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CHEMICAL CHANGES OF SELECTED HARDWOOD SPECIES IN THE PROCESS OF THERMAL MODIFICATION BY SATURATED WATER STEAM

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Abstract

This paper deals with the determining and comparison of chemical changes that occur from the hydrothermal treatment of oak (Quercus robur L.) and maple (Acer platanoides L.) wood through various steaming modes. The greatest changes from monitored chemical characteristics were occurred in the content of extractives and hemicelluloses. In the most extreme steaming treatment in mode III (t_{max} 140 °C, total duration 7.5 h), the decrease in hemicellulose content was the most dramatic. The content of extractives first slightly decreased, but with increasing temperature and extended steaming period a considerable increase in their content was observed. This changes result from degradation of most labile hemicelluloses. The contents of cellulose and lignin show only minimal changes, and their slight increase and decrease in individual modes is the result of several concurrent effects. In addition to these changes the decrease in the crystallinity of cellulose due to steaming was observed.

Key words: *oak, maple, steaming, extractives, hemicellulose, FTIR spectroscopy.*

INTRODUCTION

Hydrothermal treatment of wood by steaming is a common industrial processing of wood (production of veneer, plywood, bentwood furniture and other wood processing), which is used to improving its properties. The wood after hydrothermal treatment is less sticky, less cracks, drying faster, having a more pleasant and uniform color, increased durability and strength, and better stability (Melcer *et al.* 1983, Nikolov *et al.* 1980, Sergovskij and Rasev 1987, Setnička 1989, Trebula and Klement 2005).

Steaming causes changes in structural, physical, chemical and mechanical properties of wood. The extent of these changes depends on the hydrothermal treatment conditions (temperature, pressure, duration of action and other). In general, hydrothermal action on wood under mild conditions (shorter time, temperature below 80 °C) causes only minor changes in its main components. Deeper chemical changes occur with longer treatment times and temperatures above 80 °C, while mechanical strength of wood decreases (Kačík *et al.*1989, Kačík 1997, Melcer *et al.* 1983, 1989, Solár and Melcer 1990, 1992).

Hemicelluloses are the most thermally labile of the wood polymeric components (Hill 2006). Degradation of especially non-cellulosic polysaccharides leads to the loss of holocellulose in hydrothermally treated wood (Kačík *et al.* 1990, Kačík 2001).

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Hardwoods have a higher proportion of hemicelluloses, and the hemicelluloses of hardwoods have a higher content of acetyl groups compared to softwoods. Additionally, hardwood hemicelluloses are richer in pentosans, which are more susceptible to degradation than hexosans. Therefore, hardwoods are less thermally stable than softwoods (Hill 2006).

In lignocellulosic materials, the main components form the so-called “lignin-saccharide complex”. Cellulose microfibrils are covered with a heterogeneous hemicellulose polymer which is wrapped by amorphous lignin polymer (Volynets *et al*. 2017). According to Chen *et al.* (2010) during the initial phase of hydrothermal treatment lignin-free xylan is released, while lignin-bound xylan is dissolved in the later phase.

Several authors report that not only the carbohydrate but also the aromatic part of the wood (lignin) undergoes changes during the hydrothermal treatment. The depth of these changes depends primarily on the temperature and the time of action, as well as on the species of treated wood (Solár and Melcer 1992, Kačík *et al.* 1989, Kačík *et al*. 1990). The hydrothermal treatment causes also the formation of new chromophore structures in the lignin, which causes a change in the color of the treated material (Solár 1997).

The aim of this work was to determine and compare chemical changes occurring in the oak (*Quercus robur* L.) and maple (*Acer platanoides* L.) wood as a result of its modification in the different modes of steam.

MATERIAL AND METHODS

The samples of oak (*Quercus robur* L.) and maple (*Acer platanoides* L.) wood supplied from an industrial plant Sundermann Ltd. (Banská Štiavnica, Slovakia) were used to investigate chemical changes that occurred in different steaming treatments.

The samples with the dimensions 30 x 75 x 510 mm were thermally treated by the saturated steam in a pressure autoclave APDZ 240 (Dzurenda 2018). The temperature of the steam and duration of the processes are shown in Table 1.

The fraction of sawdust from 0.5 mm to 1.0 mm from completely disintegrated boards of the original wood and wood after steaming (including surface and center part) were used to monitor the chemical changes.

Table 1. Thermal treatment of wood

Steaming mode	Temperature of saturated water steam (°C)			Duration (h)	
	$t_{\mathrm{min}\ (\tau 1)}$	$t_{\mathrm{max}\ (\tau 1)}$	$t_{\mathrm{end}\ (\tau 2)}$	$\tau_{1\ \mathrm{(steaming)}}$	$\tau_{2\ \mathrm{(cooling)}}$
I	110	115	100	4.5	1.0
II	125	130	100	5.0	1.5
III	135	140	100	5.5	2.0

Selected chemical characteristics were measured in the samples before steam treatment and after the various modes of steaming:

Ethanol-toluene solubility	ASTM D 1107-96
Polysaccharide fraction	Chlorite isolation method of Wise (Kačík and Solár 2000)
Cellulose	Kürschner-Hoffer method (Kačík and Solár 2000)
Lignin	ASTM D 1106-96

The isolated holocellulose and dioxane lignin were analyzed using ATR-FTIR spectroscopy. The measurements were carried out using a Nicolet iS10 FTIR spectrometer equipped with a Smart iTR attenuated total reflectance (ATR) sampling accessory with a diamond crystal (Thermo Fisher Scientific, Madison, WI). The resolution was set at 4 cm^{-1} for 32 scans for each steaming technique and following analysis. The wavenumber range varied from 4000 cm^{-1} to 650 cm^{-1}. Six analyses were performed per sample. OMNIC 8.0 software (Thermo Fisher Scientific, Madison, WI) was used to evaluate the spectra.

RESULTS AND DISCUSSION

The steaming conditions of maple and oak wood have influenced not only the required color change of wood (Dzurenda 2018) but also its chemical composition (Výbohová *et al.* 2018, Geffert *et al.* 2018).

When comparing the content of extractives in the original maple and oak wood (Fig. 1), it can be seen that the original oak wood contained 2.4 times more of these substances than wood of maple. After steaming in mode I there was a decrease in the content of extractives while maintaining a ratio of 2.4. By increasing the severity of the steaming conditions, the difference in the content of extractives (after steaming in mode III) in oak and maple wood increased to 4.2.

While the content of extractives under the most demanding conditions of steaming (mode III) with respect to the original wood was higher by 33% for maple wood, the increase for oak wood was 132%.

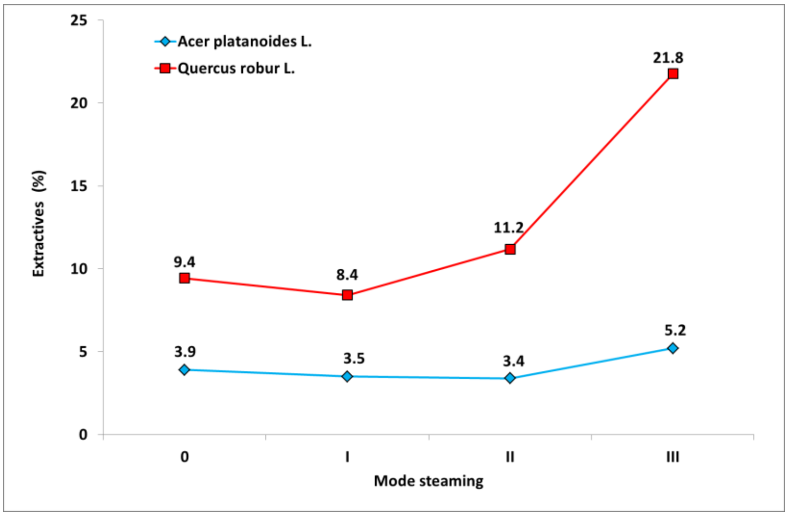

Fig. 1 Content of extractives before (0) and after steaming

With regard to the values of lignin and cellulose content by individual mode of steaming (Tab. 2) (Výbohová *et al.* 2018, Geffert *et al.* 2018), it can be stated that the increase in the content of extractives is related to the degradation of hemicelluloses and amorphous cellulose. The degradation products affected the increase in the content of extractives and thus the more intense coloring of wood samples (Fig. 2).

Table 2 Chemical characteristics

Mode		**0**	**I**	**II**	**III**
Lignin (%)	*Acer platanoides* L.	23.2	22.3	23.4	23.1
	Quercus robur L.	22.8	21.0	22.9	23.5
Cellulose (%)	*Acer platanoides* L.	45.1	46.3	45.0	45.2
	Quercus robur L.	39.1	40.0	36.7	36.9

Dzurenda (2018) in his work featured on samples oak in individual steaming modes total color differences ΔE * 3.0, 11.5 and 20.1, indicating the smallest color change in steaming mode I, a larger color shift in mode II and the largest shift in color space after mode III.

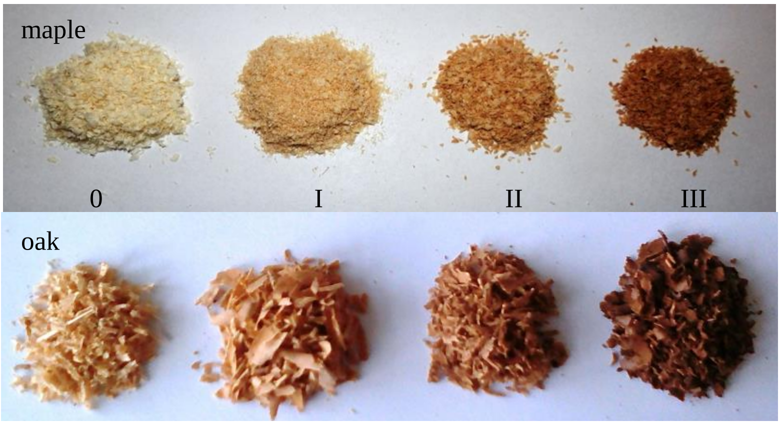

Fig. 2 Disintegrated samples of the original and steamed woods

The content of hemicelluloses in steamed wood species point to their different contents in maple and oak wood and also to the different degrading intensity (Fig. 3). The course of the change is similar.

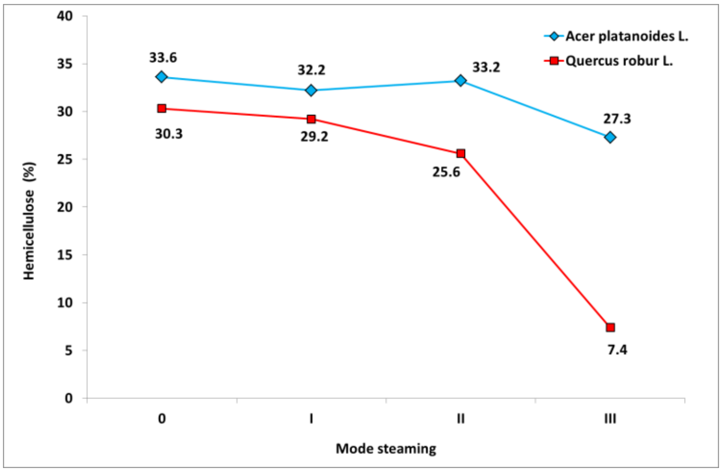

Fig. 3 Hemicellulose content before (0) and after steaming

Both wood species show the greatest decrease in hemicelluloses in mode III. While in maple wood this difference was 6.4% and represented 19% of the original wood, in oak wood the difference was 22.9%, which represented a decrease of up to 75.6%.

For both wood species, a similar course of lignin and polysaccharides ratio were also recorded (Fig. 4). Smaller changes were made again for maple wood. After steaming in mode I, the ratio decreased slightly, which may be related to the drop in content of water-soluble lignin. After two other modes, an increase of this ratio was recorded in both wood species. Although the synergistic effect of a small change of lignin and cellulose in individual steaming modes (Tab. 1) was evident, it can be clearly stated that the values of the ratio were mainly affected by the degradation of hemicelluloses.

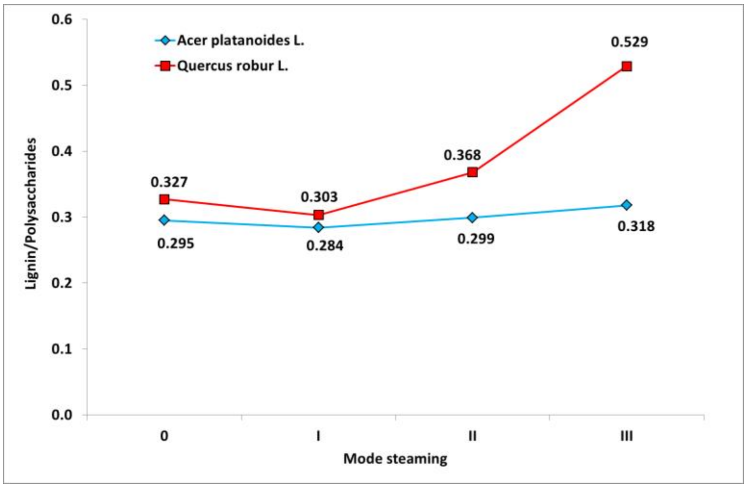

Fig. 4 Changes of lignin/polysaccharides ratio

During hydrothermal treatment of wood, various processes with different influence on the intensity of FTIR absorption bands run. On the basis of differential FTIR spectra of oak and maple wood (Fig. 5), it can be concluded, that under the most severe steaming conditions (mode III) the similar changes occurred in both examined wood species.

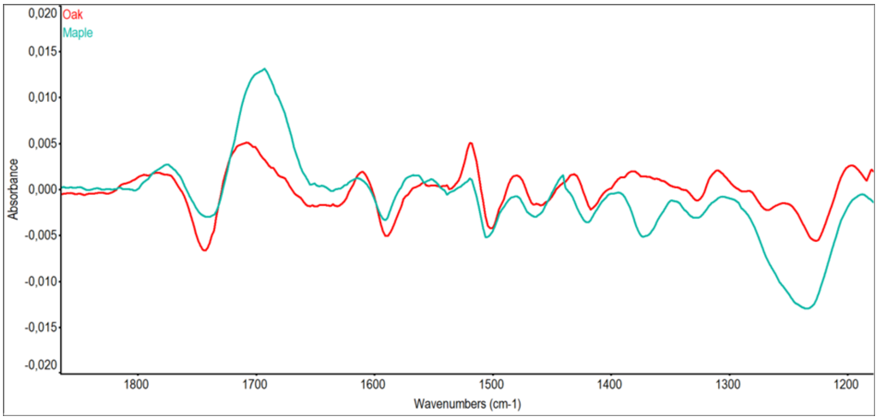

Fig. 5 Differential FTIR spectra of oak and maple wood in mode III

The decrease of intensity of absorption band at wavenumber around 1732 cm^{-1} may be caused by lignin condensation reactions, deacetylation of hemicelluloses and decomposition of aldehydes, carboxylic acids and their esters (Esteves *et al.* 2013, Özgenc *et al*. 2017, Windeissen *et al*. 2009). In the case of characteristic bands of lignin (around 1593 and 1505 cm^{-1}), the shift of peak maxima to higher wavenumber and the increase of their intensity were observed. In both cases also the intensity of absorption band between 1200 and 1300 cm^{-1} decreased. In this region absorption bands assigned to xylan and syringyl ring and C–O stretch in lignin overlapping. Considering the results of chemical analyses it can be concluded, that this decrease can be the consequence of degradation of hemicelluloses and structural changes in lignin macromolecule.

The degree of crystallinity is one of the factors, which influenced the thermal stability of cellulose (Hill 2006, Poletto *et al.* 2012). More ordered crystalline regions of cellulose exhibit low chemical reactivity, and higher thermal stability in comparison to its non-crystalline regions. In the initial stage of thermal treatment, the degradation of amorphous cellulose, and rearrangement or reorientation of quasi-crystalline regions occurred. This results in increase in cellulose crystallinity. Degradation of crystalline regions runs at increased intensity of the treatment (Bhuiyan *et al.* 2001, Kong *et al.* 2017).

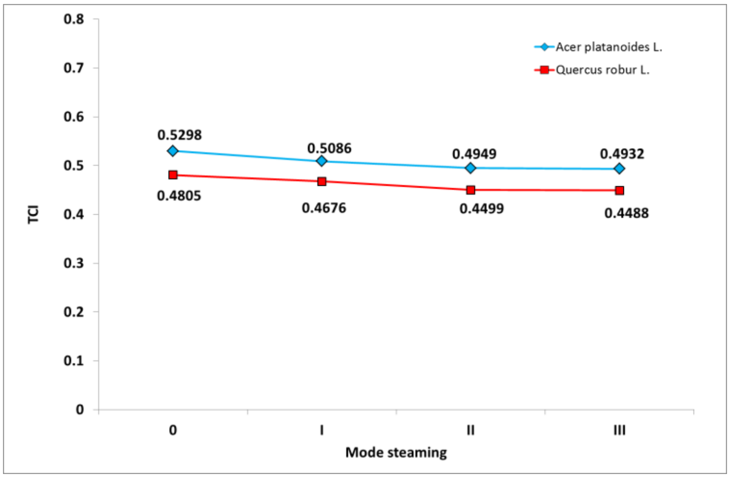

Fig. 6 Changes of the Total Crystallinity Index (TCI)

As the Figure 6 shows, the Total Crystallinity Index decreases with increased treatment severity in the case of both examined wood species. Our findings are in agreement with cited works. In our experiment, steaming times for all modes are longer, namely 5.5, 6.5, and 7.5 h. Under these conditions the degradation of microfibrillar and chain scission reactions is occurred. This reaction increased the amorphous character of cellulose, and subsequently reduced the total amount of cellulose crystalline regions.

CONCLUSION

The wood species characterized not only the content of the selected chemical characteristics but also the size of their changes during the steaming. The original maple wood contained a large amount of lignin, cellulose, hemicelluloses and a smaller proportion of extractives than oak wood.

Treatment in modes with different temperature and time of steaming resulted in minor changes monitored chemical characteristics in maple wood as the oak wood.

The largest change was determined in mode III (at the highest temperature and time of steaming) for both woods. The observed changes in the selected characteristics (a decrease in hemicellulose content and an increase in the content of extractives) were much more pronounced in oak wood than in maple wood.

The changes in the intensity of the FTIR absorption bands are the result of degradation of hemicelluloses and structural changes in lignin macromolecules and it is confirmed by the results of chemical analyses too. Degradation of crystalline regions runs at increased intensity of treatment.

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