

Impact of Steaming on the Chemical Composition of Maple Wood

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Chemical changes resulting from the thermal treatment of maple wood (*Acer platanoides* L.) through various steaming techniques were evaluated. Main wood components were isolated and characterized from the maple wood samples after steaming. Then, the isolated holocellulose and dioxane lignin were analyzed using ATR-FTIR spectroscopy. The effects of an increase in temperature and extension of the steaming period were seen primarily in the holocellulose and extractives contents, and less in the cellulose and lignin components. Certain steaming methods resulted in an increase in chemical composition, while others saw a decrease. The cellulose content of steamed maple wood was not considerably altered; however, the cellulose crystallinity did increase. The slight changes observed in this study can be attributed to several concurrent effects. While the lignin content in steamed maple wood showed only minimal changes, there were several changes in the structure of the lignin macromolecule. Demethoxylation, the decrease in the ratio of syringyl-propane to guaiacyl-propane units, and the formation of new α -C=O bonds were also observed. The hydrothermal treatment of wood also resulted in color changes of wood samples; the intensity of the change depended on the intensity of the treatment.

Keywords: Maple wood; Steaming; Extractives; Holocellulose; Cellulose; Lignin; FTIR spectroscopy

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INTRODUCTION

The steaming of wood is a hydrothermal treatment that uses water vapor. It causes structural changes in the wood, as well as changes in the wood's chemical, physical, and mechanical properties. The wood after hydrothermal treatment is less sticky, with fewer cracks, faster drying, a more pleasant and uniform color, increased durability and strength, and better stability (Melcer *et al.* 1983). The extent of these changes depends on different variables of the hydrothermal treatment (*e.g.*, temperature, pressure, and duration).

The hydrothermal treatment of wood at low temperatures does not cause marked chemical or physico-chemical changes to the main components of the wood. More notable chemical changes are correlated with an increased duration of hydrothermal treatment (Melcer *et al.* 1983; Kačík *et al.* 1989; Solár and Melcer 1990, 1992; Kačík *et al.* 1993; Laurová *et al.* 2004). Increasing the temperature of the hydrothermal action above 80 °C increases the chemical and physico-chemical changes throughout the wood. At the same time, its mechanical strength decreases in correlation with the intensity of the treatment (Melcer *et al.* 1983; Kačík *et al.* 1989, 1990; Solár and Melcer 1990).

The acidity of the environment during hydrothermal treatment increases gradually because of the splitting-off of acetyl and formyl groups of hemicelluloses. Additionally,

the formation of organic acids, such as acetic and formic acid, lowers the pH of the condensate.

This lowering of pH catalyzes various hydrolysis, dehydration, degradation, and condensation reactions of the carbohydrates and their products. Hexose dehydration leads to 5-hydroxymethyl-2-furaldehyde formation. 2-Furaldehyde is formed by degradation of pentoses, and further decomposition of furan derivatives produces levoleic and formic acids (Jönsson *et al.* 2013).

In native cellulose, monomers of glucose form microfibrils that are stabilized by hydrogen bonds, making the macromolecule highly crystalline and difficult to hydrolyze (Trajano and Wyman 2013). In contrast, hemicelluloses are heteropolysaccharides that have shorter, branched chains of saccharides. Because of their amorphous structures and the presence of acetyl groups, hemicelluloses are the most thermally labile of wood's polymeric components (Hill 2006).

Degradation of non-cellulosic polysaccharides leads to the loss of holocellulose in hydrothermally treated wood (Kačík *et al.* 1990, 2001; Laurová *et al.* 2004). Studies by Mercer *et al.* (1989) and Kačík *et al.* (1996) confirm that the hydrothermal treatment of wood first results in a relatively rapid release of hemicelluloses, while the vulnerability to hydrothermal treatment varies between wood species. In general, hardwoods have a higher proportion of hemicelluloses, so they have a higher content of acetyl groups compared with softwoods. Furthermore, hardwood hemicelluloses are richer in pentosans, which are more susceptible to degradation than hexosans. Therefore, hardwoods are less thermally stable than softwoods (Hill 2006).

The main components of maple wood are interconnected to form the “lignin-saccharide complex”. Lignocellulosic materials have chemical bonds especially between lignin and lateral branches of hemicelluloses (Volynets *et al.* 2017). According to Chen *et al.* (2010), lignin-free xylan is released during the initial phase of hydrothermal treatment, while lignin-bound xylan is dissolved in the later phase.

The carbohydrate and aromatic components of wood (*i.e.*, lignin) also undergo changes during hydrothermal treatment. The degree of change depends primarily on the temperature and action time. This process demonstrates the presence of syringaldehyde and vanillin in condensates of steaming wood (Laurová *et al.* 2004).

Relevant works indicate that the intensity of structural changes in the lignin of different wood species treated under approximately the same hydrothermal conditions can vary (Kačík *et al.* 1989, 1990; Solár and Melcer 1992).

The high temperatures of hydrothermal treatment cause depolymerization of the lignin because of the hydrolysis of the α -alkyl-aryl ether linkages. High temperatures and lengthy treatment can also initiate condensation reactions. Hydrothermal treatment causes the formation of new chromophore structures in the lignin, which changes the color of the treated material (Solár 1997). Structural change in the aromatic ring of the lignin macromolecule may occur because of oxidation, condensation, or conjugation of the double-bonded aromatic rings, while the content of carbonyl and carboxyl groups increases (Košíková *et al.* 1976).

This study sought to evaluate the various chemical changes that maple wood undergoes during a variety of steaming treatments. Conventional analytical methods were used to isolate the wood components to determine their chemical composition. The isolated holocellulose and dioxane lignin were analyzed using ATR-FTIR spectroscopy. The spectral analysis of individual wood components is critical for understanding the behavior of wood species during steam treatments.

EXPERIMENTAL

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

Each maple wood sample had the dimensions 30 X 75 X 510 mm. These samples were thermally treated by the steam in a pressure autoclave APDZ 240 (Dzurenda 2018). Treatment temperature and duration for the maple wood samples are given in Fig. 1. 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 maple wood and wood after steaming (including surface and center part) were used to monitor the chemical changes.

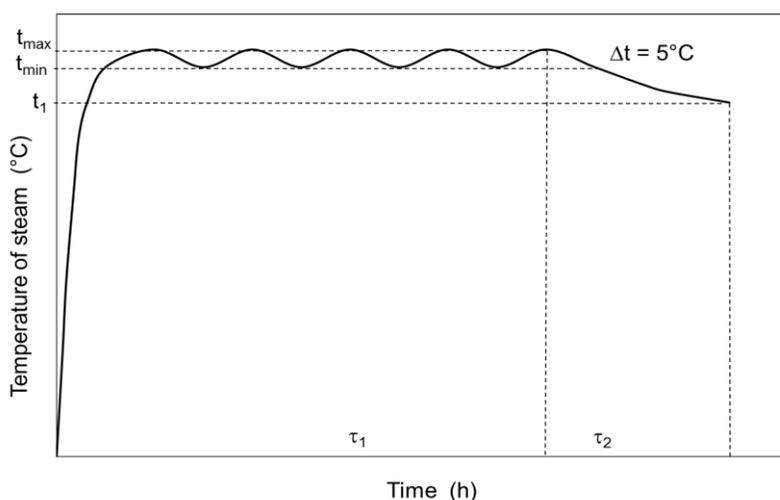


Fig. 1. Modification of maple wood samples with steam (according to Dzurenda 2018)

Table 1. Thermal Treatment of Maple Wood

Steaming mode	Temperature of saturated water steam (°C)			Duration (h)	
	t_{\min}	t_{\max}	t_1	τ_1	τ_2
I	110	115	100	4.5	1.0
II	125	130	100	5.0	1.5
III	135	140	100	5.5	2.0

Select chemical characteristics were measured in the samples before steam treatment and after the various steam treatments. These characteristics are listed in Table 2.

Table 2. Select Chemical Characteristics

Characteristics	
Ethanol-toluene solubility	ASTM D 1107 – 96 (TAPPI T-204-os-76)
Polysaccharide fraction	Chlorite isolation method of Wise <i>et al.</i> (Kačík and Solár 2000)
Cellulose	Kürschner-Hoffer method (Kačík and Solár 2000)
Lignin	ASTM D 1106 – 96 (TAPPI T-13m-54)

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 chemical composition of maple wood varies depending on the species of wood, the locality, and the methods of determination. Holocellulose content ranges from 79% to 86.9%, cellulose from 38.3% to 47.4%, lignin from 20.7% to 25.3%, and extractives from 1.9% to 2.9% (Fengel and Wegener 1984; Baloghová and Kačík 1996; Kačík *et al.* 1996). According to the results of Baloghová and Kačík (1996), maple wood holocellulose is composed primarily of D-glucose and D-xylose, while other carbohydrates (*e.g.*, L-rhamnose, L-fucose, L-arabinose, D-mannose) are present in small amounts.

The results of the chemical analysis of the samples of the original maple wood and post-treated wood for each technique are shown in Fig. 2.

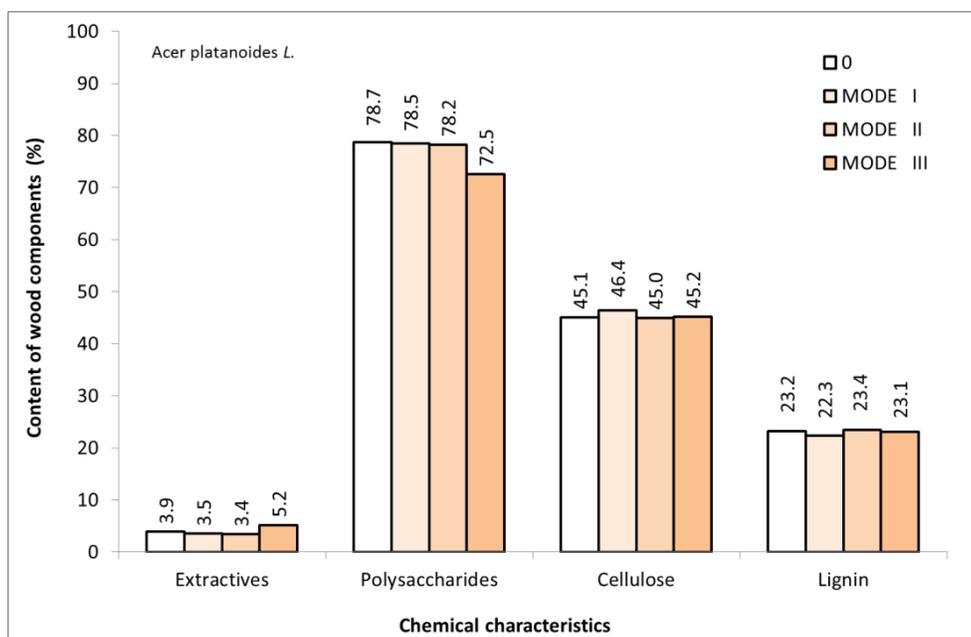


Fig. 2. Chemical characteristics of maple wood before and after steaming. Note that “0” signifies wood before steam treatment

Based on the chemical characteristics, it can be concluded that the increased intensity of the treatment was reflected primarily in the changes in holocellulose and extractives contents, and less in the contents of cellulose and lignin.

The content of extractives slightly decreased with increasing temperature and extended steaming period for modes I and II, resulting in their release or decomposition. In the most extreme steaming treatment (mode III), when temperature increased from 130 °C to 140 °C, the content of extractives increased by 33% compared with the original content and by 53% relative to the mode II conditions. This increase has previously been shown to be related to the extraction of decomposition products of other wood components (hemicelluloses, water soluble lignin, and amorphous cellulose). Baloghová and Kačík (1996) reported increased extractives in maple wood during prehydrolysis for 6 h at 160 °C, rising from 2.92% to 16.25%.

The average polysaccharide content in maple wood decreased slightly in modes I and II compared with untreated wood, and the decrease in mode III was more dramatic, reaching approximately 8%.

The FTIR analysis of isolated holocellulose was performed to characterize the changes in polysaccharides in the maple wood after hydrothermal treatment. Characteristic absorption bands of both cellulose and hemicellulose were found in the obtained spectra and assigned according to the literature, as shown in Table 3 (Hon and Shiraishi 2001; Pandey and Pittman 2003). The results are further depicted in Fig. 3.

Table 3. Spectral Records of Examined Holocellulose Samples

Wavenumber	Spectral Characteristic	Wavenumber	Spectral Characteristic
3339 cm ⁻¹	O-H stretching	1333 cm ⁻¹	OH in-plane bending
2897 cm ⁻¹	Symmetric/ asymmetric CH ₂ stretching	1316 cm ⁻¹	CH ₂ wagging
1732 cm ⁻¹	C=O stretching of acetyl or carboxylic groups	1243 cm ⁻¹	C–O stretching in xylan
1429 cm ⁻¹	C–H bending	1161 cm ⁻¹	C-O-C asymmetric bridge stretching
1371 cm ⁻¹	C–H in-plane bending	1032 cm ⁻¹	C-O stretching
		897 cm ⁻¹	Stretching at the β-(1,4)-glycosidic linkage, and C-H deformation

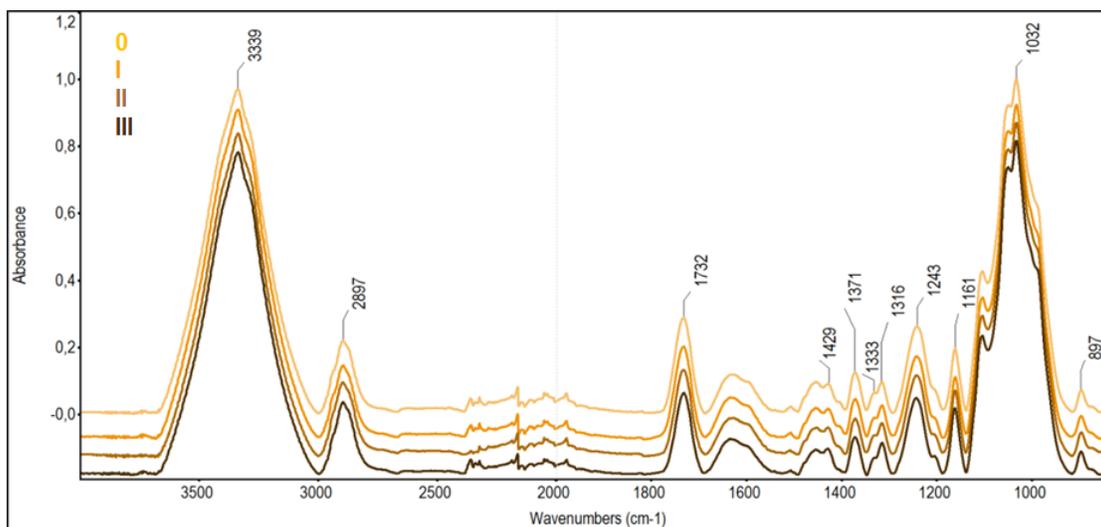


Fig. 3. Spectra of holocellulose samples isolated from maple wood

From the evaluation of the obtained spectral records, it can be stated that during the hydrothermal treatment of maple wood, the degradation of more labile hemicelluloses was observed. This is evident from the decrease in the intensity of absorption bands at 1732 and 1243 cm^{-1} (Fig. 4). This decrease is 15.1% and 10.7%, respectively, of the original intensity of said absorption bands.

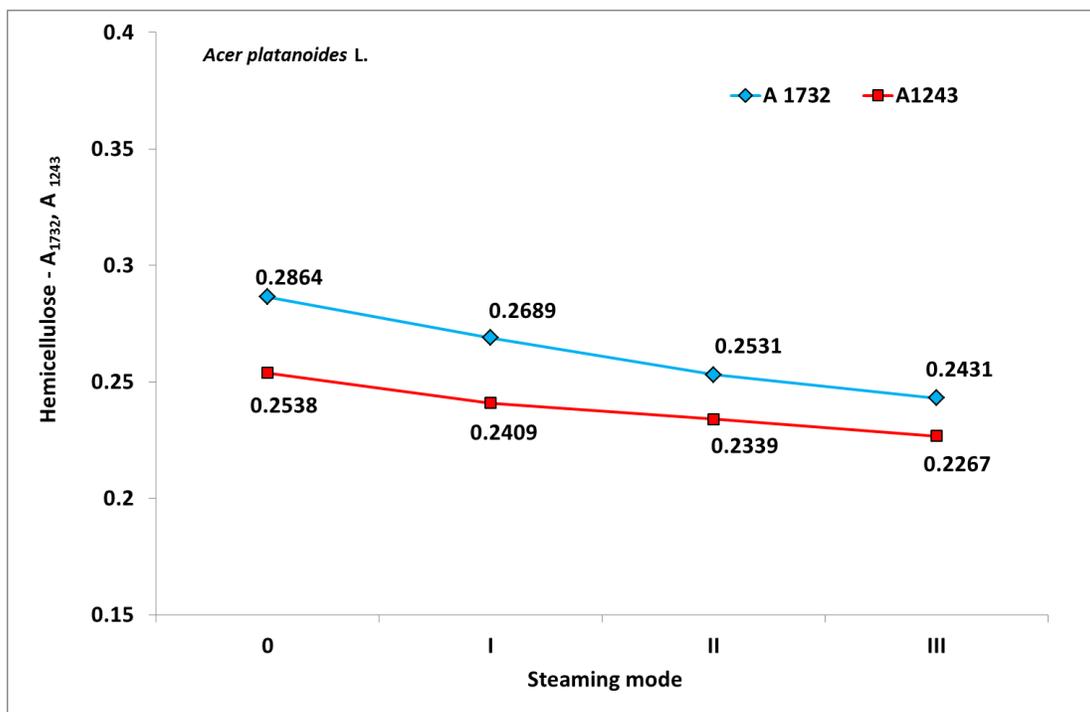


Fig. 4. The decrease in intensity of absorption bands at 1732 and 1243 cm^{-1}

According to Fengel (1966), temperature influences first the partial degradation of long hemicellulose chains into shorter ones and then the degradation through monosaccharides to volatile products. At the same time, ongoing deacetylation affects the thermal stability of hemicelluloses.

Cellulose is the most stable against hydrothermal action in the range of given temperatures. The cellulose content in maple wood under the influence of steaming did not change considerably (Fig. 2), and its slight variation in individual modes is the result of several concurrent effects: degradation of hemicelluloses or amorphous cellulose, or condensation reactions.

The results of Melcer *et al.* (1989) confirmed that during the hydrothermal treatment of the wood, there is first a relatively rapid release of hemicelluloses, then the slower release of the water-soluble part of the lignin, and later part of the amorphous cellulose.

Some authors reported a relative increase in cellulose with a prolonged hydrothermal treatment at a temperature range of 80 $^{\circ}\text{C}$ to 140 $^{\circ}\text{C}$, caused by the loss of hemicellulose and lignin components (Melcer *et al.* 1989; Solár and Melcer 1990). According to the results of Kačík (1997), the content of cellulose in hydrothermally treated wood did not usually change at temperatures up to 100 $^{\circ}\text{C}$, but above 100 $^{\circ}\text{C}$ it increased because of the degradation of hemicelluloses, which in maple wood were mostly D-xyllose and D-glucose.

From comparison of the FTIR spectra of holocellulose (Fig. 3), a decrease in the ratio of intensities of absorption bands A_{1333}/A_{1316} was observed (Fig. 5). According to Colom *et al.* (2003), the decrease in this ratio signifies an increase in the cellulose crystallinity. These changes may result from the faster degradation of the amorphous cellulose regions, but also from the reorganization of the quasi-crystalline cellulose regions at higher temperatures (Bhuiyan *et al.* 2000).

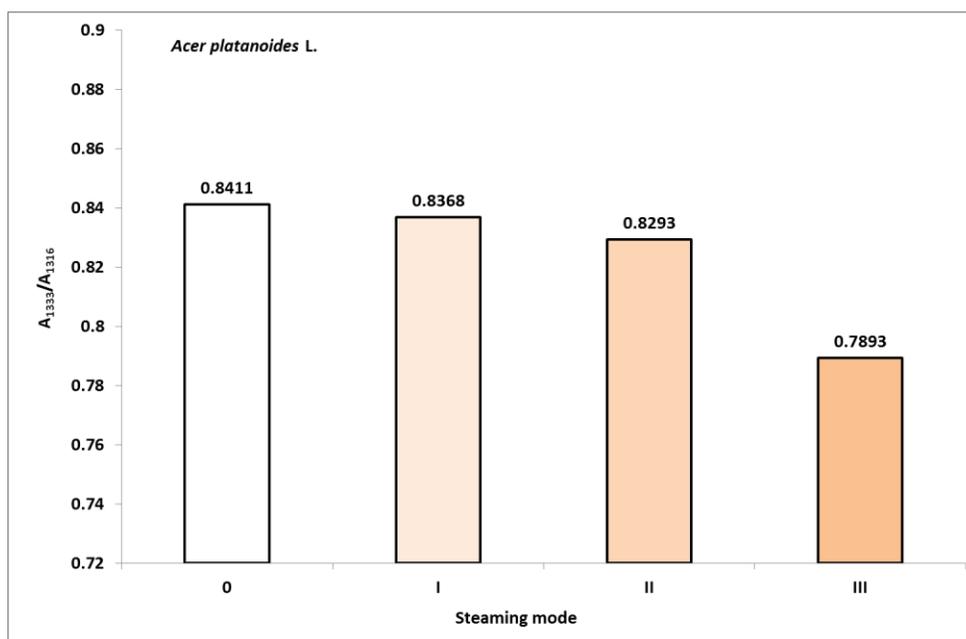


Fig. 5. Change in the ratio of A_{1333}/A_{1316}

The resulting average values of lignin content in steamed maple wood show only minimal changes (Fig. 2). Solár (1997) stated that depolymerization, reduction in the degree of lignin crosslinking, and the disappearance of bonds in the lignin-polysaccharide system predominate in the early stages of hydrothermal wood treatment. Laurová *et al.* (2004) showed the presence of syringaldehyde and vanillin in the condensates of the steamed wood, which indicates the ongoing change of the aromatic part of wood lignin.

Figure 6 shows a comparison of ATR-FTIR spectra of dioxane lignin isolated from original and hydrothermally treated (mode III) wood samples. It reflects changes in lignin structure caused by treatment under extreme conditions.

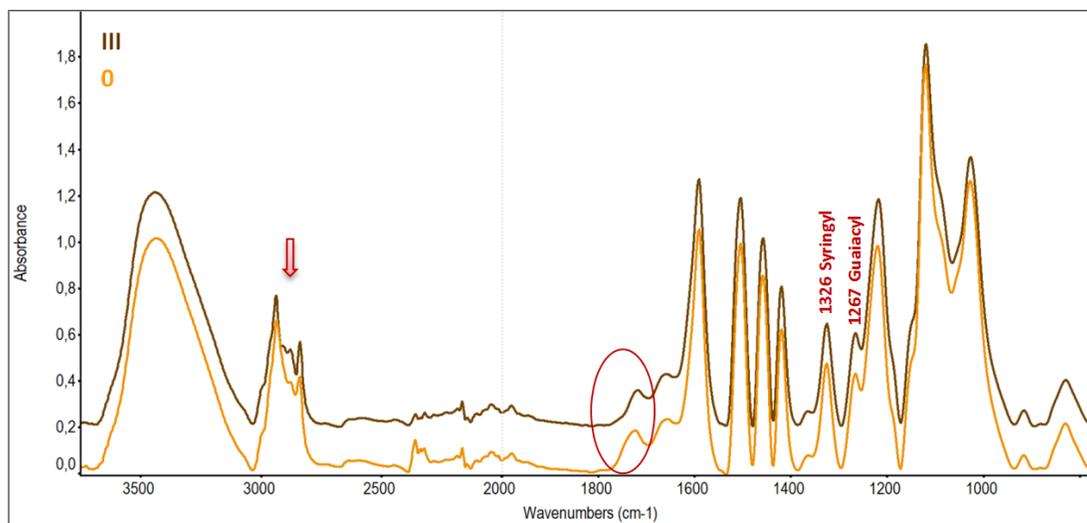


Fig. 6. Comparison of ATR-FTIR spectra of dioxane lignin

A decrease in the intensity of absorption bands can be observed in the region 3040 cm^{-1} to 2760 cm^{-1} . These bands are attributed to symmetric and asymmetric stretching vibrations of C-H in $-\text{OCH}_3$ and $-\text{CH}_2$ (Hon and Shiraishi 2001; Karmanov and Derkacheva 2013). The decrease in intensity is caused by demethoxylation of the lignin macromolecule during hydrothermal treatment. Furthermore, after treatment, a decrease in the ratio of syringyl-propane to guaiacyl-propane units was observed (Fig. 7). The partial removal of $-\text{OCH}_3$ groups and the preferential removal of syringyl to guaiacyl units in various hardwood species during autohydrolysis and steam explosion, respectively, were discussed in other works (Chua and Wayman 1979; Martin-Sampedro *et al.* 2011).

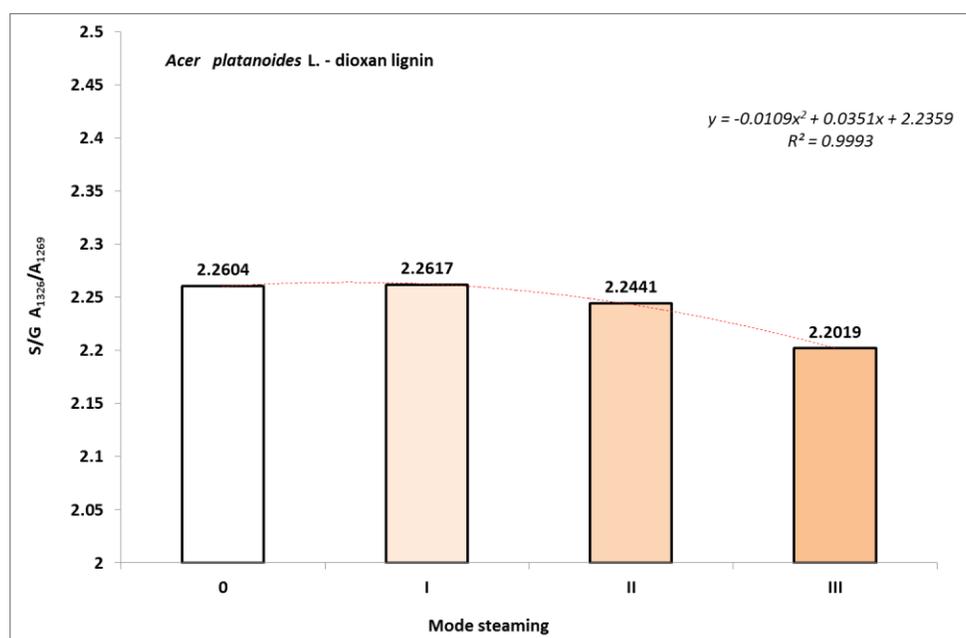


Fig. 7. Change in the ratio of syringyl and guaiacyl units

Other findings from the comparison of the FTIR spectra of lignin include the shift of the maximum absorption band, which is attributed to unconjugated C=O bonds, to a lower wavenumber as a result of treatment, *i.e.*, from 1724 cm^{-1} to 1718 cm^{-1} . According to Chen *et al.* (2012), this result suggests the formation of new $\alpha\text{-C=O}$ bonds in lignin's structure, which can contribute to the darkening of treated wood.



Fig. 8. Color changes in the original maple wood (0) after various steaming modes

The hydrothermal treatment of wood also resulted in color changes in the wood samples. The intensity of the color change depended on the severity of the treatment conditions. The photo of the disintegrated samples in Fig. 8 shows the color changes of the original and post-treated maple wood samples.

The mechanism of color change is complex, and many overlapping reactions of the basic components of wood and their decomposing products are involved (Solár 1997). Color changes are related to reactions of polysaccharide degradation products such as oxidation, dehydration, and condensation (oxidation of 2-furaldehyde, carbohydrates, and pectin reactions). They are also related to the chemical changes in lignin (quinone methide structures; free radicals; formation of new chromophoric groups; increase in phenolic hydroxyl groups) and extractives (color complexes of extracts of phenolic nature).

Similar color changes have been documented by many authors in their works on the hydrothermal treatment of various tree species by steaming or prehydrolysis (Melcer *et al.* 1983; 1989; Kačík 1997; Solár 1997; Dzurenda 2014; 2018; Barčík *et al.* 2015; Kučerová *et al.* 2016; Geffert *et al.* 2017).

CONCLUSIONS

1. Increases in temperature and duration of the steaming treatment primarily affected the holocellulose and extractives contents, and less so the contents of cellulose and lignin.
2. The decreased extractives content from steaming treatments modes I and II was a result of their release into the condensate or decomposition. However, after the mode III steam treatment, the extractives content increased by 33% compared with the original content and by 53% relative to the mode II conditions. This increase is already related to the extraction of decomposition products of other wood components.

3. The average polysaccharide ratio in maple wood decreased slightly after modes I and II treatments compared with the original sample, and decreased more sharply after mode III, by approximately 8%. The decrease in content of polysaccharides was due to the degradation of more labile hemicelluloses.
4. Cellulose is the most stable against hydrothermal action in the range of given temperatures, as its content did not change considerably after steam treatment. The cellulose crystallinity did increase during steaming.
5. The lignin content in steamed maple wood showed only minimal changes because depolymerization, or the reduction in the degree of lignin crosslinking and the disappearance of bonds in the lignin-polysaccharide system, predominate in the early stages of hydrothermal wood treatment. However, there were several changes in the structure of the lignin macromolecule. Demethoxylation, the decrease in the ratio of syringyl-propane to guaiacyl-propane units, and the formation of new α -C=O bonds were observed.
6. The hydrothermal treatment of wood also resulted in color changes in the wood samples, relative to the severity of the treatment conditions.

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