The Effect of Chemical Changes during Heat Treatment on the Color and Mechanical Properties of Fir Wood

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European silver fir (*Abies alba* L.) wood was heat-treated in an oven for 60 min at seven different temperatures of 100 °C, 150 °C, 200 °C, 220 °C, 240 °C, 260 °C, and 280 °C under atmospheric pressure in the presence of air. The effect of thermal treatment on the chemical composition, mechanical, and color properties of the wood was studied, and the mutual correlations between the investigated properties were evaluated. The bending strength/modulus of rupture (MOR) and the modulus of elasticity (MOE) were positively correlated with the total saccharides, glucose, mannose, and xylose content, where R ranged from 0.942 to 0.984. For changes in the wood color, very strong positive correlations between the total color difference and the contents of lignin and extractives were determined, where $R = 0.968$ and 0.945 respectively. Additionally, the total color difference was negatively correlated with the total saccharides, mannose, and xylose content, where R ranged from 0.876 to 0.938. The obtained data were evaluated by principal component analysis (PCA), where the components explained 93.1% of the total variance.

Keywords: Heat treatment; Silver Fir; Saccharides; Mass loss; Color traits; Mechanical properties

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INTRODUCTION

Wood is a renewable material that is widely used in different applications, especially within the construction industry. However, the utilization of natural wood in outdoor conditions has some limitations, which result from its undesirable properties such as poor resistance against biological attacks of fungi and insects, dimensional instability, and changes in appearance under atmospheric conditions. These disadvantages were overcome by the use of a durable hardwood species, particularly tropical hardwoods, or by means of wood preservation. The most common method for increasing the decay resistance of wood is the application of various chemicals (Hill 2006; Papadopoulos 2010; Wu *et al.* 2010; Chen *et al.* 2013; Xie *et al.* 2013; Han *et al.* 2015; Osvaldová *et al.* 2016), but chemical treatments may have a negative environmental impact during their production, service life, and in their disposal or recycling situations (Hill 2006; Kocaefe *et al.* 2008). Thermal treatment is a different method for the improvement of wood properties (Seborg *et al.* 1953; Alen *et al.* 2002; Militz 2002; Gurdil *et al.* 2009; Allegretti *et al.* 2012; Bazyar 2012; Cademartori *et al.* 2015; Missio *et al.* 2015; Candelier *et al.* 2016; Missio *et al.* 2016). Various thermal treatment methods have been commercialized, such as ThermoWood®, PlatoWood®, RetificatedWood®, and OHT-Wood®.

Thermal treatment removes water from wood, and it also causes significant alterations in the chemical composition of wood. The application of heat on wood results in dehydration, thermal oxidation, depolymerization, and the degradation of wood components. Hemicelluloses are the most thermally labile of the macromolecular cell wall components. Missio *et al.* (2015) observed an increase of lignin fraction and the proportional increase in cellulose content compared to hemicellulose content after heat treatment of wood.

When wood is heated, hemicelluloses degrade first, at 160 °C to 220 °C, resulting in the formation of various volatile compounds. The presence of acetyl groups in hemicelluloses leads to the formation of acetic acid, thereby causing an acid-catalyzed degradation of polysaccharides. The degradation of hemicelluloses has been proposed as the major factor for the loss of mechanical strength, affecting especially bending and tensile strength (Boonstra *et al*. 2007). In cellulose, the amorphous regions are more susceptible to thermal degradation than the crystalline phase. With an extended thermal treatment, a chain scission of the cellulose macromolecule occurs, which results in decreased degree of polymerization (DP) of cellulose (Kučerová *et al.* 2011; Kačíková *et al.* 2013; Výbohová and Kučerová 2013; Kučerová and Výbohová 2014). Degradation of the cellulose polymer was suggested to be the main cause for tensile strength losses (Boonstra *et al.* 2007). The loss of polysaccharides during heat treatment leads increased relative content of lignin in wood. Lignin is the most thermally stable component of the cell wall. However, some thermal degradation of lignin can occur at relatively low temperatures, with the formation of various breakdown products. At higher temperatures, cross-linking or condensation reactions are dominant (Nuopponen *et al.* 2004; Hill 2006; Windeisen *et al.* 2007).

The darkening of wood is one of the most visible effects of the heat treatment (Militz 2002; Esteves *et al.* 2008a; Cademartori *et al.* 2014a,b; Barcík *et al.* 2015a,b). This effect is often explained as the result of the formation of colored degradation and oxidation products from the hemicelluloses and extractives. The intensity of the discoloration depends on the severity of the treatment (Bekhta and Niemz 2003; Chen *et al.* 2012b).

The temperature of the treatment also influences the mechanical properties of wood. For example, the bending strength of birch wood in constant climate after treatment increases (compared to the strength of the wood without the treatment in the same climate) as the temperature of the treatment is augmented, reaching a maximum value after a heat treatment at 160 °C. A treatment at higher temperatures promotes a drop of mechanical properties. The length of time of the treatment has a similar effect (Poncsak *et al.* 2006). However, Yildiz *et al.* (2006) reported a decrease in the compression strength of spruce wood in the temperature range of 130 °C to 200 °C.

Relationships between changes in the chemical, physical, and mechanical properties during heat treatment of wood have been examined in several studies. There were strong correlations between degree of cellulose depolymerization and modulus of elasticity, total crystallinity index, and color characteristics, between content of hemicelluloses and modulus of elasticity, modulus of rupture, lightness, and mass loss (Kačíková *et al.* 2013), and between compression strength and the changes in chemical structure of wood components (Yildiz *et al*. 2006), color change, and the mass loss (Olarescu and Campean 2014). Other studies reported positive correlations between density and compressive strength, and modulus of elasticity (Zawadzki *et al.* 2013), and positive correlations between degree of polymerization of cellulose and compressive strength, and modulus of elasticity (Zawadzki *et al*. 2016).

A study of a wood heat treatment is still important for different wood species because it gives characterization of new material properties and provides information for optimization of wood processing and gives more insight to cause and effect of this feature.

This study investigated the effect of thermal treatment on the chemical composition, mechanical, and color properties of fir wood and evaluated their mutual correlations.

EXPERIMENTAL

Materials

European silver fir (*Abies alba* L.) wood was obtained from the Zvolen region in the Slovak Republic. A fir tree was 59 years old and the diameter at the breast height was 262 mm. From the butt end of the trunk, a radial board was cut and used for preparation of 10 mm × 10 mm × 150 mm (radial × tangential × longitudinal) samples. The samples were conditioned in a chamber at 20 ± 2 °C and 65 ± 5% relative humidity to the moisture content of about 12%. A total of 7 groups of 10 samples each were heat treated under defined conditions, and one group of 10 samples was left without treatment (20 °C).

Methods

Heat treatment

A heat treatment of the experimental samples was carried out in a preheated Binder ED 53 (Tuttlingen, Germany) laboratory heating oven at 100 °C, 150 °C, 200 °C, 220 °C, 240 °C, 260 °C, and 280 °C for 60 min under atmospheric pressure in the presence of air (Fig. 1). The time of reheating an oven to the required temperature after inserting the samples were 5 min. After the treatment, each group of samples was removed from the oven and cooled down in a desiccator, and the mass loss was determined.

Fig. 1. Influence of treatment temperature on the color of fir wood

Bending strength and modulus of elasticity

The bending strength or modulus of rupture (MOR) was evaluated using a 3-point bending test according to the modified ASTM 143-14 standard. Prior to the testing, the samples were conditioned in a chamber at 20 °C and 65% relative humidity. Due to mass loss during the thermal treatment, the cross section of a sample 10 mm × 10 mm changed before a test, and the section was measured again. The samples were loaded at the center between supports of 100 mm in distance. Tangential direction of a sample was parallel to the loading force. The loading was performed using a Testometric M250-3CT loading machine (Rochdale, UK) that measures force with the precision of ± 1 N. Samples failed within the range from 30 s to 90 s. Deflection was measured from the support movement of a loading cell with the precision of 0.001 mm. The apparent bending strength was calculated from the maximum force, $F_{\max}$, at the failure according to Eq. 1,

$$MOR = \frac{3F_{max}\, l_0}{2bh^2} \tag{1}$$

where b and h are the width and height of the samples, respectively, and l_0 is the span of the supports. The modulus of elasticity (MOE) was calculated from the following equation:

$$MOE = \frac{1}{4}\frac{Fl_0^3}{bh^3y} \tag{2}$$

The force-deflection ratio (*F*/*y*) was taken from the linear part of the force-deflection diagram. An effect of moisture content on MOE and MOR was not taken into account for readjusting the properties. A thermal treatment created new material with decreased ability to attract water vapor and dependencies of mechanical properties on moisture content were unknown. We used as homogenized groups as possible such that any effect of moisture content variation within a group would be hidden in the property variation.

Wood color

The color of the wood was measured using a standard spectrophotometer. Color was expressed in the CIELab color space system, using the space coordinates $L*$, $a*$, and $b*$. Eight color measurements were taken on each sample. A change of color due to the thermal treatment, $\Delta E*$, was defined as the CIELab space distance between the average color space coordinates of 10 untreated fir samples and the color coordinates of treated samples,

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{3}$$

where ΔL^*, Δa^*, and Δb^* denote an absolute change of the lightness, green-red chromatic coordinate and blue-yellow chromatic coordinate, respectively.

Chemical composition

Wood samples were mechanically disintegrated to sawdust. Fractions of 0.5 mm to 1.0 mm were extracted in a Soxhlet apparatus, with a mixture of ethanol and toluene, according to ASTM D1107-96 (2013). The lignin content was determined according to ASTM D1106-96 (2013). To quantify the saccharides, the extractive-free sawdust was hydrolysed by sulfuric acid as described (Saeman *et al.* 1954) and analysed by high performance liquid chromatography (HPLC) on an Agilent 1200 (Santa Clara, USA) equipped with an Aminex HPX-87P column and refractive index detector. The analysis was performed at 80 °C, using ultrapure water as an eluent at a flow rate of 0.5 mL/min. Glucose, mannose, arabinose, xylose, and galactose were detected and quantitatively determined using cellobiose as an internal standard. All measurements were carried out four times. The data were presented as percentages of the oven-dry weight of unextracted wood.

Statistical analyses

The dependency between a physical or mechanical property (P) and the content of a chemical component (X) was predicted according to the following exponential function,

$$P = a + be^{-cX} \tag{4}$$

where a, b, and c are regression parameters that were determined using the least squares method procedure in Statistica software (Tulsa, OK, USA), utilizing the efficient Levenberg-Marquardt algorithm.

Multivariate associations among 16 wood traits were analyzed using a principal component analysis (PCA; Statistica 12.0) to describe the patterns of co-variation among the examined traits.

RESULTS AND DISCUSSION

Chemical Changes

The heating of wood causes a reduction in mass and changes in its chemical composition (Table 1). The changes in the mass loss at initial stages of the treatment were associated mainly with the loss of water and volatiles (Hill 2006; Esteves *et al.* 2008b). In the experiment, a loss of major wood compounds takes place mainly above 200 °C. The thermal degradation starts by decomposition of hemicelluloses, that generally show a lower thermal stability than cellulose (Tumen *et al.* 2010; Silva *et al.* 2015).

Table 1. Chemical Analyses of Heat-Treated Fir Wood

Temperature (°C)	Mass Loss (%)	Extractives (%)	Saccharides (%)	Lignin (%)
20	0.00 ± 0.00	1.86 ± 0.03	64.42 ± 0.04	31.08 ± 0.34
100	7.88 ± 0.35	1.35 ± 0.04	67.44 ± 0.04	30.28 ± 0.07
150	9.29 ± 0.16	1.47 ± 0.02	68.15 ± 0.42	29.84 ± 0.16
200	12.32 ± 0.16	1.69 ± 0.02	67.67 ± 0.80	30.92 ± 0.47
220	14.07 ± 0.38	2.39 ± 0.01	62.66 ± 0.02	34.24 ± 0.86
240	21.45 ± 0.35	3.11 ± 0.03	60.18 ± 0.70	37.73 ± 0.20
260	33.06 ± 1.17	2.96 ± 0.03	47.64 ± 0.10	49.25 ± 0.25
280	52.40 ± 1.36	2.91 ± 0.02	13.31 ± 0.10	85.97 ± 0.16

*Note: Data represent mean values ± standard deviations

The decrease in extractives content by heat treatment up to 200 °C could be due to the removal of volatiles. Over 200 °C, the content of extractives increases in consequence of the release of degradation products of lignin and saccharides in the extraction mixture, and/or due to their condensation reactions with the extractives originally present in untreated wood. The increase in extractives during the thermal treatment was also observed in other studies (Kučerová *et al.* 2011; Missio *et al.* 2016; Severo *et al.* 2016). The decrease in extractives above 260 °C could be due to the cracking and devolatilization of lignin liquid intermediates or due to further polycondensation to form extra char (Pelaez-Samaniego *et al.* 2014).

The increase in the proportional lignin content during the heat treatment was caused by degradation of the hemicelluloses and cellulose and the condensation reactions of lignin (Wikberg and Maunu 2004; Tumen *et al.* 2010; Silva *et al.* 2013). In our experiment, an increase in the relative content of lignin was observed at temperatures over 220 °C.

The saccharide analysis showed that the degradation of hemicelluloses occurred at 100 °C and increased with the temperature of the heat treatment. This result reflects the decreased relative quantities of non-glucose saccharides in fir wood (Table 2). The D-xylose content decreased first, which indicated that the xylans, a group of the hemicelluloses, degraded more easily. This was confirmed with the decrease of the ratio of the sum of monosaccharides in xylans to sum of monosaccharides in mannans with treatment temperature (from 0.37 at 20 °C to 0.22 at 240 °C). This finding is in agreement with previously published data (Alen *et al.* 2002). The degradation of hemicelluloses starts with deacetylation reactions, followed by the formation of acetic acid that catalyzes the degradation of polysaccharides (Hill 2006; Tumen *et al.* 2010). Cellulose is more thermally stable than hemicelluloses, probably due to its crystalline structure. Cellulose degradation occurs at a higher temperature than hemicelluloses and begins in its amorphous regions (Missio *et al.* 2015). Because of the faster degradation of hemicelluloses, the relative quantity of glucose increased up until the temperature 240 °C. However, above 260 °C, its significant decrease was observed, which indicated cellulose degradation (Missio *et al.* 2015).

Table 2. Percentage Content of Monosaccharides in Heat-Treated Fir Wood

Temperature (°C)	D-Glucose (%)	D-Mannose (%)	D-Xylose (%)	L-Arabinose (%)	D-Galactose (%)
20	42.96 ± 0.16	12.32 ± 0.04	4.76 ± 0.10	2.20 ± 0.02	2.19 ± 0.04
100	45.59 ± 0.06	13.19 ± 0.04	4.30 ± 0.02	2.19 ± 0.00	2.18 ± 0.00
150	46.51 ± 0.16	13.25 ± 0.06	4.23 ± 0.02	2.11 ± 0.00	2.06 ± 0.02
200	46.30 ± 0.46	13.06 ± 0.16	4.28 ± 0.06	1.99 ± 0.00	2.04 ± 0.02
220	45.52 ± 0.02	11.45 ± 0.00	3.72 ± 0.00	1.08± 0.03	1.97 ± 0.00
240	47.90 ± 0.84	8.48 ± 0.04	2.42 ± 0.02	0.40± 0.04	1.37 ± 0.02
260	42.38 ± 0.44	3.98 ± 0.02	1.28 ± 0.04	ND	ND
280	11.51 ± 0.04	1.80 ± 0.01	ND	ND	ND

*Note: Data represents mean values ± standard deviations; ND= not detected

Color Changes

Increasing the temperature and the time of heat treatment changed the color of the fir wood (Table 3). The largest change started at the temperatures between 200 °C and 220 °C. In this temperature range, the red component, represented by the *a** coordinate, reached its maximum value. A further change of *a** coordinate was in the reverse direction toward a green color (Fig. 2). Similar behavior was shown in the yellow-blue component, represented by the *b** coordinate. Initially it changed towards a yellow color and then later back towards a blue color. The turning point was at 200 °C. The largest change of the color coordinates showed the lightness of wood *L** - wood darkened. A factor analysis showed a significant effect of the temperature on all color characteristics.

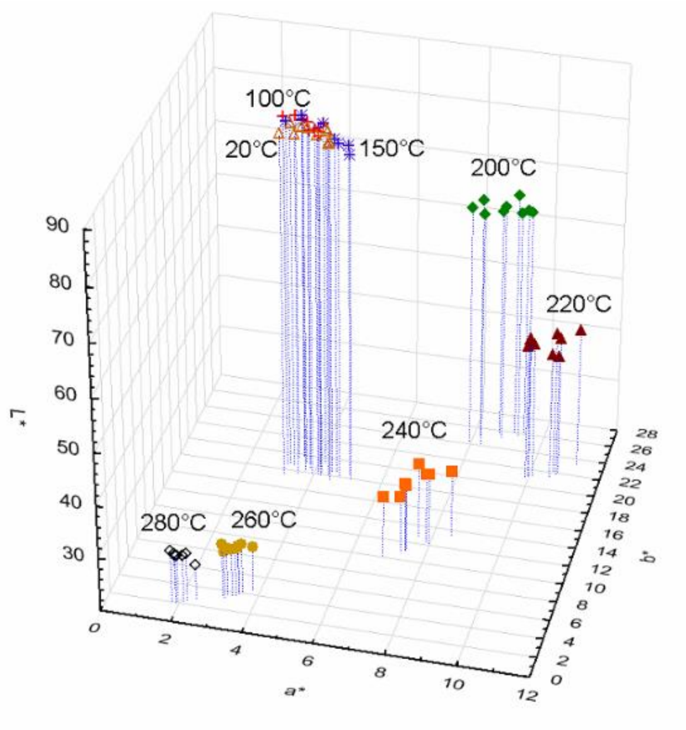

Fig. 2. Changes in the color space of fir wood due to the thermal treatment

Table 3. Color and Bending Characteristics of Heat-Treated Fir Wood

Temperature (°C)	ΔE*	L*	a*	b*	MOR (MPa)	MOE (MPa)
20	1.10 ± 0.43	84.4 ± 0.93	3.9 ± 0.51	18.3 ± 0.45	66.60 ± 4.39	6676 ± 455.4
100	1.17 ± 0.52	85.0 ± 0.48	3.8 ± 0.39	18.8 ± 0.66	79.82 ± 4.48	7480 ± 385.4
150	1.76 ± 0.58	83.6 ± 1.07	4.2 ± 0.69	19.0 ± 0.74	80.91 ± 5.03	7409 ± 471.3
200	21.95 ± 1.48	64.2 ± 1.33	8.8 ± 0.56	25.5 ± 0.85	67.05 ± 5.13	6804 ± 486.2
220	39.42 ± 1.32	45.6 ±1.32	10.4 ± 0.46	21.8 ± 0.72	67.04 ± 4.67	7665 ± 475.6
240	52.40 ± 1.16	32.5 ± 1.10	7.6 ± 0.47	11.7 ± 1.03	53.18 ± 4.12	7266 ± 206.4
260	57.27 ± 0.43	28.9 ± 0.48	3.4 ± 0.23	3.8 ± 0.38	28.26 ± 3.67	4616 ± 514.1
280	57.92 ± 0.95	28.7 ± 1.05	2.0 ± 0.21	2.3 ±0.26	7.87 ± 0.63	1735 ± 252.9

*Note: Data represent mean values ± standard deviations.
Δ*E**, total color difference; *L**, *a**, and *b** color characteristics; MOE, modulus of elasticity;
MOR, modulus of rupture or bending strength

Srinivas and Pandey (2012) described similar changes in the CIELab coordinates with the severity of the thermal treatment of silver oak and rubber wood in vacuum. Decrease in lightness L^* indicates that many components absorbing visible light are formed during heat treatment. The color darkening of the thermally modified wood is caused by the degradation reactions of hemicelluloses, and the subsequent formation of low molecular weight sugars (Poncsak *et al.* 2006; Esteves *et al.* 2008a), as well as the formation of oxidation products such as quinones (Hon and Minemura 2001; Kamperidou and Barmpoutis 2015). Moreover, an increase of extractives and relative content of lignin during heat treatment contributes to darkening of wood. According to Chen *et al.* (2012), an increase of a^* is related to condensation, degradation, and oxidation of many wood elements. The authors affirmed that substances such as lignin, and some of extractives could condense and form by-products and, consequently, contribute to the increase of red tone intensity on the wood sample. Some authors (Gierlinger *et al.* 2004; Cademartori *et al.* 2014a) referred that an increase of polyphenols content results in the increase of red tones of wood.

Changes in Mechanical Properties

The bending strength changed above 220 °C. The modulus of elasticity followed a similar trend. The MOR and the MOE slightly increased after the thermal treatment, but a more severe treatment reduced their values (Table 3). The apparent increase of mechanical properties is a result of simultaneous counter effects of thermal degradation and the increase of the properties caused by the lower equilibrium moisture content of the treated samples.

According to Silva *et al.* (2013), the increase in the MOE at lower treatment temperatures can also be caused by an increase in the crystallinity of cellulose and in the relative content of lignin. Beyond the temperature of 220 °C, the MOR of the treated wood was lower than that of the untreated wood. In the case of the MOE, lower values were obtained than the untreated wood at a temperature higher than 240 °C. At these temperatures, the saccharide content significantly decreased, suggesting holocellulose degradation. Sweet and Winandy (1999) found that hemicelluloses, especially galactoglucomannan, play an important role in determining the strength of wood.

Changes of the mechanical properties due to a higher temperature were reported also by Tankut *et al.* (2014), Boonstra *et al.* (2007), Silva *et al.* (2013), and Yildiz *et al.* (2006). However, the extent of these changes depends on the treatment conditions, *e.g.*, temperature, time, atmosphere, heating technique, size, and shape of the sample.

Correlations between Chemical Composition, Color, and Mechanical Properties of Heat-Treated Wood

The MOR and the MOE were positively correlated with the total saccharides, glucose, mannose, and xylose content (Fig. 3). The power law regressions were found to fit these trends. The coefficients of determination ranged from 0.810 to 0.984 (Table 4). It should be noted that despite the high correlation between glucose content and MOR and MOE, more data at approximately 30% of glucose content are required in order to provide more support for this correlation.

The color of wood darkened throughout the heat treatment as a result of the increased lignin and extractives content (Fig. 4). This effect was concluded on the basis of very strong positive correlations between the total color difference and the contents of lignin and extractives, where R = 0.968 and 0.945, respectively. However, the total color difference was negatively correlated with total saccharides, mannose, and xylose content (Fig. 4). These relationships of the color change were modelled as power law regressions, where the coefficients of determination ranged from 0.876 to 0.938 (Table 4). All dependencies were found to be reliable within measured range, and one should be careful in extrapolation of curves shown in Figs. 3 and 4. For example, a change of the color has limitations given by the initial color and the size of CIELab color coordinate system. Extrapolation beyond that space gives unreal results in the case of high extractives content.

González-Pena *et al.* (2009) studied the color changes after heat treatment of various wood species. In beech, total color difference had the largest correlation with hemicelluloses, followed by GluXylan; in pine the largest correlation was with lignin followed by GluMan, and in spruce with GluXylan followed by hemicelluloses. On the other hand, the color changes in heat-treated cellulose and hemicelluloses isolated from spruce wood proved that these polymers changed in color much smaller degree than lignin. These authors observed that ΔE^* was positively related to lignin, and negatively related to the other chemical components.

Table 4. Exponential Regression Analyses between Examined Characteristics of Heat-Treated Fir Wood

Equation	R
MOE = -5416 + 6249*exp (0.011*Sacch)	0.964
MOE = 970,5 + 361.1*exp (0.061*GLC)	0.942
MOE = 7363 - 11055*exp (-0.369*MAN)	0.984
MOE = 7501 - 5877*exp (-0.747*XYL)	0.967
MOR = 0.9787+3.3015*exp (0.0463*Sacch)	0.983
MOR = -4.112 + 6.160*exp (0.053*GLC)	0.810
MOR = 133.5 + -139.8*exp (-0.066*MAN)	0.984
MOR = 108.7 - 102.7*exp (-0.242*XYL)	0.968
ΔE^* = 60.74 - 0.008*exp (0.131*Sacch)	0.876
ΔE^* = 60.00 - 0.472*exp (0.361*MAN)	0.925
ΔE^* = 63.40 - 2.663*exp (0.684*XYL)	0.938
ΔE^* = 1722 - 1763*exp (-0.019*EXT)	0.945
ΔE^* = 58.69 - 92281*exp (-0.246*LIG)	0.968

MOE, modulus of elasticity; MOR, bending strength; ΔE^*, total color difference; Sacch, total saccharides; GLC, glucose; MAN, mannose; XYL, xylose; and EXT, extractives

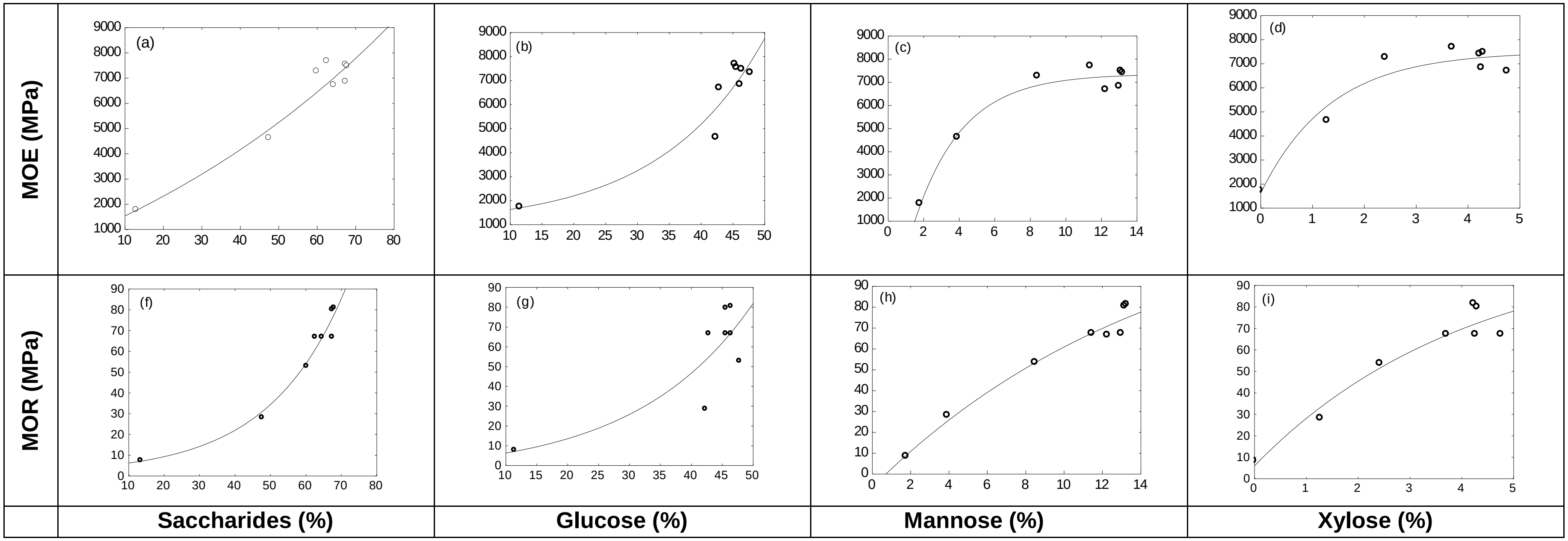

Fig. 3. Relationship between MOE and saccharides (a), glucose (b), mannose (c), and xylose (d). Relationship between bending strength and saccharides (f), glucose (g), mannose (h), and xylose (i).

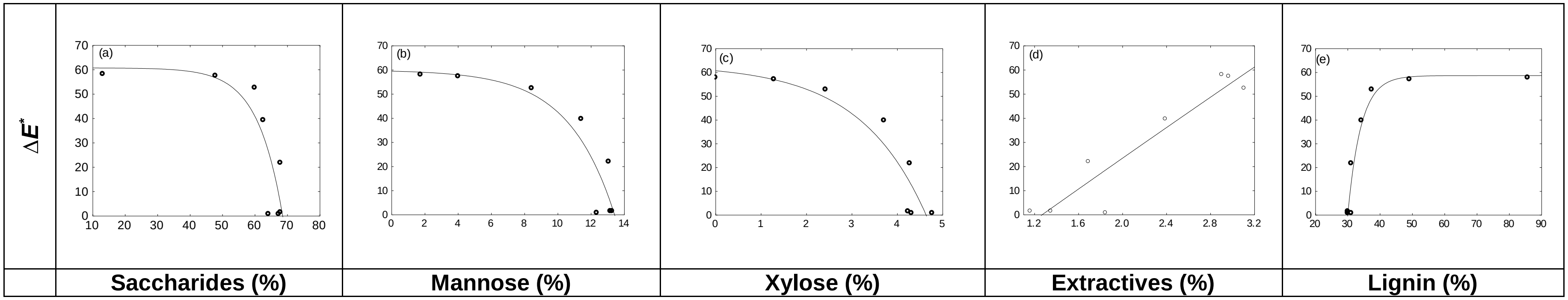

Fig. 4. Relationship between total color difference and saccharides (a), mannose (b), xylose (c), extractives (d), and lignin (e)

Principal Component Analysis (PCA)

PCA analysis was used to evaluate the data, including visualization in multiple dimensions. In the factor score plot (Fig. 5), the PC1-axis explained 78.62% of the total variance and correlated strongly and positively with *T*, EXT, Δ*m*, and Δ*E*. The total content of saccharides (SACCH), the content of the particular saccharides (GLC, XYL, MAN, GAL, ARA), and the mechanical properties (MOE and MOR) were strongly and negatively correlated with that component. Thus, the mechanical properties of heat-treated wood were mainly influenced by the saccharide content. The PC2-axis explained 14.45% of the total variance, and showed high positive correlation with the color component a. Moreover, the axis indicated positive correlations for the values of the color components *a* and *b*, and negative correlation for the color component *L*.

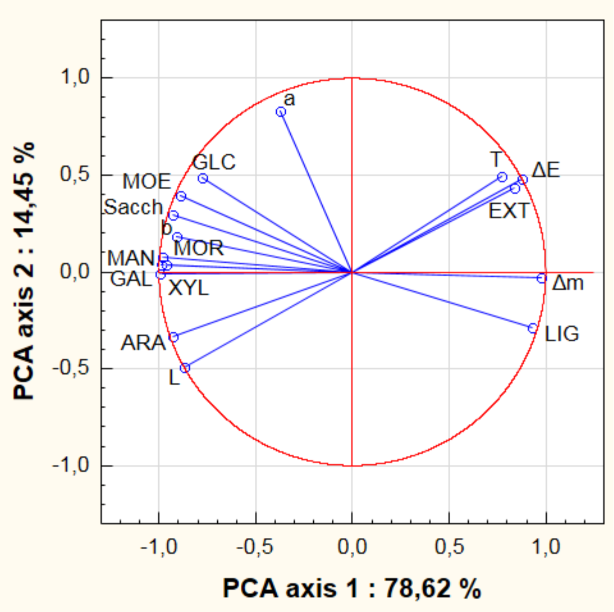

Fig. 5. Projection of the variables on the factor-plane. T, temperature; Δ*E**, total color difference; EXT, extractives; Δ*m*, mass loss; LIG, lignin; *L**, *a**, *b**, color characteristics; ARA, arabinose; XYL, xylose; GLC, glucose; GAL, galactose; MAN, mannose; Sacch, total saccharides; MOR, bending strength; and MOE, modulus of elasticity.

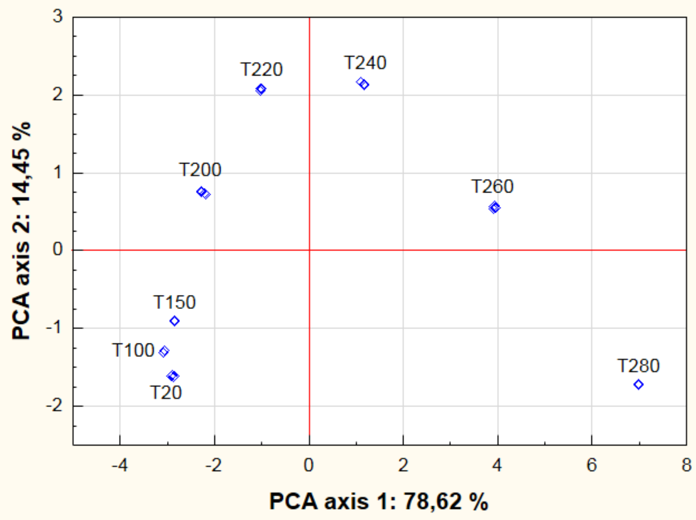

Fig. 6. Projection of the cases on the factor-plane. T20, 20 °C; T100, 100 °C; T150, 150 °C; T200, 200 °C; T220, 220 °C; T240, 240 °C; T260, 260 °C; and T280, 280 °C

In addition, the cases score plot (Fig. 6) showed that the temperatures of 20 °C, 100 °C, and 150 °C formed a compact cluster segregated from the other temperatures. This result indicates that the changes in the examined wood properties due to treatment at temperatures in the range of 20 °C to 150 °C are similarly considerable. The plot also identified the temperature of 280 °C as clearly separated from the others, which points out to a significant effect of this temperature on all properties.

CONCLUSIONS

1. The initial heating of wood causes a significant reduction in its mass, even at 100 °C, which is associated mainly with the loss of volatile extractives and bound water.
2. A slight initial decrease in the lignin content and the content of extractives occurred. In the temperature range over 220 °C, the content of these components increased, due to the release of the degradation products of lignin and saccharides, in the extraction mixture and the condensation reactions, respectively.
3. Hemicelluloses were degraded at 100°C, and its intensity increased with the increased heat treatment temperature. However, the noticeable degradation of cellulose began at temperatures over 260 °C.
4. The bending strength (MOR) and the modulus of elasticity (MOE) slightly increased in the initial stages of thermal treatment due to lack of bound water in wood. However, a more severe treatment resulted in a reduction in their values due to removal of saccharides. The MOR and the MOE were positively correlated with the total saccharides, glucose, mannose, and xylose content.
5. The largest change in the color of treated wood started at temperatures between 200 °C and 220 °C. There were very strong correlations between the total color difference and the contents of saccharides, mannose, xylose, lignin and extractives, respectively.
6. The close relationships that were found between the chemical, color, and mechanical properties of thermally modified fir wood can be used for their mutual predictions.

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