

FT-IR STUDY OF MAPLE WOOD CHANGES DUE TO CO₂ LASER IRRADIATION

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The paper reports on the wood component changes caused by laser beam irradiation. A 500 x 150 x 15 mm maple (*Acer pseudoplatanus* L.) board was irradiated by a CO₂ laser beam, at different values of exposure energy (expressed as irradiation dose). Changes in the absorption intensities due to degradation and condensation reactions of the main wood components were observed by infrared spectroscopy (FT-IR). When increasing the irradiation dose (from 18 to 57 Jcm⁻¹), the degradation of hemicelluloses was predominantly observed, while lignin was degraded at a lower irradiation dose and, at a higher energy dosage, lignin condensation occurred.

Keywords: maple, lignin, cellulose, hemicelluloses, laser, irradiation dose, FT-IR spectroscopy

INTRODUCTION

Wood is a complex of natural polymer substances: cellulose (40-45%), hemicelluloses (20-30%) and lignin (20-30%). Cellulose represents the crystalline part of wood, while the structures of hemicelluloses and lignin are amorphous. The main mechanical function of hemicelluloses and lignin is to join the cellulose fibrils. Wood is a material with wide practical utilization, applicable in its natural state, although its properties may be improved by various technological processes. Heating, electromagnetic irradiation, steaming and drying are the external factors that can induce changes in wood's main components (cellulose, hemicelluloses and lignin), as well as in the extractives, their content and relationship affecting most of its properties (*e.g.*, colour).¹ The thermal treatment is one of the currently applied methods for improving wood utilisation.^{2,3} The chemical modifica-

tions in wood structure, occurring at high temperature, are accompanied by several favourable changes in the physical structure, such as reduced shrinkage and swelling, low equilibrium moisture content, better decay resistance, enhanced weather resistance and decorative, dark colour. The thermally modified wood is used in outdoor furniture, claddings on wooden buildings, floor materials, musical instruments and a diversity of other outdoor and indoor applications.^{4,5}

The thermal treatment may be provided by electric, infrared or microwave heating.^{6,7} An unconventional source for wood surface heating is the CO₂ power laser, although its application area mostly includes cutting,⁸ engraving and marking.⁹ Laser power for surface treatments may induce desirable colour changes, although data on such utilisations lack in the specialty literature. The chemical structural changes of wood

constituents can be monitored by Fourier transform infrared spectroscopy (FT-IR), a very useful technique for analysing the structural changes induced by different treatments in wood components.¹⁰⁻¹²

The present work studies the dependence of the main wood component modifications on laser radiation energy, expressed as irradiation dose, its value varying with the scanning speed of the laser head.

EXPERIMENTAL

Materials

A 500 x 150 x 15 mm (length x width x thickness) maple wood (*Acer pseudoplatanus* L.) board was obtained by tangential cuttings from an 80 year-old tree stem, its surface being ground by coated abrasive paper (roughness no. 150), prior to the experiment. The moisture content of the board = 12%.

Irradiation

A CO₂ laser was used for the irradiation treatment of the maple board. The LCS 400 experimental equipment includes a CO₂ laser (wavelength = 10.6 μm, maximum power output = 400 W, power on the surface = 45 W), a positioning table system (permitting laser head positioning and raster scan of the laser beam) and a PC control system. The sample was placed

away from the 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 scanning speed. After scanning, the whole width of the sample was laser head-shifted in length direction (axis y). The speed was increased and the entire process was repeated.

A parallel stripped system, with 23 irradiated stripes (noted as JV10 and JV32), was created on the board surface (Fig. 2), each stripe being irradiated with a particular value of the scanning speed. In this way, each strip got a various cumulative irradiation dosage H (higher velocity, *i.e.* lower irradiation dose). The H value varied from 18 to 57 Jcm⁻² (corresponding to a carriage velocity of 1.0-3.2 cms⁻¹).

Analysis

The analytical materials were collected from the surface of each even-numbered irradiated stripe (JV10, JV12, ..., JV30), as well as from the untreated area (JVREF) – altogether 12 irradiated samples being collected. The samples of the surface material (1 mg) were finely ground and dispersed in a KBr (200 mg) matrix, followed by compression at 180 MPa, to prepare the pellets. The FT-IR spectra of the samples were obtained by the KBr technique at a 4 cm⁻¹ resolution, on a NICOLET AVATAR 330 FT-IR spectrometer.

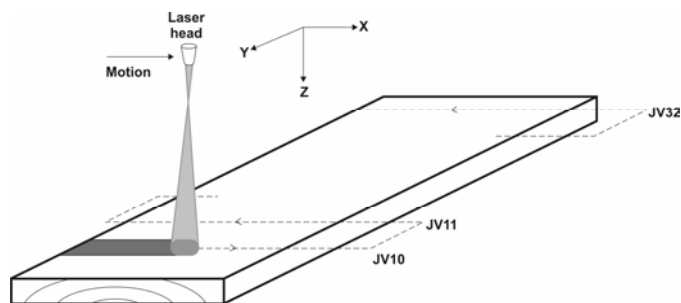


Figure 1: Wood surface laser irradiation

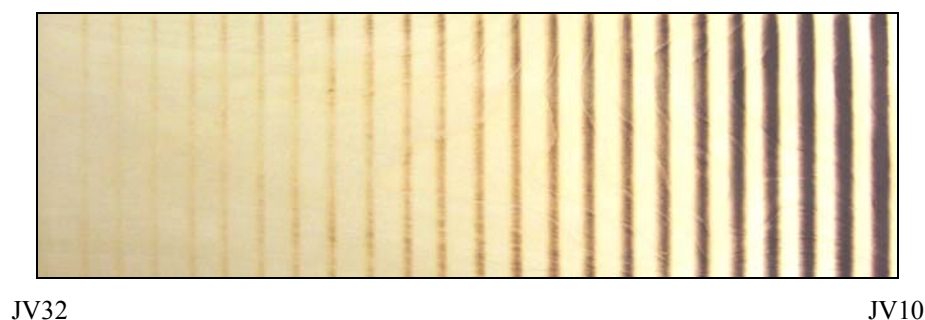


Figure 2: Maple wood surface after laser irradiation

RESULTS AND DISCUSSION

The FT-IR spectra of each irradiated and untreated reference stripe are shown in Figures 3 and 4, while Table 1 lists the relative band absorbance intensities. To normalize the obtained infrared spectra, the 1601 cm^{-1} band, assigned to the aromatic skeletal vibrations in lignin, was used. At wavenumber 1601 cm^{-1} , absorbance exhibits minimum changes after irradiation, so that it was selected as an internal standard. Table 2

shows the difference in the absorbance intensities, calculated by the formula:

$$A_d = \frac{A_i - A_{REF}}{A_{REF}} \cdot 100$$

where A_d is the difference in absorbance intensities, A_i is the relative absorbance of the irradiated sample and A_{REF} is the absorbance of the reference (untreated) stripe. The positive values refer to the increase, the negative ones – to the decrease in absorbance.

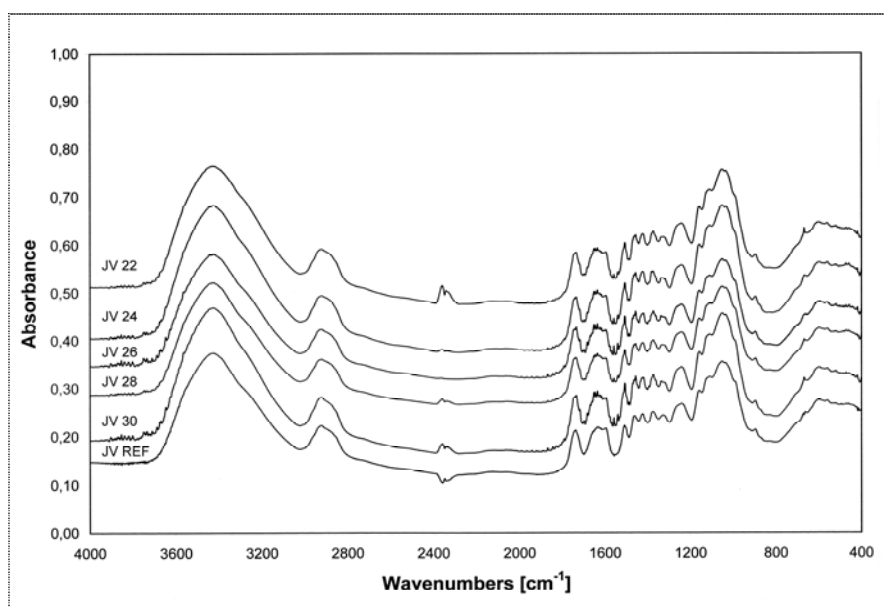


Figure 3: FT-IR spectra for the JV22-JV30 irradiated stripes and for the JVREF untreated stripe

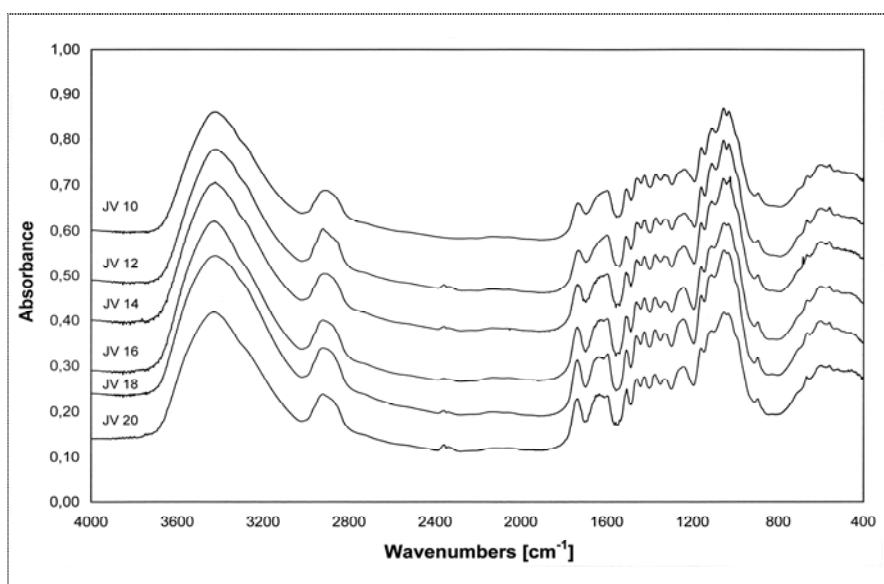


Figure 4: FT-IR spectra for the JV10-JV20 irradiated stripes

The infrared spectra evidence an increased absorbance at 3427-3438 cm^{-1} (valence vibration of the -OH groups), resulting from the cleavage of the ether bonds in lignin. At higher irradiation doses, these absorbance values decrease, which is probably due to the condensation reactions.

The absorbance at 1740 cm^{-1} (carbonyl stretching of the unconjugated β -ketone and conjugated acid/esters) initially increases, after which it markedly decreases, which agrees with other authors' observations.¹³⁻¹⁵ The increase of this band may be caused by the cleavage of the β -alkyl-aryl ether bonds

in lignin, while its decrease is probably due to the condensation reactions of lignin, as well as to the deacetylation of hemicelluloses.

At 1637 cm^{-1} (C=O stretching in conjugated carbonyls), band intensity increases at first, while, at higher irradiation doses, it decreases and finally disappears completely, which may be caused by the high reactivity of the α -sites of the side chains in lignin, with adjacent benzene nuclei, under both acid and alkaline conditions, to form diphenylmethane structures.¹⁶⁻¹⁸

Table 1
Relative band absorbance intensities in FT-IR spectra (A_i/A_{1601})

Wavenumber (cm^{-1})	Irradiated stripe [Irradiation dose in Jcm^{-2}]											
	JVREF [0]	JV30 [19.1]	JV28 [20.5]	JV26 [22.0]	JV24 [23.9]	JV22 [26.1]	JV20 [28.7]	JV18 [31.8]	JV16 [35.8]	JV14 [40.9]	JV12 [47.8]	JV10 [57.3]
A_{3430}	3.000	3.091	3.185	3.034	3.121	3.065	2.943	2.850	3.025	2.974	2.816	2.969
A_{1740}	1.036	1.152	1.111	1.172	1.091	1.097	1.029	1.000	0.950	0.895	0.789	0.813
A_{1637}	1.036	1.182	1.148	1.172	1.152	1.129	1.086	0.975	0.975	0.947	0.895	0.338
A_{1508}	1.000	1.242	1.148	1.310	1.212	1.161	1.086	1.025	0.975	0.974	0.921	0.969
A_{1464}	1.214	1.394	1.296	1.345	1.424	1.290	1.286	1.250	1.225	1.184	1.184	1.188
A_{1380}	1.250	1.333	1.333	1.345	1.394	1.323	1.314	1.325	1.250	1.237	1.211	1.219
A_{1252}	1.357	1.424	1.407	1.414	1.424	1.419	1.371	1.425	1.350	1.289	1.211	1.250
A_{1163}	1.643	1.697	1.741	1.690	1.818	1.742	1.743	1.825	1.700	1.711	1.684	1.719
A_{1060}	2.321	2.515	2.519	2.414	2.606	2.548	2.457	2.675	2.500	2.553	2.579	2.594
A_{903}	0.429	0.424	0.444	0.448	0.424	0.419	0.400	0.425	0.425	0.421	0.421	0.406

Table 2
Different absorbance intensities of the bands in FT-IR spectra (%)

Wavenumber (cm^{-1})	Irradiated stripe [Irradiation dose in Jcm^{-2}]										
	JV30 [19.1]	JV28 [20.5]	JV26 [22.0]	JV24 [23.9]	JV22 [26.1]	JV20 [28.7]	JV18 [31.8]	JV16 [35.8]	JV14 [40.9]	JV12 [47.8]	JV10 [57.3]
$A_d 3430$	3.03	6.17	1.15	4.04	2.15	-1.90	-5.00	0.83	-0.88	-6.14	-1.04
$A_d 1740$	11.18	7.28	13.20	5.33	5.90	-0.69	-3.45	-8.28	-13.61	-23.77	-21.55
$A_d 1637$	14.11	10.86	13.20	11.18	9.01	4.83	-5.86	-5.86	-8.53	-13.61	-67.37
$A_d 1508$	24.24	14.81	31.03	21.21	16.13	8.57	2.50	-2.50	-2.63	-7.89	-3.13

A _d 1464	14.80	6.75	10.75	17.29	6.26	5.88	2.94	0.88	-2.48	-2.48	-2.21
A _d 1380	6.67	6.67	7.59	11.52	5.81	5.14	6.00	0.00	-1.05	-3.16	-2.50
A _d 1252	4.94	3.70	4.17	4.94	4.58	1.05	5.00	-0.53	-4.99	-10.80	-7.89
A _d 1163	3.29	5.96	2.85	10.67	6.03	6.09	11.09	3.48	4.12	2.52	4.62
A _d 1060	8.34	8.49	3.98	12.26	9.78	5.85	15.23	7.69	9.96	11.09	11.73
A _d 903	-1.01	3.70	4.60	-1.01	-2.15	-6.67	-0.83	-0.83	-1.75	-1.75	-5.21

The intensity at 1508 cm⁻¹ (C=C vibrations of the aromatic lignin nuclei) shows a trend similar to the previous band, the initial increase being followed by a continuous decrease, which agrees with the observations of Colom *et al.*¹⁰ and Papp *et al.*¹⁹

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 which its value permanently decreases, mainly due to the degradation of hemicelluloses. Weiland and Gyuonet²⁰ also evidenced the decreasing intensity of the band at 1460 cm⁻¹ in the thermally modified pine wood. Colom *et al.*¹⁰ 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.¹⁰

Initially, the intensity at 1380 cm⁻¹ (phenolic hydroxyl groups)²¹ slightly increases, which indicates cleavage of the aryl-alkyl ether lignin bonds. The decrease observed for this band after the application of higher irradiation doses is caused by lignin condensation reactions. The decrease in absorbance at 1252 cm⁻¹ means cleavage and alterations of the carbonyl and acetyl groups.¹⁴

The modification of the cellulose environment (the 1000-1200 cm⁻¹ spectral region)²⁰ indicates changes in the cellulose structure. The decrease at 900 cm⁻¹ is caused by the cleavage of the β-(1,4)-glycosidic bonds in polysaccharides. The acetyl groups present in wood and released as acetic acid during irradiation, induce the 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 induces further condensation reactions, catalyzed by high temperature and the presence of the acetic acid.²⁰

Similar changes in the thermally modified wood were observed by other authors as well.²⁰⁻²²

CONCLUSIONS

The present work, investigating the changes induced in the main maple wood components (cellulose, hemicelluloses, lignin) by CO₂ laser irradiation of its surface, permits the following conclusions:

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

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