Effect of Thermal Treatment on the Chemical, Physical, and Mechanical Properties of Pedunculate Oak (*Quercus robur* L.) Wood

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Changes in the chemical composition and selected physico-mechanical properties of pedunculate oak (*Quercus robur* L.) wood samples were assessed after thermal treatment. Heat treatment was performed at 160, 180, and 200 °C in an oxidizing atmosphere. The contents of the extractives, lignin, cellulose, holocellulose, and saccharides, and the structural changes in the functional groups were determined. Changes in the colour traits, wood density, compression strength parallel to the grain, and compression modulus of elasticity were also determined. The decrease in the holocellulose content caused by the degradation of non-glucosic saccharides was observed during thermal treatment. The contents of both the extractives and lignin increased. The syringyl to guaiacyl (S/G) ratio in the lignin increased because of the preferential condensation of guaiacyl units. The physical and mechanical properties of pedunculate oak wood, such as density, equilibrium moisture content, colour lightness, and yellowness, decreased as the temperature increased. The compression strength and redness varied during thermal treatment, and reached maximum values during the treatment at 180 °C. The modulus of elasticity showed non-significant differences. Three groups of heat treatment clusters were distinguished in the multivariate wood trait analysis and were clearly segregated from each other.

Keywords: Pedunculate oak wood (Quercus robur L.); High temperature treatment; Wood chemical components; Infrared spectroscopy; Colour of wood; Physical properties; Mechanical properties

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INTRODUCTION

Wood properties are influenced by the modification of its main constituents by heat treatment, moisture, UV radiation, and chemical agents. Heat treatment generally improves the dimensional stability and resistance to wood-deteriorating fungi, and it can enhance some wood properties. This process was first developed in 1920 as a high temperature wood drying process and has become a wood modification process that occurs at various conditions. Heat treatment is the most advanced wood modification process that is used commercially. It causes extractives and main wood component changes due to heat transfer, which can be influenced by nanoparticles. Further development of heat treatment started in 1990 in Finland and continued across Europe for processing softwood and hardwood species, such as spruce, pine, aspen, and birch (Hill 2006; Laoutid *et al.* 2009; Sun *et al.* 2012). The American Hardwood Export council suggested thermally treating oak wood and other hardwood species used for outdoor applications with no additional protection.

The technological steps of direct heating, where heat treatment plays the most important role, are used in the process of drying or steam treatment of wood. Heating changes several physical and chemical wood properties (electrical properties, toughness, density, modulus of elasticity in tensile strength, and bending), increases the resistance to fire and biological pests, and decreases the hygroscopicity. These procedures are often used to change the wood colour. Modification of the wood structure, especially the lignin and extractives, can change its colour (Brebu and Vasile 2010; Tolvaj *et al.* 2013; Barcík *et al.* 2015; Wang *et al.* 2016; Kačík *et al.* 2016, 2017). This colour change is often viewed positively, especially in the furniture industry when processing hardwoods (Kačík and Kubovský 2011; Kvietková *et al.* 2015). Wood colour also depends on the incidence angle of illumination and is sensitive to heat and light radiation (Rinnhofer *et al.* 2003; Kubovský *et al.* 2016). Drying, heating, electromagnetic irradiation, and steam are external factors that can induce changes in the main components (cellulose, hemicellulose, and lignin) and extractives of wood, their content, and the wood properties (*e.g.*, colour) (Mitsui *et al.* 2001; Csanády *et al.* 2015). Heat treatment promotes a range of chemical changes in the different wood constituents. The chemical changes that occur in wood during heating start with deacetylation of hemicellulose. This is followed by depolymerisation, which is catalysed by the released acetic acid. Cellulose and lignin are more heat-resistant than hemicellulose (Tjeerdsma *et al.* 1998). Simultaneously, hemicellulose undergoes dehydration because of the decreased amount of hydroxyl groups (Weiland and Guyonnet 2003).

The relationship between the colour and chemical and mechanical properties of wood has been examined by several researchers (Bekhta and Niemz 2003; Yildiz *et al.* 2006; Kačíková *et al.* 2013). The chemical reactions involved during wood heat treatment, as well as the final properties of the material, depend directly on the treatment temperature, relative humidity, treatment time, and wood species used (Kačík *et al.* 2006; Popescu *et al.* 2013; Čabalová *et al.* 2016).

This work studied the effect of thermal degradation on the main wood components. The effects on the hemicellulose, cellulose, lignin, and extractives contents, and the selected physical and mechanical properties were investigated with the aim of finding a correlation between the heat treatment conditions (temperature and time) and the selected oak wood properties. This information would be useful for utilization of thermally modified wood for particular applications.

EXPERIMENTAL

Materials

Pedunculate oak (*Quercus robur* L.) is the second most abundant hardwood species in Slovakia and a heat treatment gives another option for adding to its economic value. Air-dried lumber from a trunk of a 120 years old tree was used to prepare defect-free samples that were 30 × 30 × 120 mm. To homogenize sampling, the samples were taken from one trunk only and they were randomly grouped.

Methods

Heat treatment

Prior to treatment, the samples were conditioned at a temperature of 20°C and relative humidity (RH) 65% for 4 weeks and then oven-dried at 100 ± 5 °C. Heat treatment was performed in an oven at 160, 180, and 200 °C in air. The duration of the treatment was 3, 6, 9, and 12 h. Altogether, nine groups with 11 treated samples each and one control group with 25 untreated samples were prepared. After the heat treatment, the samples were conditioned at standardized conditions (T = 20 °C; RH = 65%).

Chemical composition

In both the untreated and thermally-treated samples, the extractives content was determined according to the National Renewable Energy Laboratory (NREL) procedure by Sluiter *et al.* (2008). The saccharides and lignin contents were determined according to the NREL procedure by Sluiter *et al.* (2012). The structural carbohydrates were analysed using an Agilent 1200 HPLC chromatograph (Agilent Technologies, Santa Clara, CA, USA) equipped with an Aminex HPX-87P column (Bio-Rad Laboratories, Hercules, CA, USA) at 80 °C and a mobile phase (deionized water) flow rate of 0.6 mL/min. The acid insoluble lignin content was determined as the residue remaining on the filtering crucible (S3) after a two-step hydrolysis of saccharides. Four replicates were performed per sample.

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) analysis

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were obtained directly from the wood surface using a Nicolet iS10 FTIR spectrometer (Thermo Fisher Scientific, Madison WI, USA) equipped with a Smart iTR ATR sampling accessory and diamond crystal (Thermo Fisher Scientific, Madison WI, USA). The spectra were acquired by accumulating 64 scans at a resolution of 4 cm^{-1} in absorbance mode (A) from 4000 to 650 cm^{-1} and normalised at approximately 1032 cm^{-1} (C-H stretching vibrations). The spectra were measured using the OMNIC 8.0 software (Thermo Fisher Scientific, Madison WI, USA). Four measurements were performed per sample.

Measurements of the selected physical and mechanical properties

Changes in the colour, density, equilibrium moisture content (EMC), compression strength, and modulus of elasticity in compression parallel to the grain were determined according to standard tests. The colour values were measured with a BYK Spectro-guide 6834 spectrophotometer (Geretsried, Germany) equipped with a light source in the range of 360 to 740 nm. The scanned region was 10 mm in diameter. The colour was measured in the three-dimensional colorimetric system $L^*a^*b^*$, where L^* determines the lightness from 0 (black) to 100 (white), a^* is the ratio of red (positive) to green (negative), and b^* is the ratio of yellow (positive) to blue (negative). Eight measurements on each sample were performed, and the colour of the sample was expressed as the average value of the colour space coordinates. The difference ΔE^*, which was expressed as the distance between two points in the CIE-$L^*a^*b^*$ colour space, was calculated according to the following formula:

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{1}$$

where ΔL^*, Δa^*, and Δb^* are the differences in the lightness, green-red coordinates, and blue-yellow coordinates, respectively, between the colour of a treated sample and the average colour of the untreated samples.

The EMC was determined after conditioning the samples at the standard conditions of 20 °C and 65% RH. The density was measured at the oven-dry conditions before and after the thermal treatment. These paired measurements allowed for an evaluation of the direct effect of a treatment without the influence of the moisture content or a material variation in the density. The change in the density was expressed as the percent change based on the oven-dried density of the samples at the untreated stage. The strength in compression parallel to the grain and modulus of elasticity were measured according to ASTM 143-14 (2014) after the samples were conditioned at standard conditions. The deformation in compression was measured on a reference length of 50 mm. Twenty measurements were performed per each treating group.

Statistical analysis

The influence of the thermal treatment on the examined wood traits was statistically analysed by a nested analysis of variance (the treatment time was nested in the treatment temperature). Both the treatment temperature and time were considered fixed effect factors. Data with the same treatment temperature was analysed by a one-way analysis of variance, and Duncan's multiple range tests were used for comparison of the means. Additionally, the multivariate associations among 17 wood traits were analysed using a principal component analysis (PCA) to describe patterns of covariation among the examined traits.

RESULTS AND DISCUSSION

Changes in the Chemical Composition

Thermal treatment has statistically influenced all the examined parameters, *i.e.* chemical, physical as well as mechanical, except MOE (Table 1). In case of STR only the heat treatment (HT) at the temperature of 180 °C differed from the control sample, on contrary to the remaining two.

The chemical analysis showed that with an increasing temperature (Table 1) and duration of thermal loading (Table 2), the extractives and lignin contents increased considerably.

The yield of extractives in oak wood treated at the highest temperature (200 °C) was almost double that of the non-treated wood. This increase reflected the thermal decomposition of lignin macromolecules (Wikberg and Maunu 2004; Zachar *et al.* 2017). Lignin content increased with treatment time confirming higher susceptibility of hemicelluloses to thermal treatment (Mburu *et al.* 2008). An increase in lignin has been reported for various heating methods (Nuopponen *et al.* 2005; Inari *et al.* 2007; Windeisen *et al.* 2007).

It was also obvious that heating the samples decreased the absolute content of the hemicellulose-type saccharides (XYL, GAL, ARA, and MAN), which are the least heat-resistant saccharides, and three of these saccharides (GAL, ARA, and MAN) were almost completely degraded at 200 °C. This finding was in agreement with the fact that wood degradation starts with deacetylation of hemicellulose, and is followed by the depolymerization of polysaccharides, which is catalysed by the released acetic acid (Sivonen *et al.* 2002; Nuopponen *et al.* 2005). Sweet and Winandy (1999) found that the changes in the hemicellulose content and their structure also greatly influenced the decrease in the toughness properties of the wood, and glucomannan played the dominant role in this process. The degradation of the spruce wood saccharides in hemicellulose caused by thermal treatment was fastest for mannose. This process was slower for xylose and slowest for galactose (Čabalová *et al.* 2014).

Table 1. Effect of the Thermal Treatment on the Examined Chemical, Physical, and Mechanical Traits of the Pedunculate Oak Wood

Trait	No treatment	160 °C	180 °C	200 °C
EXT (%)	5.57 ± 0.06d	7.04 ± 0.83c	8.14 ± 1.34b	10.63 ± 0.95a
LIG (%)	21.78 ± 0.20c	21.62 ± 0.03d	24.00 ± 2.29b	27.49 ± 2.66a
S/G	1.38 ± 0.04c	1.41 ± 0.13c	1.66 ± 0.25b	2.01 ± 0.16a
GLC (%)	48.30 ± 0.03b	47.66 ± 0.84c	49.88 ± 1.77a	41.78 ± 0.67d
XYL (%)	21.44 ± 0.03a	19.55 ± 0.90b	18.54 ± 1.01c	10.69 ± 1.67d
GAL (%)	1.17 ± 0.02a	0.47 ± 0.06b	0.34 ± 0.06c	0.10 ± 0.04d
ARA (%)	1.97 ± 0.04a	1.04 ± 0.15b	0.20 ± 0.08c	0.06 ± 0.01d
MAN (%)	4.08 ± 0.15a	3.09 ± 0.09b	0.31 ± 0.08c	0.11 ± 0.05d
HOL (%)	76.96 ± 0.11a	71.37 ± 0.76b	69.28 ± 2.57c	52.73 ± 1.43d
Δ*E**	2.56 ± 0.97d	9.48 ± 2.76c	20.76 ± 2.83b	32.20 ± 2.30a
L*	63.71 ± 0.43a	54.57 ± 2.37b	43.61 ± 2.84c	33.77 ± 1.74d
a*	7.53 ± 0.01b	9.03 ± 0.11a	8.88 ± 0.19a	6.43 ± 0.51c
b*	21.64 ± 0.15a	20.51 ± 0.33b	16.76 ± 1.08c	9.91 ± 1.55d
EMC	0.11 ± 0.01a	0.09 ± 0.00b	0.08 ± 0.00c	0.06 ± 0.00d
STR (MPa)	50.80 ± 4.13b	51.54 ± 2.00b	55.96 ± 3.22a	52.56 ± 1.64ab
MOE (MPa)	11731 ± 4219a	11021 ± 350a	10846 ± 1168a	11639 ± 1028a
Δρ (kg/m^3)	0.00d	6.63 ± 0.15c	15.96 ± 3.04b	39.33 ± 9.29a

EXT: extractives; LIG: lignin; S/G: syringyl-to-guaiacyl ratio in lignin; GLC: D-glucose; XYL: D-xylose; GAL: D-galactose; ARA: L-arabinose; MAN: D-mannose; HOL: holocellulose; Δ*E**: colour difference; *L**: lightness; *a**: green-red chromatic coordinate; *b**: blue-yellow chromatic coordinate; EMC: equilibrium moisture content; STR: strength; MOE: modulus of elasticity; Δρ: change in density. The values are the mean ± the SD. Mean values that are followed by the same letters (a to d across examined treatment temperatures) were not significantly different at $P < 0.05$.

Chemical Changes after Thermal Treatment Analysed Using ATR-FTIR

During the thermal treatment, the components of the oak wood underwent chemical changes that affected several physical and mechanical properties of the wood. The FTIR spectra of the reference and heat-treated oak wood are shown in Fig. 1. The bands in the 3800 to 2750 cm^{-1} region were assigned to hydroxyl and methyl/methylene stretching vibrations in the polysaccharides and lignin. The decrease in intensity of the peak at 3343 cm^{-1} at lower temperatures represented the loss of hydroxyl groups following the dehydration of polysaccharides. The increase of this peak at 200 °C was because the lignin content increased, which was caused by carbohydrate degradation (Esteves *et al.* 2011).

The peak intensity at 1732 cm^{-1} (C=O stretching in unconjugated ketone in lignin and carboxyl groups in hemicellulose) initially increased, and then decreased as the heat treatment time increased. Li *et al.* (2015) found that the peak at 1732 cm^{-1} increased as the temperature increased (180 to 220 °C), especially at 220 °C, and did not decrease, which was probably because of the high lignin content in the analysed pine wood. Kocaefe *et al.*

(2008) and Dubey *et al.* (2012) observed a decrease in the peak at 1740 cm^{-1} during the heat treatment, which demonstrated that hemicelluloses are not stable and easily degrade at high temperatures.

Table 2. Changes in the Cell Wall Composition (% of Oven-Dry Weight per Unextracted Wood) of the Thermally-treated Pedunculate Oak Wood

T (°C)	*t* (h)	EXT	LIG	S/G	GLC	XYL	GAL	ARA	MAN	HOL
160	3	6.37 ± 0.06d	21.62 ± 0.07a	1.31 ± 0.04b	48.87 ± 0.51a	20.78 ± 0.06a	0.51 ± 0.03a	1.15 ± 0.06a	3.18 ± 0.13a	72.09 ± 3.38a
	6	6.96 ± 0.10b	21.61 ± 0.05a	1.53 ± 0.13a	47.13 ± 0.05c	19.45 ± 0.26b	0.51 ± 0.01a	1.01 ± 0.02b	3.12 ± 0.53a	71.87 ± 0.09a
	9	8.23 ± 0.11a	21.65 ± 0.08a	1.29 ± 0.05b	47.04 ± 0.16c	19.32 ± 0.08b	0.46 ± 0.02b	1.15 ± 0.09a	3.11 ± 0.20a	71.08 ± 0.08a
	12	6.60 ± 0.09c	21.58 ± 0.09a	1.52 ± 0.05a	47.62 ± 0.09b	18.64 ± 0.05c	0.39 ± 0.00c	0.83 ± 0.07c	2.96 ± 0.01a	70.43 ± 0.06a
180	3	6.30 ± 0.03d	21.98 ± 0.15c	1.56 ± 0.08b	52.49 ± 0.59a	19.35 ± 0.17a	0.41 ± 0.02a	0.32 ± 0.32a	0.40 ± 0.10a	72.97 ± 0.59a
	6	7.99 ± 0.11c	22.11 ± 0.09c	1.52 ± 0.14b	48.91 ± 0.51bc	19.24 ± 0.46b	0.35 ± 0.02b	0.17 ± 0.01a	0.35 ± 0.03ab	69.02 ± 1.01b
	9	9.03 ± 0.06b	25.48 ± 0.07b	1.49 ± 0.05b	48.67 ± 0.06c	18.40 ± 0.09b	0.36 ± 0.00b	0.18 ± 0.02a	0.26 ± 0.08bc	67.88 ± 0.19c
	12	9.22 ± 0.05a	26.43 ± 0.06a	2.05 ± 0.06a	49.46 ± 0.05b	17.16 ± 0.02c	0.25 ± 0.00c	0.14 ± 0.02a	0.23 ± 0.01c	67.24 ± 0.08c
200	3	9.95 ± 0.08d	23.80 ± 0.07d	1.89 ± 0.11b	41.92 ± 0.10b	12.36 ± 0.03a	0.08 ± 0.01b	0.06 ± 0.01a	0.16 ± 0.01a	54.59 ± 0.11a
	6	10.41 ± 0.08b	27.26 ± 0.08c	1.89 ± 0.10b	41.21 ± 0.29c	11.49 ± 0.18b	0.12 ± 0.02a	0.07 ± 0.01a	0.14 ± 0.05a	53.03 ± 0.51b
	9	12.02 ± 0.05a	29.50 ± 0.03a	2.06 ± 0.09a	41.32 ± 0.06c	10.40 ± 0.07c	0.15 ± 0.03a	0.05 ± 0.01b	0.07 ± 0.04b	51.98 ± 0.04c
	12	10.12 ± 0.05c	29.38 ± 0.04b	2.18 ± 0.14a	42.67 ± 0.24a	8.50 ± 0.07d	0.04 ± 0.03b	0.04 ± 0.01b	0.07 ± 0.01b	51.32 ± 0.31d

T: temperature; t: time; EXT: extractives; LIG: lignin; S/G: syringyl-to-guaiacyl ratio in lignin; GLC: D-glucose; XYL: D-xylose; GAL: D-galactose; ARA: L-arabinose; MAN: D-mannose; HOL: holocellulose. The values are the mean ± the SD. Mean values that are followed by the same letters (a to d across examined treatment times within the same treatment temperature) were not significantly different at $P < 0.05$.

In this study, the increase in this peak intensity was probably caused by the cleavage of ß-alkyl-aryl ether bonds in the lignin, and the subsequent decrease may have been caused by the lignin condensation reactions (Windeisen and Wegener 2008), as well as the deacetylation of hemicellulose (Solár *et al.* 1987; Srinivas and Pandey 2012).

The decrease in intensity of the 1644 cm^{-1} peak indicated the destruction of α-carbonyl groups. Similar results were observed during the thermal modification of spruce (Kačík *et al.* 2006) and beech (Timar *et al.* 2016) wood. According to Funaoka *et al.* (1990), this may have been caused by the interaction of α-sites of the side chains in lignin with the adjacent benzene nuclei, which subsequently formed diphenylmethane structures. The increase in intensity of the peaks at 1504 and 1593 cm^{-1} (C=C stretching in aromatic nuclei) and their shift to higher wave numbers (1514 and 1600 cm^{-1}, respectively) as the treatment temperature increased to 200 °C may have been because of the cleavage of propyl groups in lignin and formation of cross-links during the condensation reactions (Colom *et al.* 2003; Windeisen and Wegener 2008; Chen *et al.* 2012).

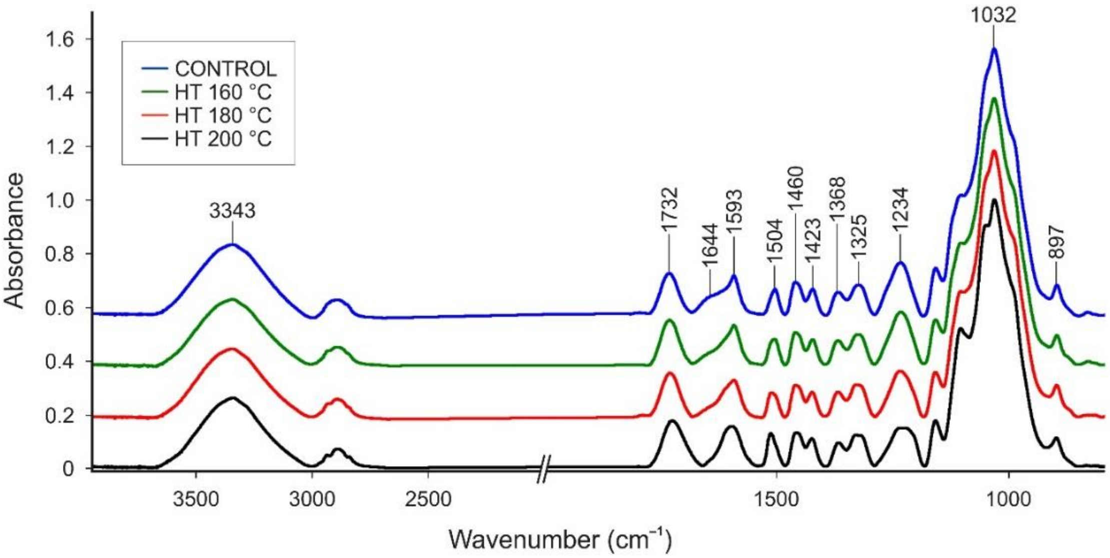

Fig. 1. ATR-FTIR spectra of the untreated and thermally-treated oak wood (20 °C control; 160, 180, and 200 °C was treated for 12 h)

The peak at 1460 cm^{-1} was assigned to asymmetric C-H deformation in the methyl and methylene groups in lignin and hemicellulose. The increase in intensity as the treatment temperature increased may have been caused by hemicellulose degradation and lignin condensation with the assistance of $–CH_2$ groups (Funaoka *et al.* 1990).

Changes in the Colour Traits after Thermal Treatment

The colour difference of the thermally-treated wood increased with the treatment temperature (Table 1) and duration (Table 3). Other colour characteristics were also affected by the temperature and duration of the treatment, especially at high treatment temperatures (180 and 200 °C). As was reported previously by Hill (2006), the most substantial change occurred in the lightness (*L**) of the thermally-treated wood. The lightness gradually decreased as both the temperature and time increased. The changes in the redness (*a**) of the investigated wood samples were similar to what was reported previously for silver fir (Kučerová *et al.* 2016) and oak wood (Barcík *et al.* 2015). The redness was higher for the samples treated at 160 and 180 °C compared with the untreated sample, and then decreased for the samples treated at 200 °C, where the values were even lower than that of the untreated wood. The yellowness (*b**) of the thermally-treated wood decreased with an increase in the temperature.

Table 3. Changes in the Physical and Mechanical Traits of the Thermally-treated Pedunculate Oak Wood

T (°C)	t (h)	ΔE^*	L^*	a^*	b^*	EMC	STR (MPa)	MOE (MPa)	$\Delta\rho$ (kg/m^3)
160	3	5.58 ± 1.81c	57.61 ± 2.41a	8.92 ± 0.80a	20.93 ± 1.15a	0.091 ± 0.002a	52.34 ± 6.92a	11440 ± 2001a	6.55 ± 1.10a
	6	8.20 ± 2.06b	54.62 ± 2.08b	9.11 ± 0.47a	20.62 ± 0.99a	0.091 ± 0.002a	53.25 ± 6.44a	10712 ± 2068a	6.79 ± 1.59a
	9	8.78 ± 3.26b	54.22 ± 3.49b	8.96 ± 0.90a	20.27 ± 1.24a	0.093 ± 0.003a	48.66 ± 10.94a	11179 ± 4285a	6.45 ± 1.49a
	12	11.00 ± 1.81a	51.84 ± 1.79c	9.14 ± 0.88a	20.23 ± 1.32a	0.093 ± 0.003a	51.93 ± 9.52a	10752 ± 2509a	6.72 ± 1.69a
180	3	17.07 ± 1.19d	47.13 ± 1.50a	9.12 ± 0.58a	18.03 ± 0.95a	0.081 ± 0.001a	57.29 ± 6.38a	12463 ± 3153a	12.30 ± 1.40d
	6	20.00 ± 1.18c	44.32 ± 1.72b	8.93 ± 0.68ab	17.08 ± 1.14b	0.079 ± 0.004a	57.19 ± 4.88a	10900 ± 2290ab	15.01 ± 1.64c
	9	21.82 ± 0.97b	42.56 ± 1.65c	8.73 ± 0.52b	16.50 ± 1.01b	0.075 ± 0.002b	51.18 ± 6.40b	9808 ± 2874b	17.10 ± 2.30b
	12	24.17 ± 1.07a	40.41 ± 1.57d	8.72 ± 0.70b	15.44 ± 1.22c	0.070 ± 0.002c	58.20 ± 5.35a	10214 ± 1658ab	19.43 ± 1.94a
200	3	29.29 ± 1.45c	36.08 ± 1.99a	7.15 ± 0.48a	11.96 ± 1.39a	0.061 ± 0.002a	54.72 ± 7.91a	12118 ± 3235a	26.59 ± 2.57d
	6	31.75 ± 1.79b	34.12 ± 2.42b	6.42 ± 0.80b	10.23 ± 1.78b	0.061 ± 0.003a	51.04 ± 9.24a	10525 ± 2370a	38.85 ± 3.89c
	9	33.58 ± 0.94a	32.67 ± 1.02c	6.06 ± 0.66b	8.93 ± 1.31c	0.062 ± 0.002a	51.56 ± 6.36a	11092 ± 2796a	43.84 ± 7.45b
	12	34.17 ± 0.75a	32.21 ± 1.05c	6.07 ± 0.61b	8.52 ± 1.21c	0.062 ± 0.002a	52.90 ± 9.88a	12822 ± 2932a	48.04 ± 4.01a

T: temperature; t: time; ΔE^*: colour difference; L^*: lightness; a^*: green-red chromatic coordinate; b^*: blue-yellow chromatic coordinate; EMC: equilibrium moisture content; STR: strength; MOE: modulus of elasticity; $\Delta\rho$: change in density. The values are the mean ± the SD. Mean values that are followed by the same letters (a to d across examined treatment times within the same treatment temperature) were not significantly different at $P < 0.05$.

Density, EMC, and Mechanical Properties

As was expected according to Horváth *et al.* (2012), the density and EMC of the treated oak wood decreased as the temperature increased (Fig. 2). The density decreased by up to 7% (12 h at 200 °C). The effect of the treatment duration was more severe at higher temperatures. The treatment caused a desirable change in the EMC for oak wood (Akyildiz and Ates 2008) and equalized the property. A better dimensional stability of the treated oak was the ultimate consequence of the change in the EMC. The duration of the treatment had no significant effect on the EMC of the wood.

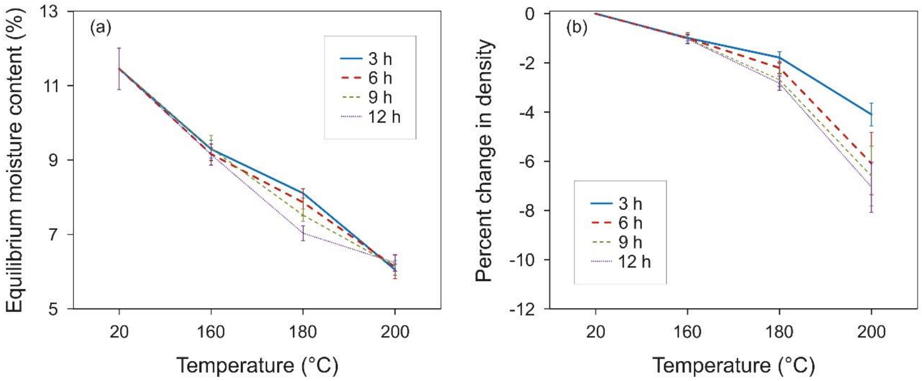

Fig. 2. Effect of the thermal treatment on the EMC and percent change in density of the pedunculate oak wood

In contrast to the shear strength of oak wood (Bakar *et al.* 2013), the compression strength of the treated oak wood increased with a maximum value at 180 °C. However, the compression strength was comparable to that of the untreated wood at 200 °C. The modulus of elasticity slightly increased with the temperature, but the variation was not large enough that an effect from the treatment temperature or duration was observed (Table 3). The relation of the total colour change and weight loss, contents of cellulose, hemicellulose, and lignin, and toughness properties has been monitored and studied by many researchers (Kim *et al.* 1998; Yildiz *et al.* 2006; Kocaefe *et al.* 2008; Kačíková *et al.* 2013). It has been observed that the mechanical properties are mostly affected by the hemicellulose degradation and decrease in the cellulose polymerization degree, and to a lesser extent, by the ramification of lignin and crystallization of cellulose.

Associations among the Wood Traits

A principal component analysis was done to evaluate how the examined traits were associated (Fig. 3). The first PCA axis explained 73% of the variation and showed strong positive loadings for the traits, such as the blue-yellow chromatic coordinate, lightness, EMC, and contents of holocellulose and xylose. The negative side of the axis indicated strong loadings for the colour difference, change in the density, extractives content, S/G ratio in the lignin, and lignin content. The second PCA axis explained 13% of the variation and showed strong positive loadings for the bending strength, glucose content, and green-red chromatic coordinate. The negative side of the axis indicated strong loadings for the contents of arabinose, mannose, and galactose. Both the examined treatment temperatures and times correlated with the first PCA axis. Three groups of heat treatment clusters were distinguished in the multivariate wood trait analysis that were clearly segregated from each other. The untreated sample, having had no thermal treatment, was positioned farthest to the right on the positive side of the first PCA axis. A cluster formed by the thermal treatments at 160 °C was on the positive side of the first axis, and a cluster formed by treatments at 180 °C was positioned on both the positive and negative sides of the first axis. Finally, the treatments at 200 °C formed the last cluster that was positioned exclusively on the negative side of the first PCA axis. Additionally, the shorter thermal treatment times within each temperature cluster were always positioned more positively on the first PCA axis than the longer thermal treatment times. The traits most highly associated with the most segregated sample that received no thermal treatment included the lightness and EMC.

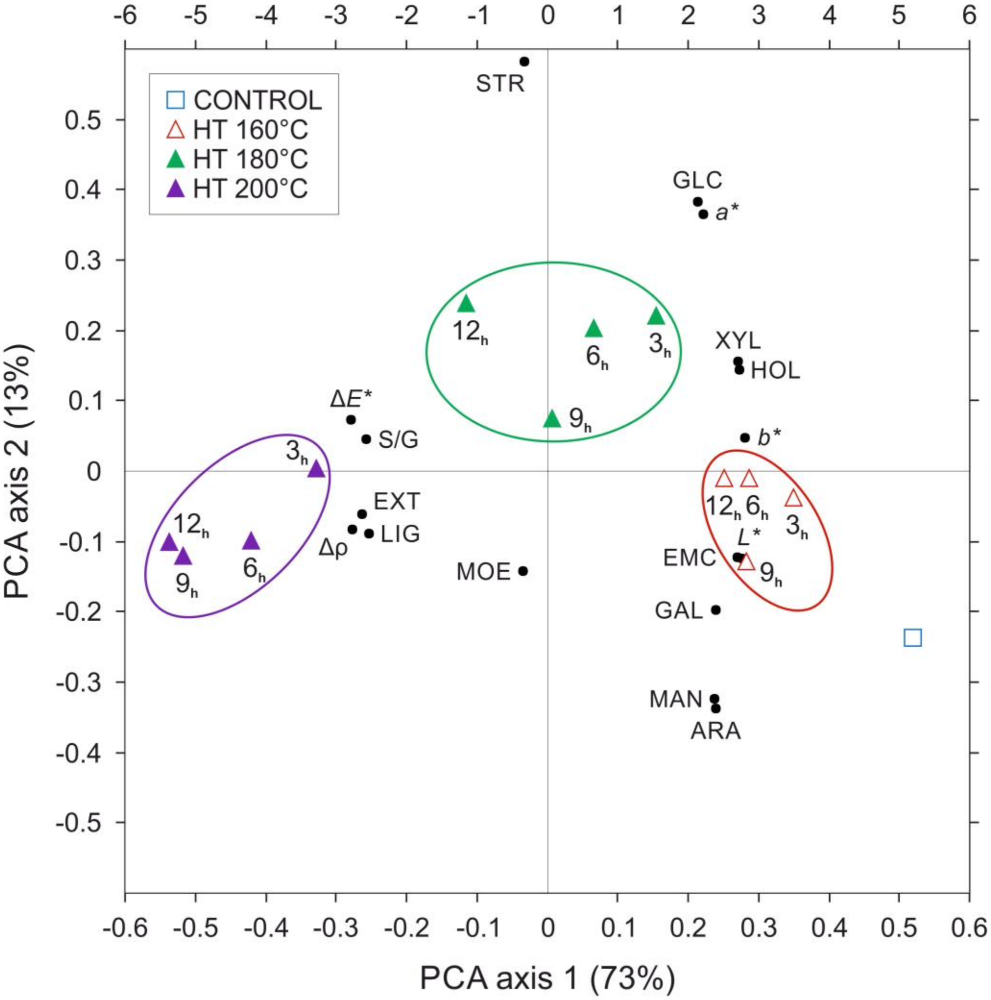

Fig. 3. Positions of 17 wood traits on the first and second axes of the PCA. The bottom and left-hand axes refer to the wood traits, and the top and right-hand axes refer to the examined treatment conditions. Trait abbreviations: *a**: green-red chromatic coordinate; *b**: blue-yellow chromatic coordinate; *L**: lightness; Δ*E**: colour difference; EXT: extractives; ARA: L-arabinose; GAL: D-galactose; GLC: D-glucose; HOL: holocellulose; LIG: lignin; MAN: D-mannose; XYL: D-xylose; S/G: syringyl-to-guaiacyl ratio in lignin; EMC: equilibrium moisture content; MOE: modulus of elasticity; STR: strength; and Δ*ρ*: change in density. The treatment temperatures are indicated in the key.

CONCLUSIONS

1. The thermal loading of oak wood caused a decrease in the relative amounts of the hemicellulose saccharides. The galactose, arabinose, and mannose were almost completely degraded by the thermal treatment at 200 °C. The resistance of the saccharides depended on the temperature, where the largest changes occurred at the highest treatment temperatures. The influence of the treatment duration was a less important factor that only affected galactose.
2. Increasing the temperature and duration caused a significant increase in the content of the extractives, which were mostly products of heat decomposition of lignin

macromolecules, and lignin, which was because of auto condensation and a higher thermal stability.

3. Over the entire temperature range, the degradation of hemicellulose was observed.
4. The compression strength and green-red chromatic coordinate varied during the thermal treatment, and maximum values were obtained at 180 °C and 160 °C, respectively.
5. The modulus of elasticity showed non-significant differences at the examined temperatures.

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