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Wood degradation caused by KrF UV-laser

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Abstract

The effect of KrF laser-produced UV-light was studied on eight wood species grown in Hungary using spectroscopic methods. The spectra of the earlywood and latewood of both the heartwood and the sapwood was investigated. The UV-laser treatment caused changes in the spectra of all samples, and the results showed that not only those changes appear in difference spectra which have been formerly observed using traditional UV sources (increase in the range of 1710 - 1760 cm^{-1} and a decrease around 1510 and 1273 cm^{-1}), but additional absorption dips appeared in our experiments around 1539, 1465, 1399 and 1147 cm^{-1}. In the case of the softwoods and maples the decrease in intensity of the former three is so intense that it overlaps the 1510 cm^{-1} band in some of the samples. The changes in spectrum are mostly attributable to the decomposition of certain chemical groups in lignin. The appearance of new bands in the difference spectra means that UV-laser light splits bonds that are not damaged by traditional UV sources.

Introduction

It has been known for centuries that wooden surfaces exposed to the elements change in color, become rough and splintery decreasing the quality and decorative value of wood. Fungi and insects, temperature changes, precipitation and sunshine all influence the degradation process. One of the most important meteorological factors is the sun's UV radiation. It is impossible to study the effects of UV radiation on wood in nature, as the degradation process is slow and the effects of UV-light cannot be separated from other factors. We must use artificial UV sources for this purpose. Xenon and mercury-vapor lamps have been commonly used in previous experiments as described elsewhere (Kalinins 1966, Chang et al.1982, , Dirckx et al. 1987a, 1987b, Anderson et al.1991, Hon 1988, 1994, Tolvaj and Faix 1995). Due to the intense thermal radiation of these sources (the surface temperature of the sample can reach 100 ^{o}C during irradiation) a rather significant thermal effect is superimposed on that of UV-light. We have used KrF laser for the UV irradiation of wood as it was written in a short communication (Barta et al. 1998). Laser has several advantages to traditional UV sources. Its usage can significantly reduce the time needed to complete the experiments. It used to take up to 200 hours of irradiation with traditional sources to cause detectable changes in the spectra (Dirckx et al. 1987a, 1987b, Tolvaj and Faix 1995). Also, with the use of laser it is possible to study degradation caused by UV only, without the disturbing thermal effects. The energy and intensity reaching the surface can be measured exactly and thus we are able to examine the changes in absorption as a function of energy or intensity rather than time. The chemical changes brought upon by UV-laser irradiation were studied using Diffusely Reflected Infrared Fourier Transformed (DRIFT) spectrometry. DRIFT spectroscopy is a widely accepted method of analyzing the spectrum of wood, wood component and pulp and to follow the changes occurring on the surface of the wood (Hon and Chang 1984, Hon and Feist 1986, Schultz and Glasser 1986, Faix and Németh 1988, Michell 1988, Owen and Thomas 1989,

Zavarin et al. 1990, Backa and Brolin 1991, Németh and Faix 1994, Pandey and Theagarajan 1997, Kosikova and Tolvaj 1998). We analyzed the changes based on the difference spectra that were obtained by subtracting the spectra of untreated samples form the spectra of irradiated ones. The purpose of the experiments presented in this article is to reveal the differences between the effects of traditional UV and laser UV sources by demonstrating the changes in the DRIFT spectrum of wood samples treated with UV-laser. We concentrated on the range of 850 - 2000 cm^{-1}, as the most pronounced changes in absorption occur in this region.

Materials and Methods

Samples were prepared from eight wood species grown in Hungary. Softwoods: Scotch pine (Pinus sylvestris.), spruce (Picea abies), larch (Larix decidua) and Douglas-fir (Pseudotsuga mensiezii). Hardwoods: beech (Fagus sylvatica), locust (Robinia pseudoacacia), silver maple (Acer saccharinum) and high ash (Fraxinus excelsior). Four samples each were chosen in case of the Douglas-fir, the spruce and the larch to represent the earlywood and latewood of both the sapwood and the heartwood. Two samples each were chosen for the other species from the earlywood and latewood of the heartwood. The samples were 2 mm thick wooden disks 12 mm in diameter. They were cut from the tangential section of the wood in a way so as for the surface to only contain one issue. The surfaces were polished smooth using fine sandpaper. No kind of thermal or chemical treatment was used before the investigation.

Irradiation by UV-laser was performed in the High Intensity Lab of the Department of Experimental Physics of the József Attila University, using a Krypton-Fluoride (KrF)-excimer laser developed here. The samples were irradiated with 5000 pulses selected from the pulse train of the laser with a wavelength of 248.5 nm and a repetition rate of 10 Hz. The pulses had a duration of 15 ns. The beam was aimed perpendicular to the surface of the samples, and was made divergent using lenses so that it irradiated the surface homogeneously. The energy of the impulse was set to 20 mJ using a filter so as to have one sample receive 100±10 J energy within 10 minutes.

Spectrum analysis: The Diffusely Reflected Infrared (DRIFT) spectra were recorded before and after irradiation using a Bio-Rad Digilab type FTS-65A/896 FTIR spectrometer located in the Vibration Spectroscopic Lab of the Division of Chemistry of the József Attila University in Szeged. The samples were arranged in the spectrometer to have the longitudinal fibers of the wood be parallel to the illuminating infrared beam. 256 interferrograms were recorded with a resolution of 4 cm^{-1} in the range of 400 - 4000 cm^{-1}. The intensity of the spectrum was given in Kubelka-Munk units. The baseline correction was done with the help of three points (3800, 1900 and 850 cm^{-1}). It is common practice to normalize the treated and untreated samples before calculating the difference spectrum. Instead of normalization, we used the fact that the absorption of CH-groups at 1373 cm^{-1} does not change (Tolvaj and Faix 1995), therefore the intensity must be the same before and after irradiation. The spectrum of treated samples was multiplied by the quotient of the blank and irradiated spectrum intensity at 1373 cm^{-1} before subtracting the spectrum of the untreated samples from the treated samples. This method has the advantage of the difference spectrum also being in Kubelka-Munk units.

Results

The treatment using a 248.5 cm^{-1} wavelength laser caused changes in all of the spectra of all samples. Our analysis was done in the wavelength range of 850-2000 cm^{-1}, as this is the range where the most characteristic changes occur (the "fingerprint" range of wood.) Usually, there are larger changes in the spectrum of the two issues of the sapwood than in the spectrum of the two issues of the heartwood. In the cases of both the sapwood and the heartwood the early

wood showed the biggest changes. Among the hardwoods the two issues of the heartwood underwent similar changes in the case of the beech, the high ash and the black locust, as some preliminary results were described elsewhere (Barta et al. 1999). In case of the other species the difference was significant. To show the characteristic features of wood spectra, the entire spectrum of earlywood of heartwood of Scotch pine is presented in the Figure 1 before and after UV laser irradiation. Around 17 major bands are roughly discernible in DRIFT spectra without using mathematical resolution enhancement. The position of the IR bands are shown by arrows. Figure 2 and 3 demonstrate how the spectral range between 2000 and 850 cm^{-1} is influenced by 248.5 nm wavelength laser irradiation for softwoods and hardwoods, respectively. The changes in the spectra of different samples are similar; they only differ in their inner ratios. Absorption increased significantly in the range of 1700 - 1800 cm^{-1}. This band consists of several overlapping bands in the difference spectrum, the two most outstanding ones being around 1722 and 1755 cm^{-1}. The increase in intensity of the 1755 band dominates the latewood. In case of the earlywood the increase in intensity of the 1722 band is dominant (Figure 2). Both bands show an increase in the number of C=O groups. The C=O group has an absorption maximum around 1650 cm^{-1}, but we found a slight decrease around here in all samples. An explanation for this is that during treatment water escapes the wood, which also has an absorption maximum around 1650 cm^{-1}. The latter of the two processes is more dominant, explaining the decrease in the spectrum and concealing the increase in intensity caused by the increase in the number of C=O groups. In case of all of the issues of the softwoods, absorption increased in the 1560 - 1620 cm^{-1} range, which has a maximum at 1598 cm^{-1} in the difference spectra. In case of the hard woods a smaller increase was observed at 1610 cm^{-1} and 1575 cm^{-1}, and a smaller decrease at 1596 cm^{-1}.

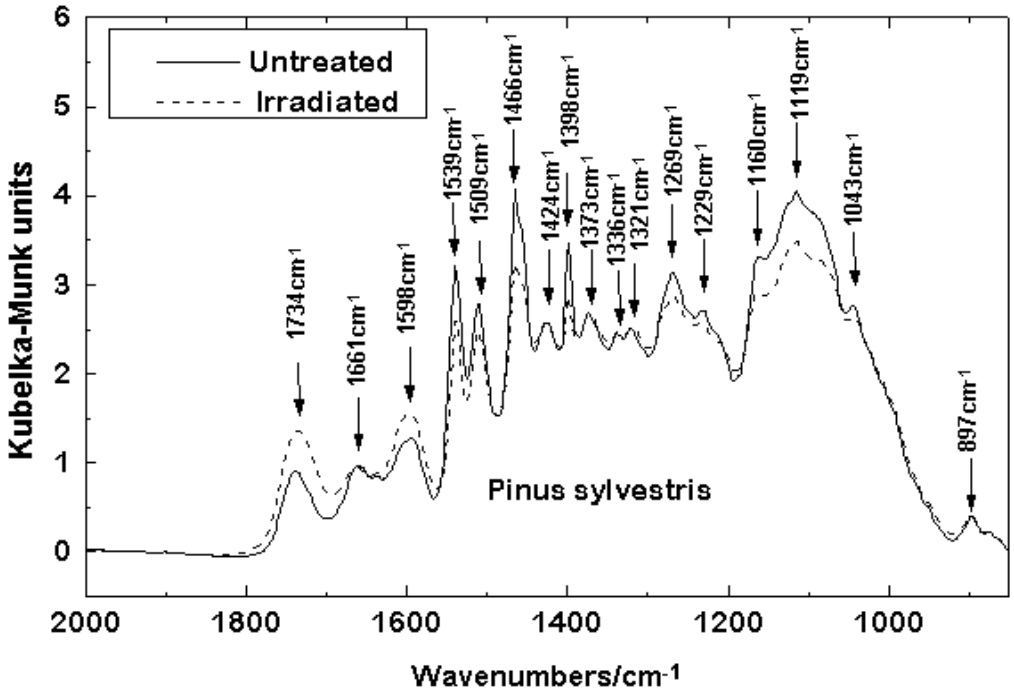

Fig. 1. The DRIFT spectrum of Scotch pine's earlywood before (___) and after (_ _ _) UV laser irradiation in the range of 2000 to 850 cm^{-1}

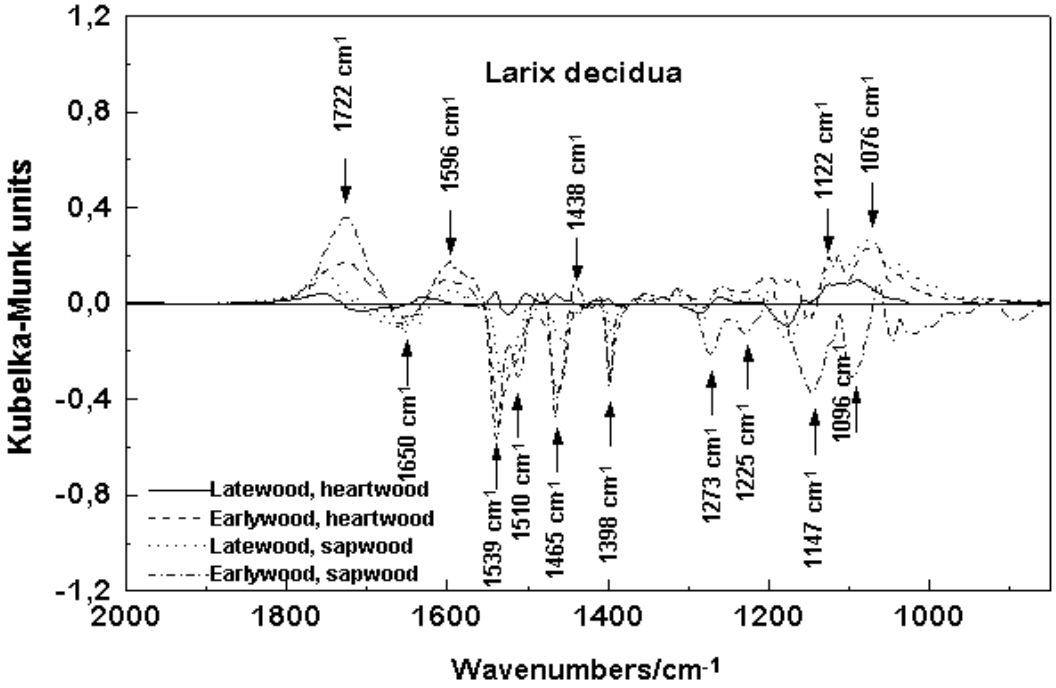

Fig. 2. DRIFT difference spectra of the type "irradiated wood minus untreated" of various issues of larch

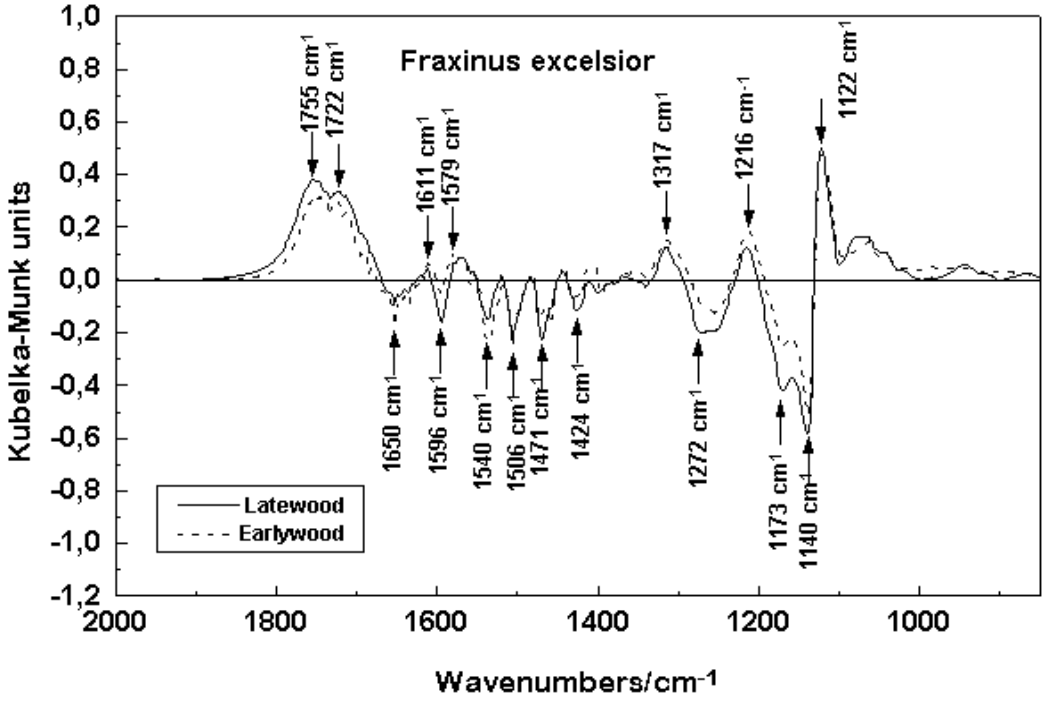

Fig. 3. DRIFT difference spectra of the type "irradiated wood minus blank" of high ash

Although both the increase and decrease in intensity is small, we have to discuss this since the difference spectra of the softwoods and the hardwoods characteristically differ in this range. Conjugated carbonyl groups have an absorption maximum at 1598 cm^{-1} and the same band corresponds to the frame resonance of the aromatic rings. The decrease in absorption at 1506-1510 cm^{-1}, in the band solely belonging to the aromatic rings, clearly indicates that aromatic rings are split by UV-light. The splitting of aromatic rings and the formation of C=O bonds are two antagonistic processes that change the absorption around 1598 cm^{-1} in opposite directions. With the softwoods the formation of the C=O groups is dominant. The hardwoods also have an increase in a relatively wide band around 1560 - 1620 cm^{-1} resulting from the same process. A decrease in a narrower band superimposes on this and "pulls down" the peak around 1598 cm^{-1} thus creating the two peaks (1610 and 1575 cm^{-1}) and a valley in between (1598 cm^{-1}) characteristic of the hardwoods (Figure 3). The effects of the decrease were also noticeable for the softwoods resulting in the flattening of the wide peak (the latewood of the heartwood in case of the scotch pine, see Fig.4) or resulting in two peaks with a slight trough in between (the latewood of the heartwood in case of the spruce, see Fig. 5). The above indicate that both the splitting of the aromatic rings and the increase in the number of C=O groups occur with both the softwoods and the hardwoods, but in different ratios. Absorption decreased significantly around 1539, 1465 and 1398 cm^{-1}. These occurred in the spectra of all samples.

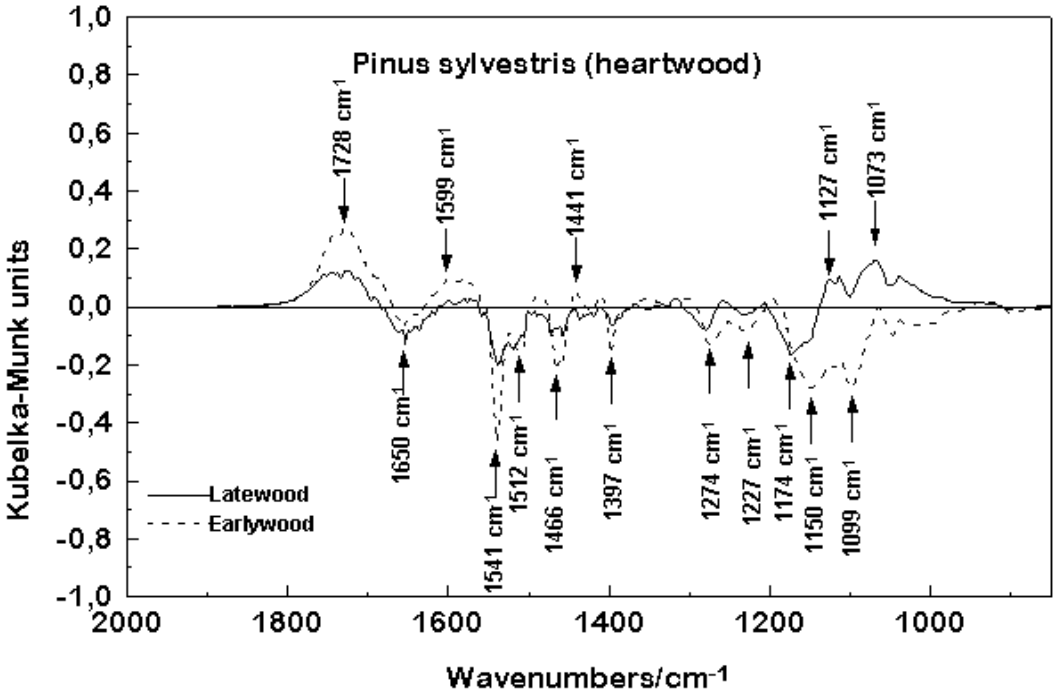

Fig. 4. DRIFT difference spectra of the type "irradiated wood minus untreated" of Scotch pine's latewood

In case of the earlywoods of the softwoods and the maple the decrease reached the value of -0.6, -0.8 in Kubelka-Munk units. The decrease was smaller in case of the beech and the locust. Characteristically, it was the latewood of the heartwood of the larch that showed the smallest change (Figure 2).

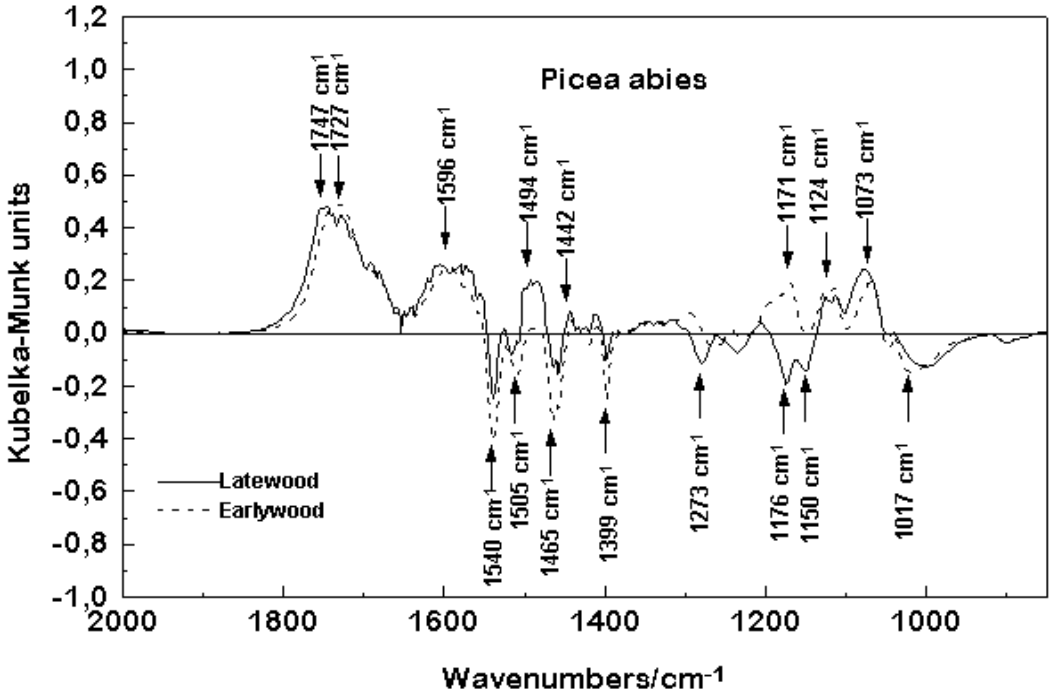

Fig. 5. DRIFT difference spectra of the type "irradiated wood minus untreated" of Spruce's heartwood

The absorption decrease appears in a narrow range and with a sharp peak in case of all three bands and it is so prominent that the 1535 cm^{-1} band overlaps the 1510 cm^{-1} band, which has shown the greatest decrease so far according to previous studies. In these cases the 1510 cm^{-1} band appears in the difference spectrum as the shoulder of the 1535 cm^{-1} band (earlywood of heartwood of larch and douglas-fir). The 1465 cm^{-1} band usually shows a double-peaked decrease (douglas-fir, scotch pine, high ash). We may conclude that UV-laser produces chemical processes that were not induced when using UV-light from xenon and mercury-vapor lamps in previous experiments. Further studies are needed to explore these processes. Except for the maple, all samples show a decrease around 1230 and 1273 cm^{-1}. The latter is in connection with the splitting of aromatic rings and the formation of C=O groups. Usually, the splitting of aromatic rings is the more dominant of the two. We also experienced changes in the lower wavelength ranges (1050 - 1200 cm^{-1}) which are the absorption region of the C-O-C and C-O-H groups. There are significant differences among the softwood species and also among the different issues within the same species. As opposed to this, the difference spectra of the hardwoods are very similar, only the maple differs in its inner ratios from the locust, beech and the high ash. In case of the hardwoods absorption increased around 1317 and 1216 cm^{-1} (CH_2 groups) for both issues and decreased around 1173 and 1140 cm^{-1} corresponding to C-O-C bonds. The latter band also represents an absorption maximum for the aromatic CH-groups which in accordance with the decrease in the bands at 1510 and 1273 cm^{-1} points to the splitting of aromatic molecules. Right next to the absorption decrease at 1140 cm^{-1} in case of the hardwoods we observed a sudden absorption decrease at 1122 cm^{-1}, of which there is no mention in the literature. We might conclude from the different changes in the spectra of the softwoods around the wavelengths 1050 - 1200 cm^{-1} that multiple chemical processes take place that change the absorption in this range. The increase or decrease in the individual bands

is determined by the sum of these processes. The splitting and forming of bonds must be the same in quality because of the fact that the changes observed always occurred in the absorption of the same wavelength ranges in the case of the softwoods. The peak belonging to the increase of the 1122 cm^{-1} band can always be found in the difference spectra of all the softwood samples. The negative peak (trough) belonging to the decrease at 1140 cm^{-1} can also be found. Because of the close proximity of these two peaks and the opposite direction of them, in case of some issues the latter pulls the former below the baseline (the earlywood of the sapwood of the larch, the earlywood of the maple). The reason behind this is that the inner ratios of forming and splitting bonds are different in case of the different issues for the softwoods and the maple. For the hardwoods however, these ratios are approximately the same for the issues of the different species.

Conclusions

Summarizing the results, we might conclude that the UV-laser not only causes the changes in the difference spectra of the wood samples that are also produced by the traditional UV-radiators, but also produces new decrease and increase bands (1122, 1140, 1398, 1465, 1535 cm^{-1}) that have never been mentioned before. We did not observe the absorption decrease at 1710 cm^{-1} that was thought significant based on former studies. This band blended into the wide band of 1722 - 1755 cm^{-1} that showed a much larger increase. It is likely that the increase at 1710 cm^{-1} was produced by the thermal effect superimposed on the UV radiation, which did not occur during UV-laser treatment. The element of wood predominantly damaged by UV-light is lignin. The absorption decrease at 1510, 1273 and 1140 cm^{-1} indicates the disintegration of the aromatic rings of lignin. The increase around 1722 - 1755 and 1598 cm^{-1} shows the forming of C=O groups. Further studies are necessary to explore the chemical changes taking place in wood as a result of UV-light that was produced by laser.

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