Effect of UV laser radiation with different wavelengths on the spectrum of lignin extracted from hard wood materials

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Abstract

The effect of different wavelength UV laser irradiation on DRIFT spectra of lignin extracted from hard wood was investigated. Changes in the spectra of lignin were studied with 308, 248.5, and 193 nm wavelength of UV laser radiation. To monitor the energy dependence, different number of laser impulses reached the sample's surface. To investigate quantitatively how the absorption does change the band damage index (BDI) is introduced. Fourier deconvolution and fit of mixtures of Gaussians and Lorentzians were used to decompose the difference spectra into two spectra containing the bands changing their intensity to opposite directions, which made us possible to identify the products and the components destroyed. Opening up of the glucopyranose ring is essential starting point of the decomposition process and all further steps are dependent on the energy and intensity of the photons.
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1. Introduction

The chemical and thermodynamic processes in the Earth atmosphere are directly or indirectly induced and/or maintained by radiation energy from the Sun. The energy of a photon (E) is given as $E = hc/\lambda$ (where $h = 6.62 \times 10^{-34}$ J s is the Planck constant, c is the speed of light, and λ is the wavelength). Thus, the highest photon energies can be found in the UV region of the radiation spectrum of the Sun; consequently photons in the UV region have the highest photochemical activity. Photons with wavelength shorter than 315 nm have primary importance in this respect. Molecules under the influence of the Sun radiation and capable of absorbing UV photons can be excited to a higher energy level and their chemical bonds might be modified as result of absorption of UV light. Artificial UV light sources have to be used for examination of UV light effect only, if the effect of other than the UV region of the Sun radiation is to be avoided. Numerous groups have already studied the effects of UV radiation on wood materials as well as on their

constituents. Xenon (Xe) and high-pressure mercury vapor lamps were used as radiation sources in studies of the effect of UV light on lignin and cellulose samples [1–4]. During the studies with usual radiation sources, the treatment was performed for hundreds of hours and radiation sources worked in a definite wavelength region instead of at fixed wavelength.

Using lasers as radiation sources [5–8], the duration of treatment can be shortened, the wavelength of radiation is known, and the energy as well as the intensity of radiation at the surface can be determined. UV lasers working at different wavelengths were used for irradiation our wood material and its constituents. Lignin is a natural polymer biologically produced through random polymerization processes. The biological role of lignin in living plants is to form, together with the cellulose and other carbohydrates of the cell walls, a tissue of excellent strength and durability. Plant lignins are concentrated mainly in the space between the cells (middle lamella) where they are deposited during the lignifications of the plant tissue [9]. Lignin lacks the regular and ordered repeating units found in other natural polymers, such as cellulose and proteins. Wood lignin composed of phenylpropane units, e.g. guaiacyl and syringyl with hydroxyl and carbonyl

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substitutions. The infrared (IR) spectrum of lignin has already been studied in many respects [10–12]. The diffuse reflection infrared Fourier transform (DRIFT) spectroscopy played an important role in the identification of the most intensive absorption bands as well as the chemical groups belonging to these absorption bands. For this technique, the sample preparation procedure is simpler and precise information can be obtained about the changes in the chemical structure of the surface of samples [2,13–15]. DRIFT technique can also be used for studying the UV radiation-caused photo-degradation of lignin [2,7,16].

In this paper, changes caused by UV laser light in the chemical structure are studied by using the DRIFT technique. The changes in the absorption spectrum of lignin will be discussed below.

2. Materials and methods

The lignin fraction of molecular mass 2000 isolated from prehydrolyzate of beech wood was impregnated on cellulose plate. Samples used were as discs with 12 mm diameter and 0.1 mm thickness. Changes in the chemical structure of lignin were studied at different wavelengths of UV radiation and at different numbers of laser impulses reached the sample surface.

The following wavelengths were used:

- 308 nm from a xenon-chloride (XeCl) Excimer laser,
- 248.5 nm from a krypton-flouride (KrF) Excimer laser, and
- 193 nm from an argon-fluoride (ArF) Excimer laser.

In cases of XeCl and KrF lasers, samples were irradiated by either 5000 impulses, or by 10,000 impulses. The energy of an impulse was 20 mJ in both cases. In case of ArF laser, the number of impulses applied was 1500 and 3000 and the energy of an impulse was 10 mJ. It was necessary to decrease the number as well as the energy of impulses in case of ArF laser emitting at shorter UV wavelength to avoid the thermal effect of such radiation.

The 5000 and 1500 impulses refer to radiation energy of 100 and 15 J, as well as 8.8×10^5 J/m^2 and 1.3×10^5 J/m^2 surface energy density, respectively. Respective values doubled at 10,000 and 3000 impulses. The surface photon density was 10 times higher at XeCl and KrF lasers at 5000 impulses than at ArF laser at 1500 impulses. DRIFT spectra were recorded between 3800 and 850 cm^{-1} with 4 cm^{-1} resolution by using a Fourier-transform infrared (FTIR) spectrophotometer modified according to our need Bio-Rad Digilab Division (FTS-65A). Base-line correction was performed in two steps: between 3800 and 1900 cm^{-1}, and 1900 and 850 cm^{-1}.

Changes caused by the UV irradiation in the chemical structure of lignin samples were investigated by the following method of treatment for the spectroscopic data. An average spectrum was produced from the spectra of untreated

samples, to avoid information loss caused by the incomplete homogeneity of the samples. The average spectrum was decomposed by Fourier deconvolution using Bessel's functions to identify the number and position of bands to fit [17]. Mixtures of Gaussians and Lorentzians were fitted to the position of the previously identified bands in case of the average spectrum to determine the expected bandwidth and Gaussian-to-Lorentzian ratio for the bands. The original spectra of untreated samples were fitted using these parameters allowing only the intensity parameters to change. If improper description of certain parts was observed, slight alteration in position, bandwidth and Gaussian-to-Lorentzian ratio was allowed at limited number of fitted bands. The spectra of the treated samples were fitted using the parameters of the corresponding untreated samples by fitting only the intensity parameters. The normalized intensities for all spectra were calculated using the integrated intensity of the reference band at 1373 cm^{-1} as usual [4]. Two types of difference spectra were calculated and synthesized for each pairs of treated and untreated samples by using the difference of the intensities of the corresponding bands and using all other peak parameters. The first one contained only the bands of gaining, while the other only those of loosing intensity in consequence of irradiation. Calculation of so-called band damage index (BDI) took place on the basis of the integrated intensities of the fitted bands defined in the text later.

Using BIO-RAD Win-IR for Microsoft Windows, Version 3.04 Level II. of Galactic Industries performed all spectral manipulations, running on a Hewlett–Packard Vectra VL2 4/50 computer.

3. Results and discussion

To reveal the qualitative spectral features, the spectrum of cellulose and the averaged spectrum of lignin are shown in Fig. 1. The main differences of composition between
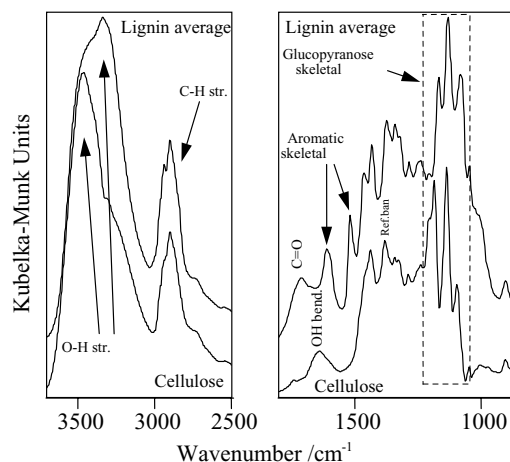

Fig. 1. Comparison of the spectrum of cellulose and the average spectrum of untreated lignin samples with the assignment of the main bands. The reference band is also marked.

cellulose and lignin can be identified in these spectra. Both contain the peaks characteristic on the glucopyranose ring around $1100\,cm^{-1}$. There is a slight shift in the position of these bands to lower wave numbers in lignin, probably caused by the change in association and in degree of polymerization for the glucopyranose rings. The aromatic components of lignin also put their marks to the spectrum; the two most important peaks of the benzene rings can be clearly identified at around 1600 and $1500\,cm^{-1}$. The C=O stretching band at around $1710\,cm^{-1}$ is a sign of the presence of carboxylic acids, esters or other oxo-compounds. There are significant differences in the X–H stretching region. The broad band of the cellulose belongs to the O–H stretching modes. The higher maximum lower of the broad band in the spectrum of lignin might originate from OH stretching of aliphatic hydroxyl-groups. The lower maximum of this band can be ascribed [18] to the phenolic hydroxyl-groups of lignin.

Although, the irradiation energy with XeCl and KrF lasers were 100 and 200 J s, and 15 and 30 J s with ArF laser, the intensity changes in the absorption spectra were in the same order of magnitude after the treatment of samples with the lasers of either three wavelengths.

Usual treatment of compound spectra, to reveal the spectral changes of the sample in consequence of various treatments, is to subtract them from each other. The difference spectra show positive and negative bands in accordance with the decomposition of the original components and positive bands corresponding to the compounds formed. The information supplied by the difference spectra is usually satisfactory to identify the essential changes. Unfortunately there is a hidden source of error involved in this simple process, which can be avoided in case of relatively low number of known components by comparing the difference spectra to the spectra of the pure components. On the other hand, spectra recorded of very complex samples can feature overlapping bands with extremely different width. The result of subtraction is a bit dubious between bands like these. Furthermore, difference spectra are rarely fit to use for quantitative measurements. A process, described in the experimental section was worked out to overcome these types of problems. Obviously, it needs a more laborious treatment of data than a simple spectral subtraction, but tremendously lessens the errors in interpretation of changes. Furthermore, it provides two synthetic spectra, separating all the influences causing gain and loss of intensity in the sample. These spectra can be searched in databases etc. The parameters of the fitted bands can be used for the quantification of spectral changes and can be used to reveal hidden correlations. Two regions of our spectra were treated by this method. The X–H stretching range between 3700 and $2500\,cm^{-1}$ and the other containing the most informative part of the spectra, between 1800 and $850\,cm^{-1}$, the XY stretching and the X–H bending modes (X and Y can be either C or O). The most important step of the above treatment to decide about the number and position of bands to fit. All conventional methods can be used,
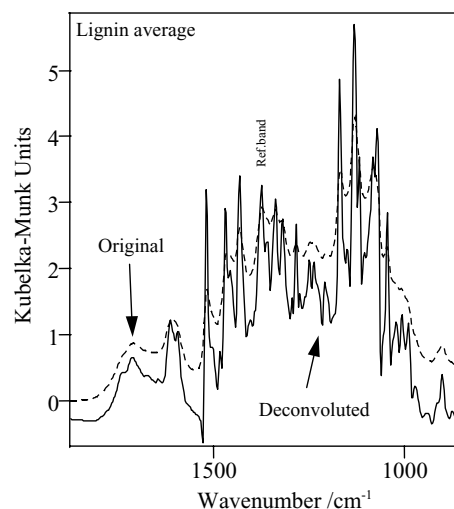

Fig. 2. The deconvoluted spectrum (solid line) of the average lignin spectrum (dashed line) with the reference line at $1373\,cm^{-1}$ marked.

e.g. second derivative of the spectrum etc. but our choice was Fourier deconvolution, because it keeps the integrated intensity of the spectrum, only limits the bandwidth of the bands to a lower but uniform value. The result of the deconvolution of the lower, XY stretching range is given in Fig. 2.

There were no differences between the results of deconvolution in numbers of peaks for the individual spectra of untreated samples, only slight shift in position of certain peaks occurred. The most intense peaks were used to set up the starting parameters of the curve fitting. Some components were excluded during the fitting because the program causing a baseline like behavior or resulting in zero intensity tuned the peak parameters. Finally, fits of 16 peaks were the minimal requirement for proper description of the higher X–H stretching region and fit of 27 peaks for the lower XY stretching region. The difference spectra synthesized from the parameters of the bands gaining intensity are given in Fig. 3. It can be seen that treatment with low and high power resulted in two clearly distinguishable set of spectra. While the spectra derived from the spectra of the samples treated with high power proved to be more or less uniform and simple, the low power treatment caused more compound spectral alterations, featuring a band between 2700 and $2750\,cm^{-1}$ and another between 1750 and $1650\,cm^{-1}$ showing minimum at the sample treated by KrF laser.

The synthetic difference spectra of the same samples from the bands loosing intensity depicted in Fig. 4. The similarities between the spectra divides them again into two groups, but this time the low power treatment produced the simpler more uniform spectra, while the high power treatment caused more complicated alterations.

Comparison of the spectra given in Figs. 3 and 4 brings to attention that although this treatment gives much better chance to understand the changes at a molecular level than simple subtraction of spectra, but it is necessary to keep in mind that the intensity change of a given band is the overall
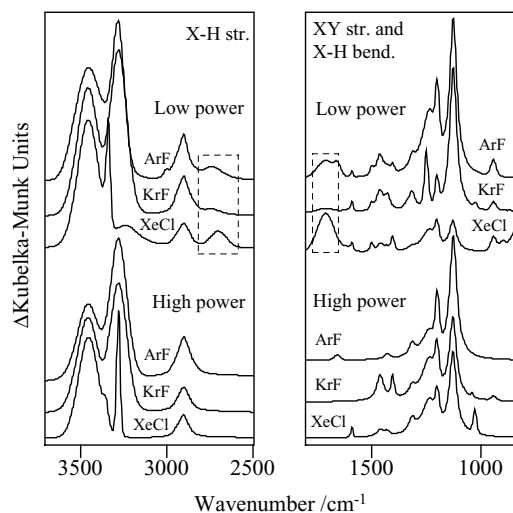
Fig. 3. Synthetic difference spectra composed from the parameters of the bands gaining intensity as a result of treatment. Framed regions contain bands changing intensity more or less parallel.

result of the changes in concentration of the various components, but the final result is depends on the molar absorbance coefficients of those components. The OH stretching bands are the best examples. It would be tempting to assign the positive and negative bands to certain species, but there is no real meaning of the two peaks in the spectra of Fig. 3 and the single maxima in Fig. 4. The only reliable conclusion is that the treatment causes increases in the concentrations of those types of species, which have higher intensity in this region, and those, which decompose, have lower absorption coefficients. It might have a kind of jolting effect but if we take into consideration that the intensity is closely connected with the square of the transition dipole moment caused by the vibration of atoms, we can conclude that the main result of the treatment, the fragmentation of the polymeric components, containing O–H groups. More specific
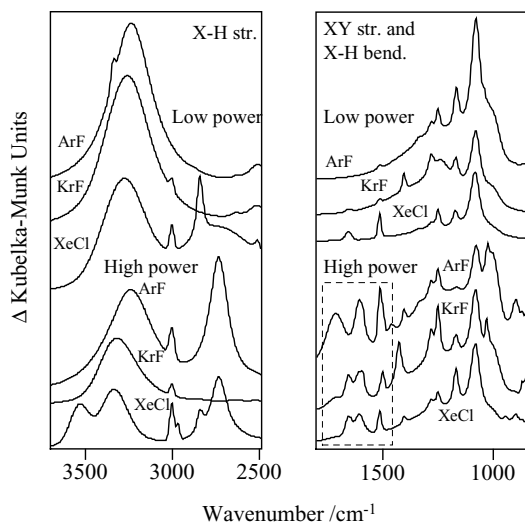

Fig. 4. Synthetic difference spectra composed from the parameters of the bands loosing intensity as a result of treatment. Framed region contains bands for the most common UV chromophores.
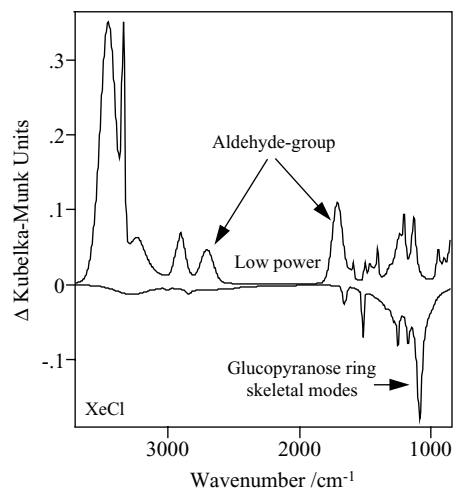

Fig. 5. Spectral differences caused by the treatment of lignin by XeCl laser at low power. Intensity changes suggest opening of the glucopyranose rings resulting the aldehyde form of the polymeric hydrocarbons.

conclusions can be deduced from certain pairs of synthetic different spectra. The most obvious pair is given in Fig. 5 for the treatment with XeCl laser with low power. The band at $1710 \, cm^{-1}$ suggests that species containing oxo-group have been formed, but the band at $2702 \, cm^{-1}$ which characteristic only on the aldehyde group from the possible candidates makes possible to conclude that the opening of the glucopyranose rings dominates the effect. The negative bands in the glucopyranose skeletal region reinforce it. The most intense change belongs to the band at $1080 \, cm^{-1}$, which usually assigned as the mode dominated by the –C–O–C– stretching among the skeletal modes of the glucopyranose ring.

Similar features can be identified in the corresponding difference spectra of the samples treated by KrF and ArF lasers at low power. Although the energy delivered by a single pulse increases in the XeCl, KrF, ArF, the intensity changes in the bands characteristic on the aldehyde group is the biggest in the spectrum derived from the sample treated by the XeCl laser. The other two lasers caused more or less the same intensity change in these bands. On the other hand, the loss in intensity of the bands characteristic on the glucopyranose ring follows the energy of the photons. It is the highest in case of ArF. The essential difference is in the influence of the high power treatment that the bands characteristics on the possible UV chromophores are also loosing intensity. The bands for possible chromophores, the aromatic rings and C=O groups can be identified in the spectra given in Figs. 6–8.

The negative relative intensity of the aromatics and the oxo-groups increases by the photon energy while the band of esters remains more-or-less the same. There is a plausible explanation that the longer treatment prevented the distribution of the delivered energy along the molecules. So, the repeated hits by the photons caused the dissociation of the chromophores themselves.
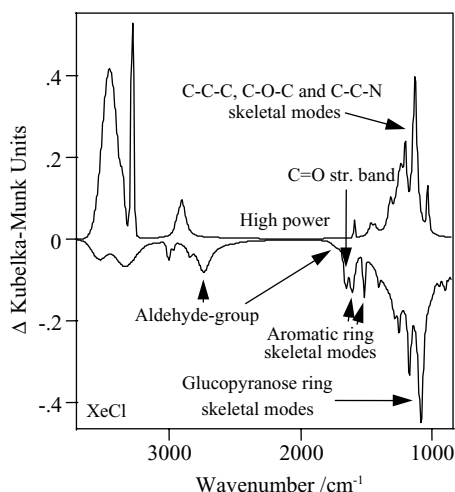
Fig. 6. Spectral differences caused by the treatment of lignin by XeCl laser at high power. The decomposition of the aromatic and ester-type chromophores is well expressed.

The intensity loss in the skeletal bands of the glucopyranose ring is still present in the spectra. So, the fragmentation of the cellulose-like parts still occurs in lignin. It has a minimum when KrF laser is used.

When the synthetic difference spectra are calculated, we obtain summarized information about the spectral changes. To see this synthesized information to be decomposed for the components, the band damage index is introduced. It is defined as follows:

$$\text{BDI} = \frac{\int_{k_1}^{k_2} \Delta S(x)\, dx}{\int_{k_1}^{k_2} S(x)\, dx},$$

where $S(x)$ and $\Delta S(x)$ are the spectrum of lignin and the difference spectra, respectively in the $[k_1, k_2]$ interval. Further-
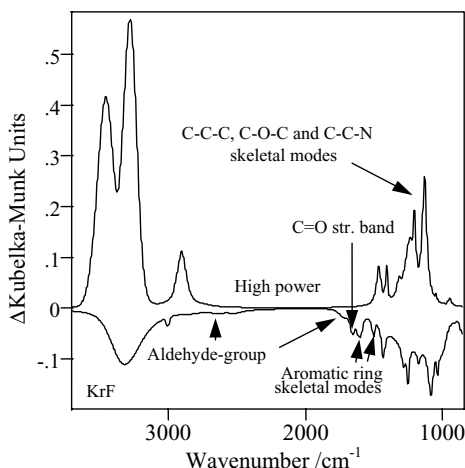

Fig. 7. Spectral differences caused by the treatment of lignin by KrF laser at high power. The decomposition of the aromatic and ester-type chromophores is well expressed, but there is a slight change in the skeletal modes of the glucopyranose ring.
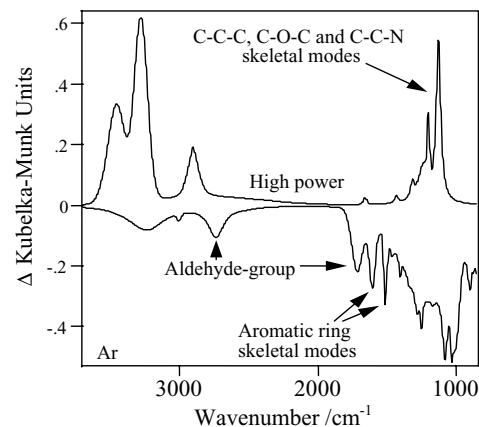

Fig. 8. Spectral differences caused by the treatment of lignin by ArF laser at high power. The decomposition of the aromatic and oxo-type components is well expressed, but they hide the ester band.

more, BDI makes possible to investigate quantitatively, how the absorption changes of the components by doubling the number of laser impulses. It also makes possible to monitor the influence of the laser wavelength change. For example the influence of the number of pulses can be recognized at the band at $1200\,\text{cm}^{-1}$ where the BDI increases by the doubling of impulses independently from the wavelength (see Table 1, row A). The bands at 1607 and $1516\,\text{cm}^{-1}$ are sensitive to the wavelength of the laser (see Table 1, row B). The dependence shows a minimum—practically zero, at the KrF [8] and more or less the same for the other two. It can be the indication of our previous assignment, that they are the skeletal modes of the aromatic ring (see Figs. 6–8). On the other hand, the band at $1083\,\text{cm}^{-1}$ shows very low sensitivity either on the number of pulses or the wavelength of the laser, against that it is the most intense negative peak in all synthesized spectra (see Table 1, row C). A seemingly contradictory behavior can be observed at $1710\,\text{cm}^{-1}$ (see Table 1, row D). The BDI indicates a gain at low and a loss at high number of pulses, in intensity for all lasers, but the gain is much higher for the XeCl laser and the loss is for the ArF than for the KrF. It is possible to resolve this contradiction if two processes are taken into account, having opposite influence to this region. The opening up of the glucopyranose ring increases the band intensity, while the decomposition of the aldehyde and C=O containing (e.g. carboxylic acids and

Table 1
BDI values for a few selected bands showing characteristic behavior

Row	Band (cm^{-1})	XeCl		KrF		ArF	
		Low	High	Low	High	Low	High
A	1200	0.164	0.663	0.364	0.521	0.205	0.849
B	1607		−0.134		−0.055		−0.140
	1516		−0.140		−0.001		−0.129
C	1083	−0.099	−0.150	−0.099	−0.068	−0.102	−0.078
D	1710	0.295	−0.027	0.023	−0.025	0.033	−0.149

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.

4. Conclusions

The deconvolution of the DRIFT-spectra combined with the curve fitting allowed us to get a deeper insight into the processes occurred as a consequence of the irradiation by various laser wavelengths. It made easier the band assignment. The decomposition of the difference spectra into two spectra containing the bands changing their intensity to opposite directions made us possible to identify the products and the components destroyed. The band damage index, defined as a relative change in integrated intensity within a wavenumber interval supplied quantitative information on the behavior of each individual band. The influence of the photon energy and intensity on the IR-spectra of lignin was discussed and possible explanations of the processes were proposed. Opening up of the glucopyranose ring is essential part of the process (see negative bands around 1100–1000 cm^{-1}). All further steps are dependant on the energy and intensity of the photons. All available chromophores—benzene rings and organic acid derivatives—are influenced and produce non-cyclic saturated compounds. The intensity changes in the C=O stretching region can be interpreted as an overall result of two independent processes with opposite effect.

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