The Effects of CO₂ Laser Irradiation on Color and Major Chemical Component Changes in Hardwoods

Ivan Kubovský,[a] František Kačík,[a,b,]* and Veronika Veľková [a]

The influence of laser radiation was evaluated relative to the color and major chemical component changes of three hardwood species. The surfaces of maple (*Acer pseudoplatanus* L.), beech (*Fagus sylvatica* L.), and lime (*i.e.* linden, *Tilia vulgaris*) wood were exposed to radiation from a CO_2 laser (wavelength = 10.6 µm, output power = 45 W). It was observed that increased doses of irradiation resulted in a decrease in the lightness (L^*), increase in the total color difference, and a drop in the total polysaccharide content. Compared with the non-irradiated specimens, the ΔL^* values at the highest irradiation doses were −56 (maple), −46.8 (beech), and −50.5 (lime). The trends observed in the FTIR spectra also showed there was a relationship between the breaking of C=O and C=C bonds in important functional groups in the lignin, hemicellulose, and carbohydrates. A highly linear correlation (R^2 from 0.902 to 0.987) was observed between the increase in the ΔL^* and decrease in the hemicellulose content, which degrades faster than other basic wood components. Such a phenomenon may have been related to the formation of new chromophore structures, which caused the color changes in the wood.

Keywords: Maple; Beech; Lime wood; Laser irradiation; Color; Saccharides

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INTRODUCTION

Maple, beech, and lime (*i.e.* common linden) wood are deciduous trees that grow in temperate zones and are exploited for various purposes. Maple wood is an important species from an industrial perspective. It can be used for making furniture components, interior cladding, and acoustic cabinets for various musical instruments. Beech is utilized mainly for the production of decorative veneers, bent furniture parts, floor parts, and staircase components. Additionally, a small proportion of beech wood is used for the production of toys, jewelry, and sporting equipment. Because of its low density and exceptional workability, soft lime wood is traditionally used for the production of musical instruments, carvings, and souvenirs. Surface treatment is the last stage in the production of wooden objects. It is commonly performed through the application of coatings, which fulfill protective and aesthetic functions. Furthermore, the color of wood can be modified by exposure to heat, moisture, ultraviolet (UV) radiation, and certain chemicals (Tolvaj *et al.* 2015; Cirule *et al.* 2016; Nemeth *et al.* 2016). Technological procedures utilizing heat have been adopted during the process of heating, drying, and steaming of wood (Frühwald 2007; Tooyserkani *et al.* 2013). Thermal treatment helps to improve mechanical, physical, and chemical wood properties, lowers the absorbability, and increases the resistance to biological pests (Bekhta and Niemz 2003; Mitsui and Tsuchikawa 2005; Esteves and Pereira 2009; Cademartori *et al*. 2013; Kačíková *et al.* 2013; Guo *et al*. 2015; Kubš *et al.* 2017). The aforementioned procedures are often employed to purposefully change the wood color. Heating can be achieved by different means, such as by an electric current, UV radiation, and microwave irradiation (Bourgois and Guyonnet 1988; Kačík *et al.* 2006; Dömény *et al.* 2014). A CO_2 laser, which is intended for cutting, drilling, and engraving, is a rather unconventional method that initiates color modification of wood surfaces. For that reason, scientific sources that discuss its use for color changes are relatively rare (Kačík and Kubovský 2011; Kubovský and Kačík 2014; Kubovský *et al.* 2016). The heat generated during the operation of a CO_2 laser promotes processes that induce chemical changes in the main components of wood (cellulose, hemicellulose, and lignin) and extractive substances. The lignin content decreases as it condenses, and subsequently demethoxylation occurs (Funaoka *et al.* 1990; Esteves and Pereira 2009; Özgenç *et al.* 2017). The degradation of cellulose is accompanied by its depolymerization and crystallization (Sundqvist *et al.* 2006; Poletto *et al.* 2012; Özgenç *et al.* 2017). The decay of polysaccharides to monosaccharides takes place in the hemicellulose complex, and their overall content simultaneously decreases (Nuopponen *et al.* 2005; Kačík *et al.* 2015). The decay of unstable polysaccharide chains, such as hemicellulose, causes the formation of low molecular weight carbohydrate compounds that subsequently undergo dehydration and condensation reactions to form colored products (Beyer *et al.* 2005). Thermal treatment of wood also causes changes to its original color. Color changes in wood are triggered by certain molecular structures contained in lignin that are able to absorb electromagnetic radiation in the visible region of the light spectrum (Ayadi *et al.* 2003; Johansson and Morén 2006).

The aim of this study was to find the relationship between color changes in wood and the degradation of polysaccharides in hardwoods caused by the irradiation of their surfaces with a CO_2 laser.

EXPERIMENTAL

Materials

The experiments examined three wood species: maple (*Acer pseudoplatanus* L.), beech (*Fagus sylvatica* L.), and common linden (*Tilia vulgaris* L.). Wood samples with the dimensions 15 mm × 140 mm × 500 mm (thickness × width × length) were obtained by a tangential cut from a tree trunk. Before the experiment, the surface, which was free of dust and impurities, was sanded with sandpaper (grit no. 150). The samples were dried to a 12% moisture content.

Irradiation of the Samples

Irradiation was performed by means of a LCS 400 laser system (VEB Feinmechanische Werke, Halle, Germany). The wood samples were placed away from the lens focus of the laser head. The laser beam (wavelength = 10.6 μm, Transversal Electromagnetic Mode TEM_{00}) was directed perpendicularly along the surface of the samples and tangential cut plane, and moved across the width of the sample (X-axis) at a selected speed (Fig. 1). The scanning speed range of the laser head was chosen based on the preliminary experiments. After the beam passed across the sample, the laser head shifted along the longer side of the sample (Y-axis), the scanning speed was changed, and the whole process was repeated. Modification of the scanning speed resulted in the formation of isolated areas (stripes) that were irradiated by various amounts of energy (Fig. 2, Tables 1 to 3), which were expressed as a dose of irradiation (H, J/cm^2). The H ranges were chosen to obtain comparable color differences for the three different wood species. The effective power of the laser was 45 W and the width of the stripes was 8 mm. The power was measured on the surface of each specimen with a Laser Power Meter (No 201, Coherent Radiation Laboratories, Palo Alto, USA). The focal distance of the lens from the wood surface was kept constant. After the whole system of stripes was created, the samples were divided into smaller pieces (Fig. 2).

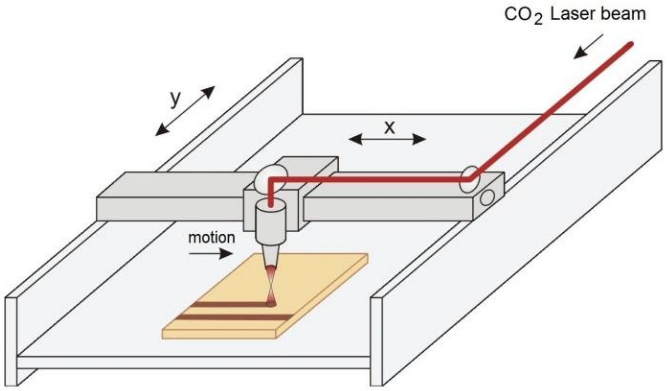

Fig. 1. Scheme for wood surface laser irradiation

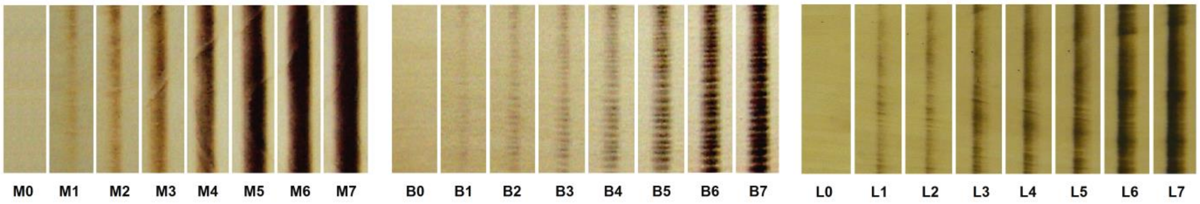

Fig. 2. Picture of the created stripes after irradiation (left to right: maple, beech, and lime wood)

Color Measurement

The color was measured with a CM 2600d spectrophotometer (Konica Minolta, Osaka, Japan). The measurements were made using a Specular Component Included (SCI) lighting system with a D65 standardized light source that simulated daylight over the wavelength range of 360 nm to 740 nm. The optical aperture of the sensor head was 8 mm in diameter. To quantify the color, the colorimetric $L^*a^*b^*$ (CIELAB) system was used. This color space is based on the fact that a color cannot simultaneously be red and green or blue and yellow because these colors are the opposite of each other. The model of this system consists of three mutually perpendicular axes, where the L^* axis determines the lightness, the a^* axis determines the ratio of red to green, and the b^* axis specifies the ratio of yellow to blue. To assess the color difference before and after the laser treatment, the total color difference (ΔE^*) was used, which expressed the distance between two points in the CIELAB system,

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

where ΔL^*, Δa^*, and Δb^* are the differences in the individual axes (differences between the values measured after and before laser treatment were calculated by:

$$\Delta L^* = L^* - L_{\mathrm{REF}}^*,\ \Delta a^* = a^* - a_{\mathrm{REF}}^*,\ \Delta b^* = b^* - b_{\mathrm{REF}}^*) \qquad (2)$$

First, the color was measured at 30 uniformly distributed points on an unirradiated surface. The results were used as reference values that had the subscript “REF”. The color values of each selected irradiated stripe, which are listed in Tables 1, 2, and 3, were then measured (125 measured points on the whole length of a stripe). From the measured values, the arithmetic averages for each stripe were calculated. All of the color values are given in Tables 1, 2, and 3, and they are valid with a 95% confidence interval.

Analysis of the Saccharides

The qualitative and quantitative analyses of the saccharides in the wood samples were performed using high-performance liquid chromatography (HPLC) according to the NREL procedure by Sluiter *et al.* (2008). Briefly, the samples were hydrolyzed in a two-stage process; during the first stage, 72% (w/w) H_2SO_4 at 30 °C was used for 1 h, and for the second stage, the formed oligomers were hydrolyzed to monosaccharides after dilution to 4% (w/w) H_2SO_4 at 121 °C for 1 h. The analyses were performed with an Agilent 1200 HPLC chromatograph (Agilent Technologies, Santa Clara, CA, USA) equipped with an Aminex HPX-87P (300 mm × 7.8 mm) column (Bio-Rad Laboratories, Hercules, CA, USA) at 80 °C and a mobile phase (deionized water) flow rate of 0.6 mL/min. Two samples were hydrolyzed in parallel, and each hydrolysate was analyzed twice.

ATR-FTIR Analysis

FTIR spectra of the wood surface were recorded on the Nicolet iS10 FT-IR spectrometer, equipped with Smart iTR using an attenuated total reflectance (ATR) sampling accessory attached to a diamond crystal (Thermo Fisher Scientific, USA). The spectra were from 4000 to 650 cm^{-1} at a spectral resolution of 4 cm^{-1}, and 64 scans were used. Measurements were performed on four replicates per sample.

RESULTS AND DISCUSSION

Color Changes

The color values of the stripes created by the laser, as well as the corresponding differences, are shown in Tables 1, 2, and 3.

Because of the absorption of the CO_2 laser irradiation by the wood surface, nearly all of its energy was converted into heat (Zhou and Mahdavian 2004). This resulted in the thermal degradation of the surface structures of the wood, especially saccharides, which is similar to other heat treatment methods (Kačík *et al.* 2006). Although various quantities of irradiation energy were applied to the different wood species, all of the examined samples exhibited virtually identical trends. Increasing values of the irradiation dosage caused a continuous decrease in the L^* (Tables 1, 2, and 3). Lower irradiation doses ($H < 26$ J/cm^2 for maple and beech, $H < 11$ J/cm^2 for lime) resulted in a minimal change in the lightness. There was an almost linear trend observed for the ΔL^*, and at the highest doses of irradiation the ΔL^* reached its highest values, which were −56 (maple), −46.8 (beech), and −50.5 (lime). These irradiation values blackened the surface of all of the samples, which might have occurred because of incipient carbonization of the wood. The Δa^* and Δb^* changed to brown shades. The ΔE^* had a consistently increasing trend, and it was influenced mainly by variations in the ΔL^*; thus, in essence, the ΔE^* followed the trend of ΔL^* (in absolute terms).

Table 1. Color Values of the Maple Wood Depending on the Irradiation Dose

STRIPE	**M0**	**M1**	**M2**	**M3**	**M4**	**M5**	**M6**	**M7**
H (J/cm^2)	0	22.0	26.1	28.7	35.8	40.9	47.8	57.3
L^*	85.93	82.27	75.24	66.99	50.10	37.59	34.07	29.93
a^*	2.54	4.35	7.51	9.38	8.59	5.76	4.29	2.72
b^*	18.46	24.16	25.70	24.91	17.78	10.98	7.51	4.58
ΔL^*	0	-3.66	-10.69	-18.94	-35.83	-48.34	-51.86	-56.00
Δa^*	0	1.81	4.97	6.84	6.05	3.22	1.75	0.18
Δb^*	0	5.70	7.24	6.45	-0.68	-7.48	-10.95	-13.88
ΔE^*	0	7.01	13.83	21.14	36.34	49.02	53.03	57.69

Table 2. Color Values of the Beech Wood Depending on the Irradiation Dose

STRIPE	**B0**	**B1**	**B2**	**B3**	**B4**	**B5**	**B6**	**B7**
H (J/cm^2)	0	20.5	26.1	28.7	31.8	35.8	47.8	57.3
L^*	78.55	71.71	62.58	54.03	47.63	40.29	30.72	31.72
a^*	6.25	7.06	7.16	7.14	6.59	5.42	1.74	1.11
b^*	16.70	15.15	15.13	14.40	13.11	10.47	2.62	1.95
ΔL^*	0	-6.84	-15.97	-24.52	-30.92	-38.26	-47.83	-46.83
Δa^*	0	0.81	0.91	0.89	0.34	-0.83	-4.51	-5.14
Δb^*	0	-1.55	-1.57	-2.30	-3.59	-6.23	-14.08	-14.75
ΔE^*	0	7.06	16.07	24.64	31.13	38.77	50.06	49.37

Table 3. Color Values of the Lime Wood Depending on the Irradiation Dose

STRIPE	**L0**	**L1**	**L2**	**L3**	**L4**	**L5**	**L6**	**L7**
H (J/cm^2)	0	9.7	10.8	14.0	16.4	19.8	24.9	28.7
L^*	78.48	68.97	68.83	61.19	49.96	40.85	28.11	27.98
a^*	6.43	9.03	8.93	10.19	10.45	9.39	3.79	2.34
b^*	26.25	26.45	25.75	24.57	21.45	17.47	5.83	3.50
ΔL^*	0	-9.51	-9.65	-17.29	-28.52	-37.63	-50.37	-50.50
Δa^*	0	2.60	2.50	3.76	4.02	2.96	-2.64	-4.09
Δb^*	0	0.20	-0.50	-1.68	-4.80	-8.78	-20.42	-22.75
ΔE^*	0	9.86	9.98	17.78	29.20	38.76	54.41	55.53

Regarding the lightness, the total color difference also reached its highest values at the maximum irradiation doses, and were 57.7 (maple), 49.4 (beech), and 55.5 (lime). Irradiation of the surface caused the formation of stripes with a colored tint that ranged from light brown through brown to dark brown (Fig. 2).

Changes in the Saccharide Complex

Hemicellulose is a wood component that is considered most volatile when exposed to various influences (Windeisen *et al.* 2009; Esteves *et al.* 2013). Its degradation rate is approximately two times faster than that of cellulose (Turner *et al.* 2010; Kačík *et al.* 2015).

The results showed that as the amount of energy from the CO_2 laser on the wood surface increased, the saccharides content in the wood decreased. Despite having the same trends, certain differences between the individual wood species were observed. In the case of the maple wood, the decrease in the saccharides content was negligible if the irradiation dose was lower than 26 J/cm^2 (Table 4).

Table 4. Changes in the Maple Wood Saccharides Content Depending on the Irradiation Dose

STRIPE	*H* (J/cm^2)	ARA (%)	XYL (%)	MAN (%)	GLC-H (%)	GLC-C (%)	GAL (%)	Hemi-cellulose (%)	Saccharides Yield (%)
M0	0	0.67	16.28	1.49	11.88	46.95	0.67	31.00	77.95
M1	22.0	0.51	14.55	1.96	10.62	48.15	0.48	28.12	76.27
M2	26.1	1.02	14.15	2.23	10.33	41.69	0.31	28.02	69.71
M3	28.7	0.93	13.26	1.46	9.68	43.52	0.58	25.91	69.43
M4	35.8	0.86	12.65	0.79	9.23	40.22	0.47	24.02	64.24
M5	40.9	0.24	6.21	0.88	4.53	31.43	0.21	12.08	43.51
M6	47.8	0.34	6.11	0.66	4.46	28.58	0.27	11.84	40.42
M7	57.3	0.38	4.35	0.77	3.17	22.64	0.30	8.97	31.61

Note: ARA – arabinose, XYL – xylose, MAN – mannose, GLC-H – glucose in the hemicellulose, GLC-C – glucose in the cellulose, GAL – galactose, H –dose of irradiation

The beech wood exhibited a more remarkable decrease in the saccharides content if the irradiation dose exceeded 26 J/cm^2 (Table 5). A noticeable drop in the saccharides content in the lime wood occurred at 10 J/cm^2 (Table 6). This effect may have been because of the degradation of hemicellulose, as well as the amorphous region of cellulose. The thermal degradation of saccharides produces various volatile substances, especially methanol, acetic acid, propionic acid, furan, carbonyl compounds, levoglucosan, *etc.* (Košík *et al.* 1968; Fengel and Wegener 1983). Faster losses of hemicellulose compared with cellulose were also observed by Turner *et al.* (2010). Higher levels of irradiation doses caused a gradual decrease in the saccharides content in the wood and a noticeable loss of hemicellulose, which may have been caused by the degradation of a part of the hemicellulose and amorphous regions of cellulose. Higher doses of radiation also led to considerable degradation of the cellulose itself.

Table 5. Changes in the Beech Wood Saccharides Content Depending on the Irradiation Dose

STRIPE	*H* (J/cm^2)	ARA (%)	XYL (%)	MAN (%)	GLC-H (%)	GLC-C (%)	GAL (%)	Hemi-cellulose (%)	Saccharides Yield (%)
B0	0	0.75	25.90	1.24	3.74	42.15	0.47	32.09	74.24
B1	20.5	0.60	22.49	0.97	4.05	45.70	0.53	28.63	74.33
B2	26.1	0.65	18.95	1.13	3.40	38.41	0.61	24.75	63.16
B3	28.7	0.63	15.64	1.93	2.57	28.96	0.36	21.12	50.08
B4	31.8	0.49	13.37	0.42	2.42	27.34	0.29	17.00	44.34
B5	35.8	0.41	11.11	1.01	2.47	27.87	0.22	15.23	43.10
B6	47.8	0.24	7.22	0.59	2.10	23.66	0.13	10.27	33.93
B7	57.3	0.39	4.41	0.77	2.11	23.80	0.30	7.97	31.77

Table 6. Changes in the Lime Wood Saccharides Content Depending on the Irradiation Dose

STRIPE	*H* (J/cm^2)	ARA (%)	XYL (%)	MAN (%)	GLC-H (%)	GLC-C (%)	GAL (%)	Hemi-cellulose (%)	Saccharides Yield (%)
L0	0	7.19	11.86	4.01	4.29	46.75	1.81	29.15	75.90
L1	9.7	8.64	12.56	3.43	3.74	44.52	1.37	29.73	74.25
L2	10.8	4.77	11.24	5.33	3.28	44.30	2.92	27.54	71.84
L3	14.0	5.46	6.53	3.53	2.46	47.99	0.97	18.95	66.94
L4	16.4	4.10	5.59	2.47	3.27	49.11	0.94	16.37	65.48
L5	19.8	3.54	4.94	2.29	2.16	49.20	0.51	13.44	62.64
L6	24.9	3.21	4.23	2.12	2.02	48.57	0.24	11.82	60.39
L7	28.7	2.48	4.29	1.74	1.62	44.47	0.51	10.64	55.11

Changes in the FTIR Spectra

As was expected, higher irradiation doses were found to cause more color changes to the wood surface for all of the specimens. This behavior occurred because several chemical changes take place in the wood when thermal treatment is applied (Chen *et al.* 2014). During the thermal treatment process, some components of wood are degraded or modified through different reactions, such as dehydration, hydrolysis, oxidation, decarboxylation, and trans-glycosylation (Kocaefe *et al.* 2008). Several changes were observed in the FTIR spectra (Figs. 3, 4, and 5), which were assigned to changes in the hemicellulose and lignin structures. Initially, the hemicellulose degraded with the treatment. This was indicated by a decrease in the peak intensities at 1740 cm^{-1}, which was attributed to non-conjugated carbonyl stretching in hemicellulose (Srinivas and Pandey 2012). The mechanism of the color changes was explained as a consequence of heat-induced degradation changes in the polysaccharide structure that led to a reduction in the hemicellulose content. This process is associated with the degradation of carbonyl groups present in hemicellulose, where the cleavage of C=O bonds affects the change in the chromophores content responsible for coloring the wood surface.

It was observed that the band at 1740 cm^{-1}, which was assigned to the C=O stretching vibration in acetyl, carbonyl, and carboxyl groups, decreased with an increase in the laser radiation energy. This indicated that cleavage of acetyl side chains in hemicellulose occurred (Popescu *et al.* 2013). The decreased intensities of the peaks at 1740 cm^{-1} and 1650 cm^{-1} for the heat-treated samples might have resulted from the decreased hemicellulose content in the heat-treated wood samples. Similar observations were also made in heat-treated and control samples by Nuopponen (2005) and Miklečić *et al.* (2011). Özgenç *et al.* (2017) discovered that the thermal treatment of wood induced the degradation of hemicellulose, which was accompanied by a decrease in free hydroxyl groups.

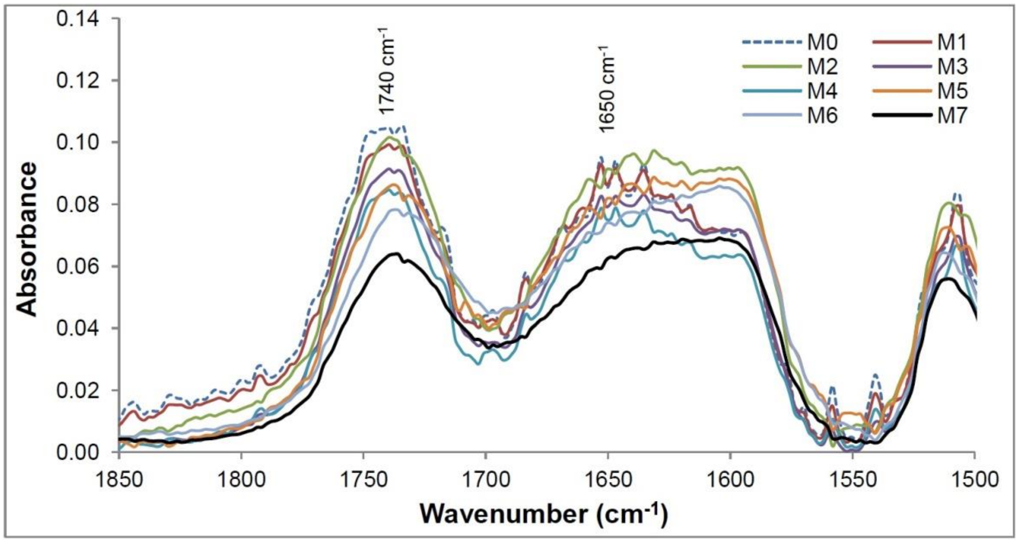

Fig. 3. FTIR spectra of the carbonyl groups in the maple wood

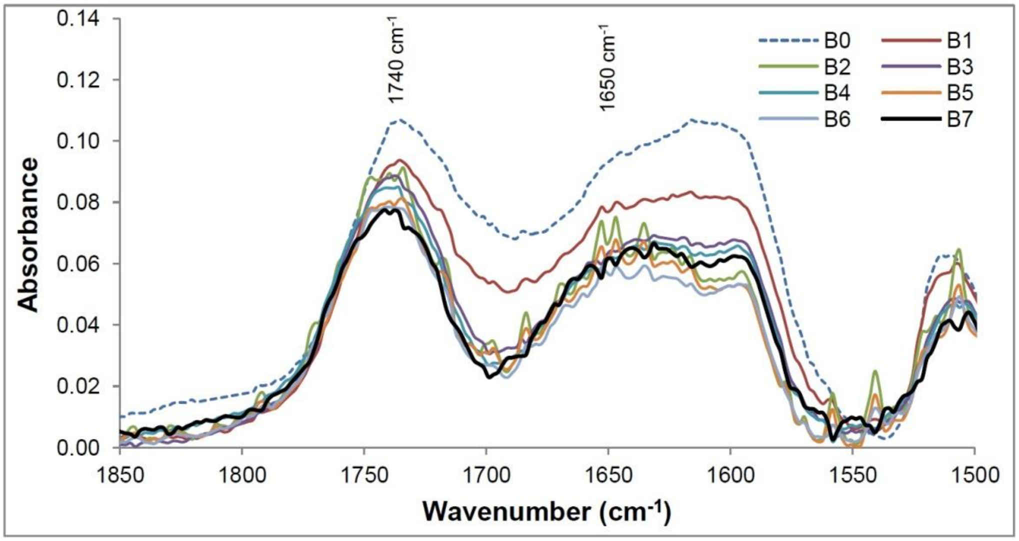

Fig. 4. FTIR spectra of the carbonyl groups in the beech wood

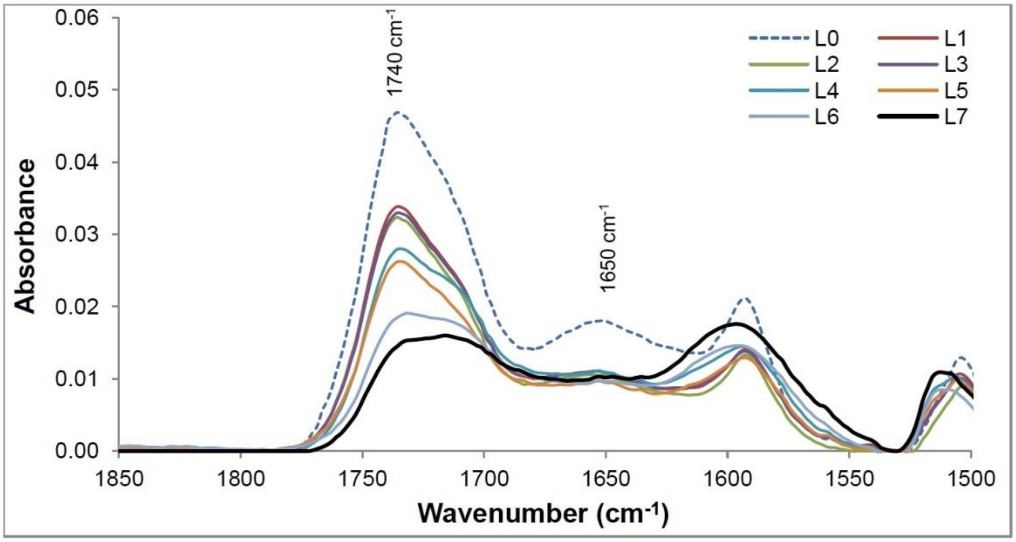

Fig. 5. FTIR spectra of the carbonyl groups in the lime wood

Dependence of the Color on the Saccharide Complex Changes

Thermal treatment of the wood resulted in the degradation of lignin and hemicellulose and a darkening of the wood color, which becomes greater as the temperature increases (Huang *et al.* 2012). The graphs shown in Figs. 6, 7, and 8 show the dependence of the Δ*L** on the hemicellulose degradation (Tables 1 to 6).

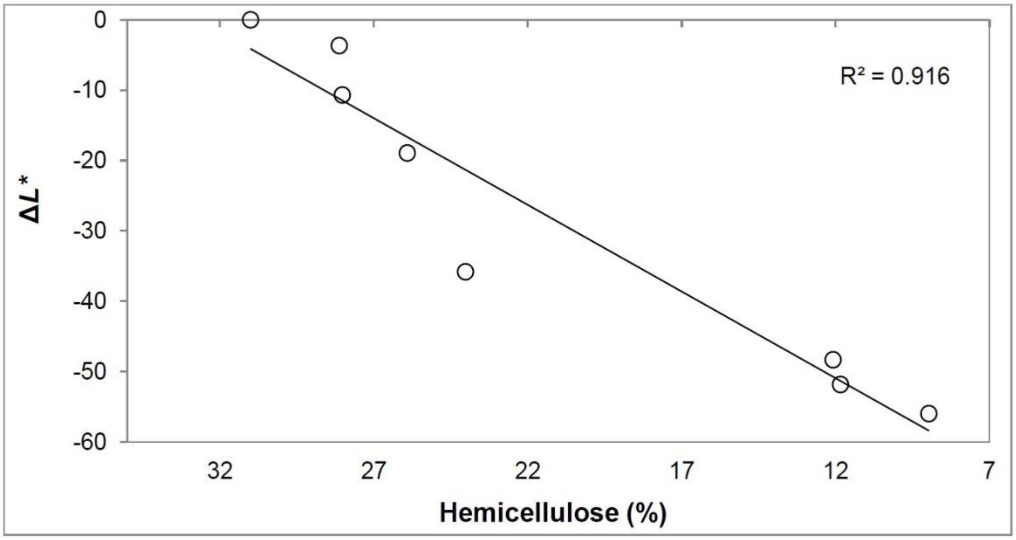

Fig. 6. Dependence of the Δ*L** on the hemicellulose content for the maple wood

The gradual increase in the irradiation dose caused an increase in the color differences for all of the studied species, while the hemicellulose contents decreased. The obtained results confirmed the findings of other researchers (Beyer *et al.* 2005; Kačík *et al.* 2015). A strong linear relationship with coefficients of determination (R^2) of 0.916 (maple wood), 0.987 (beech wood), and 0.902 (lime wood) was observed. Although the surface of each wood species was irradiated with different radiation dose ranges, the colors of all three lines were almost identical. This may have been because of the fact that the irradiation doses were selected on the basis of the preliminary experiments, which obtained similar color ranges for all of the studied wood species.

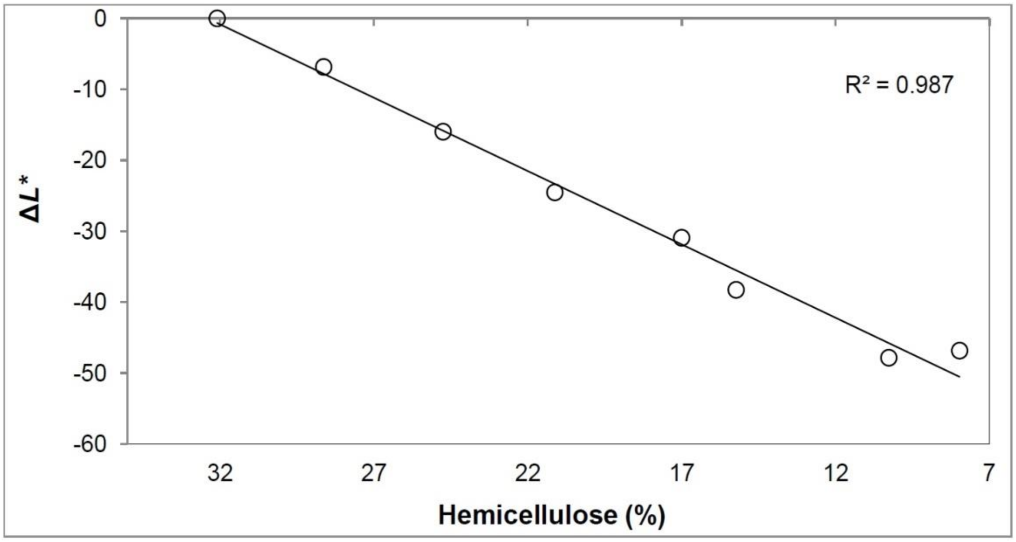

Fig. 7. Dependence of the Δ*L** on the hemicellulose content for the beech wood

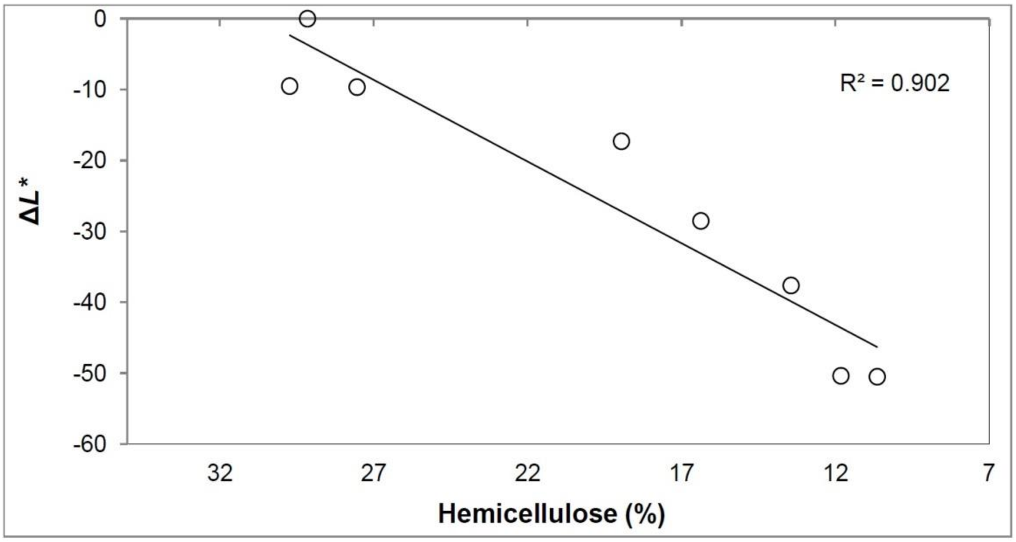

Fig. 8. Dependence of the Δ*L** on the hemicellulose content for the lime wood

Thermal decomposition of the hemicellulose and carbohydrates revealed the cleavage of the original bonds and the formation of new bonds that formed the chromophores. These groups are the ones that remarkably affect the physical properties of wood and are ultimately responsible for its color. The presence of functional groups, such as carbonyls, quinoid structures, lignin structures, and hemicellulose, may play an important role in the formation of colored substances during thermal treatment (Yildiz *et al*. 2013), which was seen in the signals obtained in the band at 1740 cm^{-1} that was associated with carbonyl groups. The relationship between the color changes and changes in the main components of the wood can also be used to predict and determine some of its physical properties. It has been determined that color changes in spruce, pine, and beech wood can be used to predict the properties of heat-treated wood (Johansson and Morén

2006; Brischke *et al.* 2007; González-Peña and Hale 2009). Some authors have focused on studying color changes in relation to the density, modulus of elasticity, and modulus of bending strength of wood (Bekhta and Niemz 2003; Todorović *et al.* 2012; Kačíková *et al.* 2013). Using statistical methods (*e.g.* the partial least squares method), it has been confirmed that the color can be an important indicator of the wood quality.

CONCLUSIONS

1. The L^* values noticeably decreased with an increase in the irradiation dose. This ultimately manifested as an increase in the ΔL^* and ΔE^*. The values representing chromaticity (a^* and b^*) changed color hue, and ranged from light brown through brown to dark brown, except for the blackened stripes that were created by the maximum irradiation doses.
2. The analysis of the saccharides content exhibited a declining trend in relation to the irradiation dose. The hemicellulose degraded faster, although some changes were noticeable in the cellulose too. As was assumed, the most considerable loss of saccharides was observed at the highest doses of irradiation. This was a proportional decrease compared with the content of saccharides in the untreated wood samples.
3. All of the studied wood species exhibited a strong correlation between the ΔL^* and hemicellulose degradation in the irradiated wood. The findings also showed that there was a relationship between the color and breaking of C=O and C=C bonds in important functional groups in the hemicellulose, carbohydrates, and lignin. This resulted in the formation of certain types of chromophoric structures contained in the lignin macromolecule, such as unsaturated structures conjugated with a benzene nucleus (quinones, stilbenes, phenolics, and coniferyl aldehydes). Chromophores may have also formed in the hemicellulose because of the breaking of C=O bonds during the process of thermal decomposition and deacetylation. Such structures induced color changes in the wood, the surface of which was thermally treated by means of laser radiation.
4. The results demonstrated that the energy of a CO_2 laser was capable of changing the surface composition of the wood. There is a range of potential applications for these findings, especially in surface treatments, such as the coloring of wood or replication of surface patterns of exotic wood species.

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