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CHANGES IN THE CHEMICAL COMPOSITION OF OAK WOOD DUE TO STEAMING

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ABSTRACT

Monitoring the chemical changes resulting from hydrothermal treatment of English oak (*Quercus robur* L.) through various steaming modes is presented in the paper. The greatest changes were observed in the polysaccharide content (holocellulose). In the most extreme steaming treatment in mode III (t_{max} 140 °C, total duration for 7.5 h), the decrease in their content was the most dramatic reaching approximately 36%. This decrease is the result of degradation of the most labile hemicelluloses. Only minimal changes in cellulose and lignin content were observed, and several concurrent effects result in the slight increase and decrease in individual modes. Firstly, the content of extractives decreased slightly, but with increasing temperature and extended steaming period a considerable increase in their content occurred. In the initial stages of steaming, new carbonyl and carboxyl groups in carbohydrates are formed by oxidation. Consequently, the deacetylation and degradation of hemicelluloses occurred. In addition, the decrease in the crystallinity of cellulose due to steaming was observed.

Key words: oak wood, steaming, extractives, holocellulose, cellulose, lignin, FTIR spectroscopy.

INTRODUCTION

Hydrothermal treatment of wood by steaming or water vapor is a common industrial processing of wood, 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 colour, increased durability and strength, and better stability (MELCER *et al.* 1983, DZURENDA and DELIISKI 2000, DZURENDA 2013).

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 (SOLÁR and MELCER 1990, 1992, MELCER *et al.* 1983, 1989, KAČÍK *et al.*1989, KAČÍK 1997, DZURENDA 2018a, 2018b).

The increase in the acidity of the condensate under hydrothermal treatment on wood is caused by the cleavage of acetyl and formyl groups of hemicelluloses and the formation of organic acids (particularly acetic acid and formic acid) which catalyze different hydrolysis, dehydration, degradation, as well as condensation reactions of carbohydrates and their products. 5-hydroxymethyl-2-furaldehyde is formed by dehydration of hexoses, and 2-furaldehyde is formed by degradation of the pentoses. Further decomposition of the furan derivatives produces levulinic acid and formic acid (JÖNSSON *et al.* 2013).

Hemicelluloses are heteropolysaccharides with branched and shorter chains of saccharide units. Because of its amorphous structure and the presence of acetyl groups, 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, 2001).

The resistance of different wood species to hydrothermal treatment is not the same (MELCER *et al.* 1983, 1989, KAČÍK *et al.* 1996). 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.

In contrast to hemicelluloses, the monomers of glucose in native cellulose form microfibrils stabilized by hydrogen bonds, thus making the macromolecule highly crystalline and more difficult to hydrolyze (TRAJANO and WYMAN 2013). The thermal stability of cellulose mainly influenced on its degree of crystallinity, crystallite size, and degree of polymerization (POLETTO *et al.* 2012, KIM *et al.* 2010). The rate of cellulose degradation is reduced if water is present, which is assumed to be due to the enhanced ability of the amorphous regions to change structure to produce more thermally stable crystalline regions (FENGEL and WEGENER 1989). With extended heating, chain scission of the cellulose occurs, producing oligosaccharides, with a concomitant decrease in the degree of polymerization as well as degree of crystallinity of cellulose (HILL 2006). According to other studies (BHUIYAN *et al.* 2000, KONG *et al.* 2017), the crystallinity increases at the initial stage and decreased at the later stages of heat treatment under moist conditions.

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 colour of the treated material (SOLÁR 1997).

The aim of this work was to determine and evaluate chemical changes occurring in the oak (*Quercus robur* L.) wood as a result of its modification in the different modes of steam, using conventional analytical methods as well as ATR-FTIR spectroscopy.

MATERIAL AND METHODS

KLEMENT *et al.* (2010) characterized oak wood as hard, tough, solid, with poor impregnation and staining. In terms of physical, mechanical and technological properties it is an important raw material for industrial processing.

The samples of oak wood supplied from industrial plant Sundermann Ltd Banská Štiavnica were used to investigate chemical changes that occurred in different steaming treatments. The samples with the dimensions 30 × 75 × 510 mm were thermally treated with saturated steam in the pressure autoclave APDZ 240 (Dzurenda 2018a). The modification mode of oak wood is given in Figure 1 and temperature of saturated water steam and duration of the technological process are shown in Table 1.

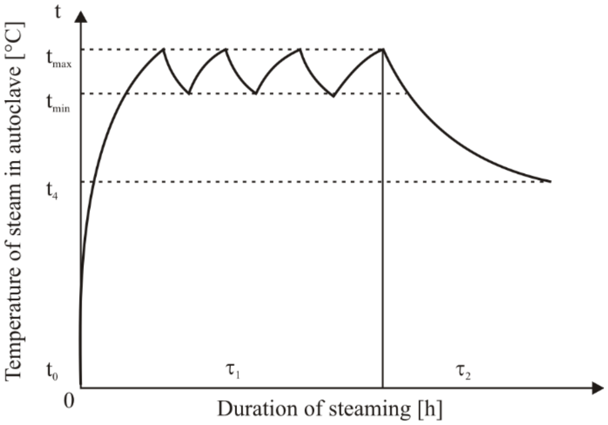

Fig. 1 Modification mode of oak wood with saturated water steam (Dzurenda 2018a).

Tab. 1 Thermal treatment of the oak wood.

Mode steaming	Temperature of saturated water steam (°C)			Duration (h)	
	t_{min}	t_{max}	t_4	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

Disintegrated samples of the original oak wood and wood after steaming (Figure 2) were used to monitor the chemical changes.

Fig. 2 Samples of the original (0) and steamed oak wood samples (mode I, mode II, mode III).

The selected chemical characteristics in the samples of the original oak wood and the wood treated through various steaming techniques were determined in the fraction of sawdust from 0.5 mm to 1.0 mm prepared from completely disintegrated boards (including surface and center part):

Tab. 2 Select chemical characteristics.

Ethanol-toluene solubility	ASTM D 1107 – 96
Polysaccharide fraction	Chlorite isolation method of Wise *et al.* (Kačík and Solár 2000)
Cellulose	Kürschner-Hoffer method (Kačík and Solár 2000)
Lignin	ASTM D 1106 – 96
Seifert´s cellulose	Acetylacetone method (Seifert 1956)

Note: The content of hemicelluloses was determined as the difference between the holocellulose and cellulose content.

The samples of wood, as well as isolated holocellulose and Seifert´s cellulose were analyzed using ATR-FTIR spectroscopy. The measurements were performed 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. The wavenumber range varied from 4000 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 results of the chemical analysis of the samples of the original oak wood and the wood after the steaming in each modes are depicted in Figure 3**.**

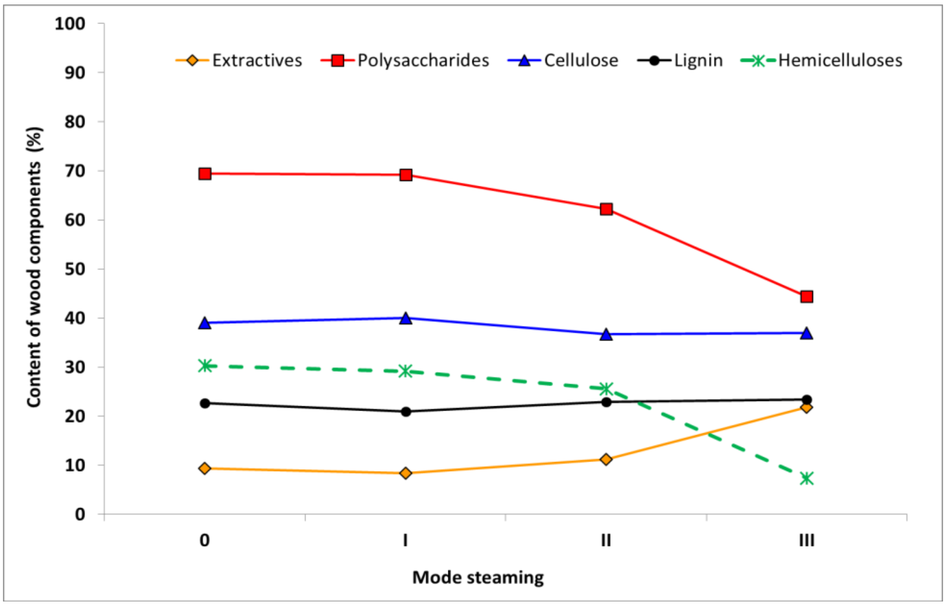

Fig. 3 Chemical characteristics of oak wood before and after steaming.

The observed values of the monitored characteristics for the original oak wood are within the ranges of values cited by various authors (KOLLMAN and FENGEL 1965, GEFFERTOVÁ *et al*. 2006, GEFFERTOVÁ and HANZEL 2007, GEFFERTOVÁ and GEFFERT 2007, ČABALOVÁ *et al*. 2018, LAUROVÁ *et al.* 2007) for various species of oak. The differences can be related not only to the type of wood, but also to the locations and places of sampling. The content of extractives ranges from 2.3 to 5.6%, holocellulose from 73.2 to 83.3%, cellulose from 36.7 to 46.6 %, and lignin from 17.6 to 25.3%. According to the results of ČABALOVÁ *et al.* (2018) in English oak wood polysaccharides primarily glucose (48.30%) and xylose (21.44%), less mannose (4.08%), arabinose (1.97%) and galactose (1.17%) are present.

On the basis of the observed chemical characteristics of oak wood after various steaming modes it can be stated that the greatest changes were occurred in the polysaccharide content (holocellulose). At the lowest temperatures and the shortest period of steam (mode I) only a slight decrease in the polysaccharide fraction was recorded. By the following increasing of the intensity of the steam treatment, the polysaccharide content decreased by 10% in mode II and by 36% in mode III compared to the average value in the original oak wood.

According to FENGEL and WEGENER (1989), temperature influences first depolymerization of long hemicellulose chains into oligosaccharides and monosaccharides, which are dehydrate to form volatile compounds. At the same time, ongoing deacetylation affects the thermal stability of hemicelluloses (FENGEL 1966).

The content of cellulose in oak wood after steaming by mode I grew by 2.3%. This is a relative increase because of the reduced hemicellulose content in the sample. In other steaming modes, the cellulose content slightly decreased, whereby the decrease represents about 6% relative to the original sample. The slight increase and decrease in individual steaming modes is the result of several concurrent effects - degradation of hemicelluloses or amorphous cellulose and condensation reactions. Some authors report a relative increase in cellulose with a prolonged hydrothermal treatment time at a temperature range from 80 to 140 °C because of the loss of hemicelluloses and lignin (SOLÁR 1997).

According to KAČÍK (1997), the content of cellulose in hydrothermally treated wood does not usually change at temperatures up to 100 °C, but at temperatures above 100 °C, it increases because of the degradation of hemicelluloses. The results of some authors (SOLÁR 1997, MELCER *et al.* 1983, MELCER *et al.* 1989) confirm that during the hydrothermal treatment of the wood, there is first a relatively rapid release of hemicelluloses, then the slower release of water-soluble part of the lignin, and later also part of the amorphous cellulose.

While after steaming mode I the hemicellulose content decreased only by 1.1% compared to the original oak wood, after mode II it was already by 4.7%, and after the most intense steaming treatment in mode III it decreased by 22.9%, which means 75% reduction in hemicellulose content.

Considering the determined content of lignin in oak wood it can be stated that in mode I the water-soluble lignin content is likely to decrease. More intense steaming conditions caused degradation and condensation reactions of lignin and their synergistic effect was reflected by an increase in the lignin content by 3.5% compared to the original oak wood sample. SOLÁR (1997) states 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.

The content of extractives after steaming in mode I decreased from 9.4% to 8.4%, which is related to their release into the condensate from steaming or their decomposition. In other steaming modes a considerable increase in the extractives was observed. After the most intense steaming (mode III), the content of extractives in the oak wood sample grew 2.3 times (from 9.4% to 21.8%) compared to their original oak wood content. This increase is already related to the release of decomposition products of other wood components into the extraction mixture.

Based on the determined chemical characteristics it can be concluded that the increased severity of the steaming conditions was reflected primarily in the change of content of holocellulose and extractives, less the content of cellulose and lignin.

In the FTIR spectra of wood absorption bands appertaining to all wood components are observable. Assignment of them is in the Table 3. Due to steaming several changes in their intensities are occurred (Table 4). In spectra of oak wood steamed by mode I intensities of characteristic absorption bands of lignin (at 1593 and 1504 cm^{-1}) slightly decreased. After steaming at higher temperatures and with the increase of steaming time their intensities increased. These changes suggest that the content of lignin firstly decreased and with rising of treatment severity increased. Similar trend was found also by determination of lignin content using conventional method by ASTM D 1106 – 96. Similarly, the increase in intensity of characteristic absorption bands of lignin by thermal treatment of pedunculate oak (ČABALOVÁ *et al.* 2018) and eucalyptus wood (ESTEVES *et al.* 2013) was reported.

Tab. 3 Assignment of infrared absorption bands in wood spectrum (according to HON *et al.* 2001, PANDEY and PITMAN 2003).

Wavenumber (cm^{-1})	Peak assignment
3345	O–H stretching
1735	C=O stretching of acetyl, carboxylic groups and aldehydes
1593	Aromatic skeletal vibrations in lignin
1504	Aromatic skeletal vibrations in lignin
1458	C–H deformations in lignin and carbohydrates
1422	C–H deformations in lignin and carbohydrates
1364	C–H in-plane bending in carbohydrates
1232	syringyl ring and C–O stretch in lignin and xylan
1032	C-O stretching in polysaccharides
898	stretching at the β-(1,4)-glycosidic linkage, and C-H deformation

Tab. 4 Relative intensities of absorption bands Ai/A1032 of FTIR spectra of wood.

Wavenumber	wood - original	wood – mode I	wood – mode II	wood – mode III
3345 cm^{-1}	1.0157	1.0256	1.1890	1.1392
1735 cm^{-1}	0.3904	0.3944	0.5327	0.3978
1593 cm^{-1}	0.3099	0.2838	0.2998	0.3192
1504 cm^{-1}	0.1756	0.1226	0.1663	0.1799
1458 cm^{-1}	0.1740	0.1589	0.1637	0.1612
1422 cm^{-1}	0.0997	0.0791	0.0801	0.0860
1364 cm^{-1}	0.1185	0.1160	0.1399	0.1289
1232 cm^{-1}	0.2309	0.2266	0.2162	0.2037
898 cm^{-1}	0.0697	0.0701	0.0696	0.0806

During hydrothermal treatment on wood, more processes with different influence on the intensity of the absorption band around 1733 cm^{-1} run. The increasing its intensity may be due to opening of the glucopyranose ring, formation of new carbonyl and carboxyl groups, or cleavage of β-alkyl-aryl ether linkages in lignin. On the other hand, a decrease in its intensity may be caused by lignin condensation reactions, deacetylation of hemicelluloses and decomposition of aldehydes, carboxylic acids and their esters (ÖZGENC *et al.* 2017, ESTEVES *et al.* 2013, WINDEISSEN *et al.* 2009). In the FTIR spectrum of wood, the absorption bands of the different wood components overlap in this wavelength region. In order to better elucidate ongoing processes, we analyzed not only samples of wood, but also the samples of isolated holocellulose. Assignment of absorption bands in spectra of holocellulose is in the Table 5.

Tab. 5 Assignment of infrared absorption bands in holocellulose spectrum (according to HON *et al.* 2001, PANDEY and PITMAN 2003).

Wavenumber (cm^{-1})	Peak assignment
3339	O-H stretching
1732	C=O stretching of acetyl or carboxylic groups
1427	C–H bending
1371	C–H in-plane bending
1333	OH in-plane bending
1317	CH2 wagging
1244	C–O stretching in xylan
1161	C-O-C asymmetric bridge stretching
1032	C-O stretching
898	stretching at the β-(1,4)-glycosidic linkage, and C-H deformation

In Table 6 relative intensities of absorption bands of FTIR spectra of holocellulose are shown. The intensity of absorption band at 1732 cm^{-1} firstly increases due to increased temperature and extended period of steaming (mode I and mode II). In the hardest degree of steaming (mode III), the height of this peak decreased. We saw the same changes in the spectrum of wood. It can be concluded that changes in FTIR spectrum of wood in range 1770 to 1550 cm^{-1}are a sign of changes in polysaccharides.

Tab. 6 Relative intensities of absorption bands Ai/A1032 of FTIR spectra of holocellulose.

Wavenumber	HC - original	HC – mode I	HC – mode II	HC – mode III
3339 cm^{-1}	1.0241	1.0396	1.0630	1.2282
1732 cm^{-1}	0.2770	0.3175	0.3756	0.1988
1427 cm^{-1}	0.1039	0.0896	0.0934	0.1155
1371 cm^{-1}	0.0858	0.0910	0.1071	0.1110
1333 cm^{-1}	0.0555	0.0568	0.0570	0.0629
1317 cm^{-1}	0.0882	0.0925	0.0933	0.1251
1244 cm^{-1}	0.1959	0.2207	0.2621	0.1334
1161 cm^{-1}	0.1851	0.1860	0.1921	0.2407
898 cm^{-1}	0.0664	0.0811	0.0890	0.0917

In our experiment, the initial increase in intensity of absorption band at 1732 cm^{-1} may be due to formation of new carbonyl and carboxyl groups in carbohydrates by oxidation. The followed decrease may be due to deacetylation and degradation of hemicelluloses. Özgenc *et al.* (2017) reported opposite changes due to heat-treatment in the intensity of peak at 1730–1732 cm^{-1} for deciduous and coniferous woods. While the bands at 1730–1732 cm^{-1} increased for heat-treated beech wood, they decreased for heat-treated spruce and pine wood. Sikora *et al.* (2018) reported the increase and shifting absorbance at around 1730 cm^{-1} to smaller wavenumber with increasing treatment severity in the case of heat treatment of spruce and oak wood. Čabalová *et al.* (2018) found that the peak intensity at 1732 cm^{-1} in spectrum of heat-treated oak wood initially increased, and then decreased as the treatment time increased. Based on the above it can be concluded that changes in the intensity of this peak depend on the hardness of the treatment as well as on the kind of wood. Also it should be emphasized that samples of wood and not of isolated components were analyzed in the cited works. Therefore, the findings in these cases are the result of running the different processes in all wood components.

The changes in crystallinity were determined from FTIR spectra of Seifert´s cellulose as two parameters – the Total Crystallinity Index (TCI) according to Nelson and O´Connor (1964) and the ratio of intensities A_{1334}/A_{1315} according to Colom *et al.* (2003). Values of these parameters are shown in Table 7. The decrease in the crystallinity of cellulose due to steaming is obvious from the decrease in the total crystallinity index (TCI) and also from the increase in the ratio A_{1334}/A_{1316}.

Tab. 7 Parameters characterized cellulose crystallinity.

Steaming mode	TCI	A_{1334}/A_{1316}
0	0.4805	0.7528
I	0.4676	0.7572
II	0.4499	0.7671
III	0.4488	0.7702

Kong *et al.* (2017) monitored the effect of steaming time on the cellulose crystallinity in eucalyptus wood. The authors found that crystallinity increased, reaching a maximum after 2 h, and then decreased. They examined the decrease in cellulose crystallinity due to increased numbers of chain scission reactions that increased the amorphous character of cellulose, and subsequently reduced the total amount of cellulose crystalline regions. Furthermore, acetic acid which is formed by hydrolysis of hemicelluloses can cause the degradation of microfibrillar. Our findings are in agreement with cited work because in our experiment steaming times for all modes are longer, namely 5.5, 6.5 and 7.5 h.

CONCLUSION

In this paper the chemical changes that occur from the hydrothermal treatment of English oak (*Quercus robur* L.) wood through various steaming modes were examined. Increase in temperature and extension of the steaming period primarily affected the holocellulose and extractives contents, and less so the contents of cellulose and lignin.

The holocellulose content due to steaming decreased, the decrease reaching approximately 36% in the case of most extreme steaming treatment. Cellulose content in oak wood under the influence of steaming not greatly changed and its slight increase and decrease in individual modes is the result of several concurrent effects. Consequently, the decrease in holocellulose content is the result of degradation of most labile hemicelluloses. The content of hemicelluloses reduces by about 75%.

The content of extractives first slightly decreased, but with increasing temperature and extended steaming period a considerable increase in their content was observed. This increase is already related to the release of decomposition products of other wood components into the extraction mixture.

The lignin content in steamed oak wood shows only minimal changes. In the early stages of hydrothermal treatment its content slightly decreased, but at more intense conditions the 3.5% increase in its content was observed.

Based on the results of FTIR analyses it can be concluded that in the initial stages of steaming new carbonyl and carboxyl groups are formed in carbohydrates by oxidation. Consequently, the deacetylation and degradation of hemicelluloses are occured. In addition, the decrease in the crystallinity of cellulose due to steaming was observed.

As can be seen from Figure 2 the hydrothermal treatment of wood also resulted in darkening of wood samples. The intensity of change is dependent on the severity of conditions. The mechanism of colour change is complex and a number of overlapping reactions of the basic components of wood and their decomposing products are involved.

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