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Chemical changes of beech wood due to CO_2 laser irradiation

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ABSTRACT

The paper deals with color changes and wood component changes caused by laser beam irradiation. A 500 mm × 150 mm × 15 mm beech (*Fagus sylvatica*, L.) board was irradiated by the CO_2 laser beam at different exposures (expressed as the irradiation dose). The color changes were measured by the spectrophotometer and described in the CIELAB color system. Changes in the main wood components were observed by the Fourier transform infrared spectroscopy (FTIR) and carbohydrates were analysed by the gas chromatography of their aldonitrilacetates. With increasing the irradiation dose (from 14 to 57 $J\,cm^{-1}$) was observed a continual growth of the total color difference (ΔE^*). Predominantly hemicelluloses degradation was observed, while at a higher energy dosage lignin condensation occurred.

1. Introduction

Dry wood is primarily composed of cellulose (40–50%), lignin (20–30%), hemicelluloses (20–30%) and extractives (3–10%). A different structure of the individual components of wood affects mechanical, physical, and chemical properties. To modify the wood in order to improve the utility of various methods are used, for example, high temperature, humidity, light, UV radiation or various chemicals. Color change is required in several areas of the use of wood, especially in the furniture industry. One of the factors that influence the color change of wood is electromagnetic radiation absorbed by the wood in a relatively wide range of wavelengths. The wood polymers show a different capacity in absorbing UV light to form radicals. Lignin is extremely susceptible to UV irradiation, which leads to the formation of aromatic free radicals (phenoxyl radicals) which further react with oxygen to produce carbonyl and carboxyl groups, these being related to wood discoloration by the occurrence of unsaturated carbonyl compounds (quinones) [1,2]. Cellulose and hemicelluloses do not absorb a visible light. Native lignins that are isolated with minimum chemical or physical changes are pale yellow. Moreover, many woods absorb light beyond 500 nm due to the presence of phenolic substances such as flavonoids, stilbenes, lignans, tannins, and quinones [3]. Absorption of electromagnetic radiation by wood leads to its photodegradation. The biggest influence on this process is shown by UV radiation, of which 80–95% is able to absorb lignin [4]. Lignin has an absorption maximum at 280 nm which gradually decreases up to 400–600 nm [5]. Degradation causes forming of free radicals which react with oxygen and form a chromophores with a great impact on wood discoloration [6,7]. The UV-irradiation of spruce wood decreased the lignin content on the surface by up to 20% of the original values and photo yellowing correlates very well with the lignin degradation [8].

Several works are devoted to research into the interaction of laser irradiation with the wood. The changes in chemical structure of wood irradiated by UV laser depend mainly on the amount of absorbed energy [9]. The rate of degradation by UV laser is usually very high [10]. Thermal effects like melting and also carbonizing of cellulose were found for IR- and also UV-laser wavelengths [11].

Absorption of electromagnetic radiation tends to increase temperature. This causes degradation of lignin, cellulose, hemicelluloses, and extractives and it also creates chromophore groups which are responsible for coloring the wood. According to Bourgois et al. [12] heat can cause the decrement in lightness and the increment in the color differences resulting from heat treatment at 240–310 °C.

The thermal treatment may be provided by electric, infrared, or microwave heating [13]. An unconventional source for wood

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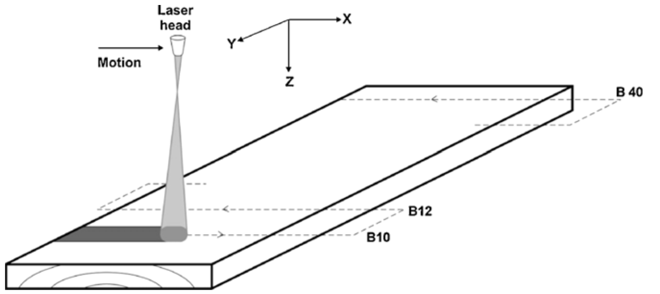

Fig. 1. Wood surface laser irradiation.

surface heating is the CO_2 power laser, although its application area is especially for cutting [14], engraving, and marking [15]. Laser power for surface treatments may induce desirable color changes, although the literature is lacking in data on such utilisation. The effect of the CO_2 laser on wood can be used as a new coloring method.

Use of the CO_2 laser irradiation in wood has several advantages. Unlike conventional methods of dyeing, we can change color (in the typical range of wood colors) only by delivering energy in the form of electromagnetic radiation. In the case of the use of the industrial CO_2 laser, we can easily change the amount of input energy – either by changing the distance from the irradiated surface from the output focus lens or by the change of the feed speed of the laser head. By measuring the intensity of irradiation, we can precisely define quantity of energy supplied. In other technological procedures used to change the color of wood (steaming, drying, cooking), it is usually quite difficult.

Chemical structural changes of wood constituents can be monitored by the Fourier transform infrared spectroscopy (FTIR), a very useful technology for analysing the structural changes caused by different treatments in wood components [16–18].

The present work is focused into the dependence of the main beech wood component modifications on laser radiation energy, expressed as the irradiation dose, its value varying with the scanning speed of the laser head. The aim is also to compare the impact of CO_2 laser with other types of radiation which cause discoloration of wood (UV, VIS, sunlight).

2. Experiments

2.1. Materials

The 500 mm × 150 mm × 15 mm (length × width × thickness) beech wood (*Fagus sylvatica* L.) board was obtained by tangential cuttings from the 80 year-old tree stem. The moisture content of the board was 12%.

2.2. Irradiation

The CO_2 laser was used for the irradiation. The LCS 400 experimental equipment includes the CO_2 laser (wavelength of 10.6 μm, maximum power output of 400 W, power on surface of 45 W), the positioning table system (permitting the laser head to position itself and raster of the laser beam) and the PC control system. The sample was placed away from lens focus of the laser head (Fig. 1). The spread laser beam (7.8 mm in diameter) stroked perpendicularly on the sample surface and the laser head carriage moved along the width (axis x) at a certain rastering speed. After rastering of the whole width of the sample, the laser head was shifted in the length direction (axis y). The speed was increased and the entire process was repeated.

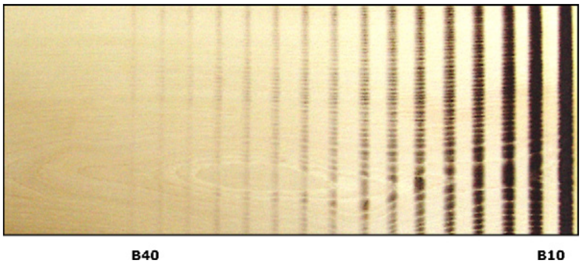

Fig. 2. Beech wood surface after laser irradiation.

A parallel stripped system with 16 irradiated stripes (denoted as B10 and B40, corresponding to the carriage velocity $v = 1–4\ \mathrm{cm\ s^{-1}}$, with the step of $0.2\ \mathrm{cm\ s^{-1}}$) was created on the board surface (Fig. 2). Each stripe being irradiated with a particular value of the scanning speed v (Table 1). In this way, each strip got a various cumulative irradiation dose H (the value varied from 14 to $57\ \mathrm{J\ cm^{-2}}$ – lower velocity, *i.e.*, higher irradiation dose).

2.3. Color measurement

The color of the specimen surface was measured with the portable spectrophotometer CM 2600d (Konica-Minolta). Measurements were made using the SCI (Specular Component Included) lighting system with the D65 light source by simulating the daylight in the wavelength range from 360 to 740 nm. The sensor head was 6 mm in diameter. The color differences ΔL^*, Δa^*, Δb^* and the total color difference ΔE^* were calculated as reported previously [19].

2.4. Analysis

The analytical materials were collected from the surface of each even-numbered irradiated stripe (B10, B12, . . ., B24 and B28, B32, B36) and also from the untreated area (BREF) – altogether 12 samples. The samples of the material surface (1 mg) were finely ground and dispersed in the KBr (200 mg) matrix, followed by compression at 180 MPa to prepare the pellets. The FTIR spectra of the samples were obtained by the KBr technique at $4\ \mathrm{cm^{-1}}$ resolution on the NICOLET AVATAR 330 FTIR spectrometer. The carbohydrate analysis was performed after acid hydrolysis of irradiated beech wood samples. After derivatization to aldonitrilacetates, carbohydrates were analysed by the gas chromatography. Separation was performed on the capillary column DB-5, 30 m × 0.32 mm ID, and the film thickness of 0.25 mm. The injector and detector temperatures were 250 °C, the temperature programme: 175 °C for 4 min, then gradient at $4\ \mathrm{°C\ min^{-1}}$ to 225 °C; helium was used as a carrier gas [20].

3. Results and discussion

With increasing the irradiation dose we observed a continual growth of the total color difference ΔE^* values (Fig. 4). From the irradiation dose of $22\ \mathrm{J\ cm^{-2}}$ to $36\ \mathrm{J\ cm^{-2}}$, the brightness ΔL^* increased almost linearly (Fig. 3). The value of irradiation dose over $40\ \mathrm{J\ cm^{-2}}$ causes a marked darkening. The color difference Δa^* is quasi invariable up to the irradiation dose of $24\ \mathrm{J\ cm^{-2}}$ where it slightly decreased to -5.7. The color difference Δb^* decreased from the value of irradiation dose of $26\ \mathrm{J\ cm^{-2}}$ to -15.5 (Fig. 3).

The FTIR spectra of selected irradiated and untreated sample are shown in Fig. 5. Table 2 lists the relative band absorbance intensities. To normalize the obtained infrared spectra, the $1601\ \mathrm{cm^{-1}}$ band assigned to the aromatic skeletal vibrations in lignin was used. As an internal standard also other wavenumbers are used, for

Table 1
The values of irradiation dose depending on the rastering speed.

Irradiated stripe	B40	B38	B36	B34	B32	B30	B28	B26	B24	B22	B20	B18	B16	B14	B12	B10
v (cm s^{-1})	4.0	3.8	3.6	3.4	3.2	3.0	2.8	2.6	2.4	2.2	2.0	1.8	1.6	1.4	1.2	1.0
H (J cm^{-2})	14.3	15.1	15.9	16.9	17.9	19.1	20.5	22.0	23.9	26.1	28.7	31.8	35.8	40.9	47.8	57.3

Table 2
Relative band absorbance intensities in the FTIR spectra (A_i/A_{1601}).

H (J cm^{-2}) (J cm^{-2}) Analysed stripe	0 BREF	15.9 B36	17.9 B32	20.5 B28	23.9 B24	26.1 B22	28.7 B20	31.8 B18	35.8 B16	40.9 B14	47.8 B12	57.3 B10
A 3430	2.440	2.520	2.360	2.607	2.759	2.346	2.731	2.607	2.645	2.667	2.535	2.537
A 2930	1.080	1.120	1.080	1.000	1.034	1.000	1.000	1.107	1.129	1.056	1.023	0.981
A 1740	1.120	1.120	1.160	1.286	1.207	1.192	1.231	1.143	1.129	1.111	0.907	0.778
A 1637	1.040	1.040	1.040	1.179	1.103	1.038	1.154	1.000	0.968	0.972	0.930	0.926
A 1505	0.880	0.880	0.920	1.214	1.034	1.038	1.115	0.893	0.903	0.944	0.953	0.870
A 1464	1.160	1.120	1.120	1.357	1.241	1.192	1.269	1.179	1.161	1.222	1.209	1.148
A 1380	1.200	1.160	1.160	1.250	1.276	1.192	1.231	1.214	1.226	1.278	1.233	1.167
A 1252	1.320	1.320	1.280	1.393	1.448	1.346	1.385	1.357	1.387	1.417	1.279	1.222
A 1163	1.480	1.440	1.440	1.536	1.586	1.462	1.538	1.500	1.516	1.611	1.558	1.574
A 1117	1.720	1.720	1.720	1.821	1.759	1.769	1.885	1.857	1.871	2.000	2.047	2.093
A 1060	1.920	1.920	1.920	2.143	2.241	2.000	2.192	2.107	2.129	2.306	2.419	2.556
A 1040	1.880	1.880	1.880	2.107	2.207	1.962	2.154	2.071	2.097	2.278	2.372	2.463
A 903	0.440	0.400	0.440	0.429	0.448	0.462	0.462	0.464	0.452	0.472	0.419	0.352

example 2900 cm^{-1} [21], 1900 cm^{-1} [22], 1050 cm^{-1} [23], 1036 cm^{-1} [16], 1373 cm^{-1} [24,25], 1515 cm^{-1} [26,27] or the spectra are evaluated without using an internal standard [40]. At the wavenumber of 1601 cm^{-1}, absorbance shows minimum changes after irradiation, so that it was selected as an internal standard in this work.

The absorbance at 1740 cm^{-1} (carbonyl stretching of the unconjugated β-ketone and conjugated acid/esters) initially increases, then it markedly decrease, which is in accordance with observations by other authors [26–30]. The increasing of this band may be caused by the cleavage of the β-alkyl-aryl ether bonds in lignin, while its decrease is probably caused by the condensation reactions of lignin [26] as well as by hemicelluloses deacetylation [29]. According to Papp et al. [24], two processes are taken into account, having an opposite influence on this area. The opening up of the glucopyranose ring increases the band intensity, whereas the decomposition of the aldehydes and C=O containing (e.g., carboxylic acids and their ethers) components result in a loss of intensity. At low photon energy and intensity the first is the dominant, while at high photon energy and intensity, the second determines the overall effect. Deacetylation of hemicelluloses in thermally modified beech wood, hornbeam, ash wood, and pine wood was confirmed by the decrease in absorbance at 1740 cm^{-1} in the FTIR spectrum and decrease at the peak of 175 ppm in the NMR spectra [30–32].

At 1637 cm^{-1} (C=O stretching in conjugated carbonyls), band intensity first increases, while at higher irradiation doses it decreases – a possible result of the high reactivity of the α-sites of the side chains from lignin, with adjacent benzene

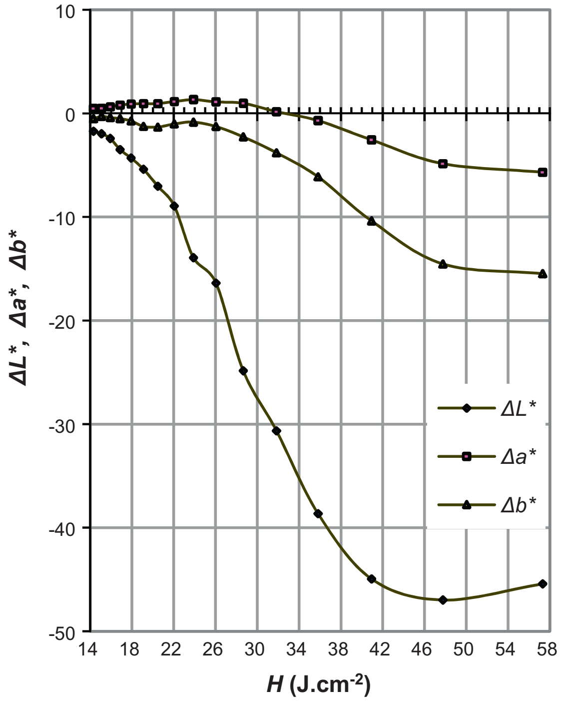

Fig. 3. Resulting values of color differences ΔL^*, Δa^*, Δb^* with irradiation dose.

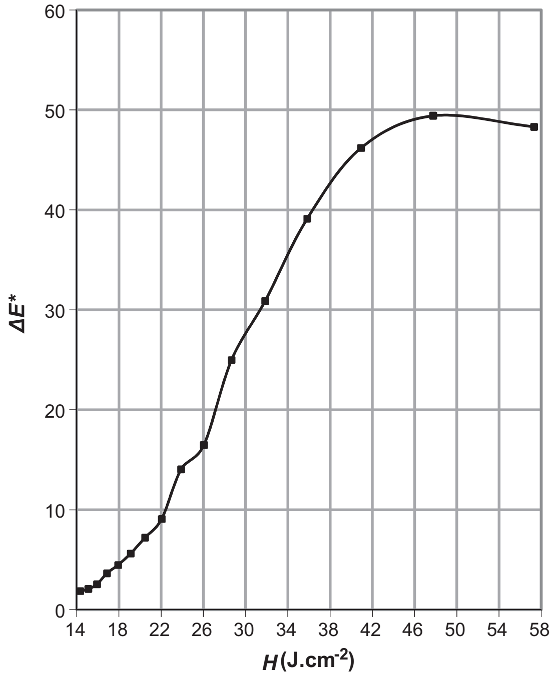

Fig. 4. Resulting values of total color differences ΔE^* with irradiation dose.

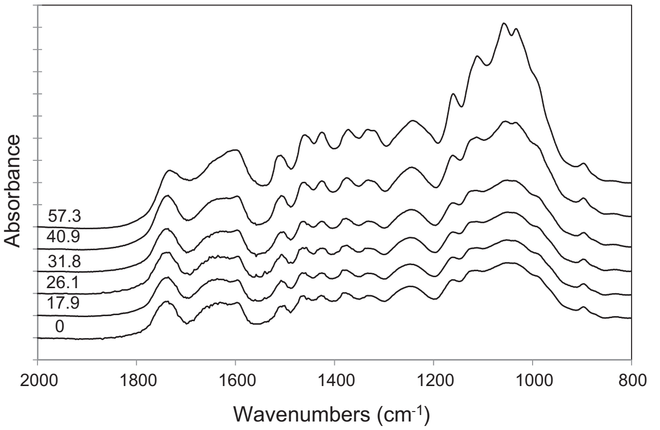

Fig. 5. FTIR spectra for the untreated stripe ($H = 0\,\mathrm{J\,cm^{-2}}$) and for the selected irradiated stripes (numbers at spectral lines represent values of the irradiation dose H from 0 to 57.3 J cm^{-2}).

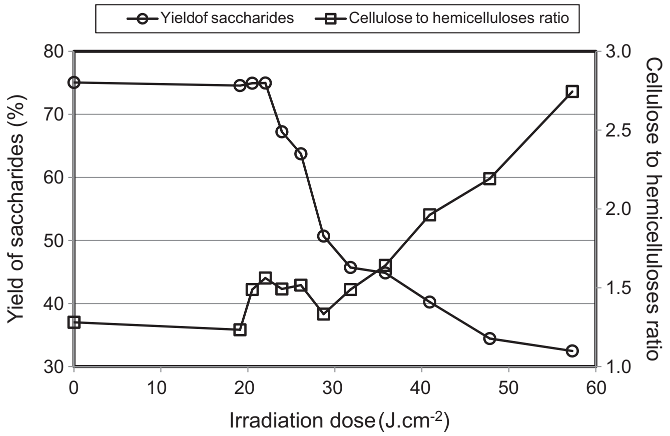

Fig. 6. Carbohydrate yield and the changes of the cellulose–hemicelluloses ratio in beech wood.

nuclei under both acid and alkaline conditions, there are formed diphenylmethane structures [33–35]. This is consistent with the results of our previous research for thermally modified spruce wood [36] and CO_2 laser irradiated maple wood [37], respectively.

The intensity at 1505 cm^{-1} (C=C vibrations of the aromatic lignin nuclei) shows a similar trend as the previous band, the initial increase being followed by a continuous decrease, which corresponds to the observations of [9,16]. According to Colom et al. [16] photodegradation of aspen wood, the guaiacyl nuclei (1510 cm^{-1}) are more sensitive to the artificial ageing process than the syringyl nuclei (1595 cm^{-1}). Higher intensity of this peak and its shift to 1510 cm^{-1} can be caused by the splitting of aliphatic side chains in lignin and/or condensation reactions [23,27,39].

The absorbance at 1464 cm^{-1} (asymmetric C–H deformation in the methyl and methylene groups in lignin and hemicelluloses) increases at lower irradiation doses, after that its value slightly decreases, mainly due to hemicelluloses degradation. The intensity increase of the band at 1460 cm^{-1} supports the assumption of lignin condensation through $-CH_2-$ groups. Weiland and Guyonnet [40] evidenced the decreasing intensity of the band at 1460 cm^{-1} in the thermally modified pine wood. Colom et al. [16] have reported that the band at 1465 cm^{-1} completely disappears after 20 weeks of sunlight irradiation of both aspen (*Populus tremula*) and box wood (*Buxus sempervirens*) indicating the degradation produced in the structure of the lignin polymer [16].

The decrease of absorbance at 1252 cm^{-1} after the application of higher irradiation doses signifies cleavage and alterations of the carboxyl and acetyl groups. Similar results were obtained using different types of thermal treatment of beech wood [23,27].

Modification of the cellulose environment (the 1000–1200 cm^{-1} spectral region) indicates changes in polysaccharides [40]. The increase of intensity in 1040–1060 cm^{-1} is consistent with observations by other authors [9,38]. Decrease in the peak intensity at 900 cm^{-1} (C1 group frequency in cellulose and hemicelluloses) [41] may be due to thermal degradation of β-(1,4)-glycosidic bonds. On the other hand, with UV laser irradiation were observed no changes in this band [9].

The acetyl groups present in wood and released as acetic acid during irradiation, cause depolymerization of the wood polysaccharides (mostly hemicelluloses and the amorphous part of cellulose). The acidic hydrolysis of lignin alters the ether linkages to form carbonium ions. The presence of carbonium ions causes further condensation reactions catalyzed by high temperature and the presence of acetic acid [40].

Similar changes in the thermally modified wood were observed by other authors [17,40,42]. Works dealing with color changes of wood under the action of radiation in the visible and ultraviolet regions show that these types of radiation are mainly caused by changes in lignin [10,43]. UV–VIS radiation causes electron transitions, while the CO_2 laser (far infrared range) gives rise to particular vibrational changes in the molecules leading to thermal action, to which saccharides, especially hemicelluloses and amorphous part of cellulose are less stable.

The analysis of saccharides results in the fact that irradiation of wood surface by the CO_2 laser causes a decrease in saccharides of the beech wood depending on the size of energy operating on wood surface. An irradiation dose less than 22 J cm^{-2} has only a minor effect on the loss of saccharides (Table 3, Fig. 6). Over this value occurs a significant decline in the amount of saccharides in the

Table 3
Changes in the amount of carbohydrates depending on their radiation dose.

H (J cm^{-2})	RHA (%)	ARA (%)	XYL (%)	MAN (%)	GLC (hemi) (%)	GLC (cel) (%)	GAL (%)	Yield of carbohydrates (%)
0	0.82	0.75	25.90	1.24	3.74	42.15	0.47	75.06
19.1	0.84	0.72	26.12	1.43	3.65	41.18	0.63	74.57
20.5	1.52	0.65	22.36	1.10	3.97	44.83	0.50	74.94
22.0	0.64	0.60	22.49	0.97	4.05	45.70	0.53	74.97
23.9	1.45	0.57	19.87	1.04	3.57	40.26	0.47	67.24
26.1	0.58	0.65	18.95	1.13	3.40	38.41	0.61	63.74
28.7	0.60	0.63	15.64	1.93	2.57	28.96	0.36	50.68
31.8	1.37	0.49	13.37	0.42	2.42	27.34	0.29	45.71
35.8	1.76	0.41	11.11	1.01	2.47	27.87	0.22	44.86
40.9	0.24	0.24	10.24	0.26	2.36	26.65	0.24	40.24
47.8	0.52	0.24	7.22	0.59	2.10	23.66	0.13	34.45
57.3	0.70	0.39	4.41	0.77	2.11	23.80	0.30	32.47

Note: RHA, L-rhamnose; ARA, L-arabinose; XYL, D-xylose; GLC (hemi)-D-glucose in hemicellulose; GLC (cel), D-glucose in cellulose; GAL, D-galactose.

irradiated samples. It may be due to degradation of the hemicelluloses and the amorphous cellulose proportion as evidenced by the ratio of cellulose to hemicelluloses (Fig. 6). Hemicelluloses–cellulose ratio increases due to their rapid removal compared with thermally more stable cellulose [29,44]. A deacetylation of hemicelluloses and cleavage of glycosidic bonds were observed by the FTIR also after CO_2 laser irradiation of maple wood [37]. This is in accordance with the analysis of carbohydrates performed in this work.

In the photodegradation of poplar has been found that radiation with wavelengths from 295 to 400 nm causes the biggest changes in lignin, where guaiacyl structural units are more susceptible to the degradation process than syringyl units [16]. Changes were also observed in the amorphous and crystalline parts of cellulose, which corresponds to our results.

The analysis of changes in beech wood after CO_2 laser irradiation (color change, changes in the FTIR spectra and changes in the composition of carbohydrates) results in the fact that irradiation at lower doses (up to about 22 $\mathrm{J\,cm^{-2}}$) causes changes in the total color difference (ΔE^*) but they are mainly due to changes in brightness (ΔL^*). In addition to changes in color differences Δa^* and Δb^*, higher irradiation dose also changes in the composition of carbohydrates, where mainly occurs the degradation of hemicelluloses. Changes in the FTIR spectra are characterized by a decline in the 1637 $\mathrm{cm^{-1}}$ (C=O valence vibrations in conjugated carbonyl) and 1740 $\mathrm{cm^{-1}}$ (C=O vibration of the acetyl and carboxyl groups). In addition to partial changes in lignin, these relate mainly to changes in hemicelluloses. Change in the color in a small irradiation dose may be caused by changes in the extractive substances.

4. Conclusions

Investigating the changes induced in the main components (cellulose, hemicelluloses, lignin) of beech wood by CO_2 laser irradiation of its surface brings the present work to the following conclusions:

- the polysaccharide structures were considerably modified depending on the increased irradiation dose,
- hemicelluloses degradation, together with decarboxylation (mainly deacetylation) reactions were observed,
- bond cleavage occurs in lignin especially in the β-aryl–alkyl ether bonds,
- the degradation products of the woody polymers react together inducing subsequent condensation reactions,
- the FTIR data indicate that the value of exposure has a considerable influence on the changes produced in the main wood components.

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