Changes in DRIFT spectra of silver maple and lignin extracted from the same wood caused by 248.5 nm laser

György Papp[+], **László Tolvaj, Edit Barta**

Institute of Physics, University of Sopron
H-9400 Sopron, Ady E. ut 5. Hungary

ABSTRACT

The effect of UV-light produced by laser on silver maple wood and lignin extracted from the same wood species has been monitored by diffuse reflectance infrared Fourier transform (DRIFT) spectrometry. The results showed that the photodegradation caused by 248.5 nm wavelength laser are not in agreement with the results of degradation caused by traditional UV sources. Independently on the energy dose the aromatic part did not suffer changes around 1510 cm^{-1} in the extracted lignin, while in the case of silver maple the decrease of this band is covered by other band decrease in the difference spectrum.

Keywords: Degradation, UV-laser, lignin, silver maple

INTRODUCTION

The effects of UV-light on wood and lignin can be studied by artificial UV-light sources. Experiments with traditional UV-sources (xenon and mercury vapour lamps) has been done by several research groups as described elsewhere (Dircx et al. 1987; Németh, Faix 1994; Tolvaj, Faix 1995). Only a few attempts have been done with UV-laser (Barta et al. 1998a, Stehr et al. 1998). The laser has several advantages compared to traditional UV-sources. Utilising laser the time of interaction can be shortened, the degradation caused by UV-light can be studied, excluding the thermal effects originating from warms up of the surface. The wavelength of irradiation, the energy dose and the intensity of irradiation can be determined exactly. The effect of irradiation by light of different wavelength were studied in the case of thermomechanical pulp by Kimura et al. (1994). It was established that the aromatic ring structure in lignin and the C-O and C-H bonds in the wood carbohydrates decreased much more rapidly at shorter irradiation wavelengths for both unbleached and bleached samples. Recently, Barta et al.(1998) reported the photodegradation of some wood species using excimer UV-laser for irradiation. The changes reported in this study are considerably different from the previous observations generated by traditional light sources. In the present study Diffuse Reflectance Infrared Fourier Transform (DRIFT) technique was used to determine chemical changes of lignin and silver maple caused by UV-laser. This method is useful to determine changes on the surface of the examined samples. Many scientist used this technique to analyse the chemical changes of wood, pulp and paper (Schultz et al. 1986, Michell et al. 1989, Backa and Brolin 1991, Tilly et al.1993, Pandey and Theagarajan 1997, Kosikova and Tolvaj 1998). In this report the special UV photodegradation of silver maple and of lignin impregnated into cellulose plate has been studied.

MATERIALS AND METHODS

The examined lignin samples were isolated from water prehydrolyzate of silver maple wood, than it was impregnated into a cellulose plate. For the investigation of degradation of wood, samples were cut from the earlywood and latewood of heart wood of silver maple. The samples were irradiated by 5000 pulses selected from the pulse train of 248.5 nm wavelength krypton fluoride excimer laser operated at 10 Hz repetition rate. The pulses had 15 ns duration and 20 mJ energy. In the case of lignin we have investigated the energy dependence of degradation also therefore some of the samples were irradiated by 10000 pulses. The effect of irradiation was examined by DRIFT method. Diffuse reflectance spectra were recorded before and after irradiation using Bio- Rad Digilab FTS-65A/896 FTIR- spectrophotometer. 256 interferogramms were collected with 4 cm^{-1} resolution. The spectral intensities were calculated in Kubelka- Munk units. The spectra were baseline corrected by a linear algorithm and were normalised to the band between 1352 and 1406 cm^{-1}. The spectrum of the untreated sample was subtracted from the spectrum of the irradiated one, to obtain the difference spectrum.

RESULTS AND DISCUSSION

To demonstrate the shape, Fig. 1a and Fig. 1b show the lignin and wood spectra in the range of 3800-2000 cm^{-1} . The IR spectrum both of lignin and silver maple showed a broad band around 3350 and 3394 cm^{-1} , respectively. This band is associated to the vibration of hydroxyl groups being in different position. The C-H stretching vibration of the lignin appeared as a broad band in the region 3000-2800 cm^{-1} and of wood appeared as two sharp absorption band in the same range.

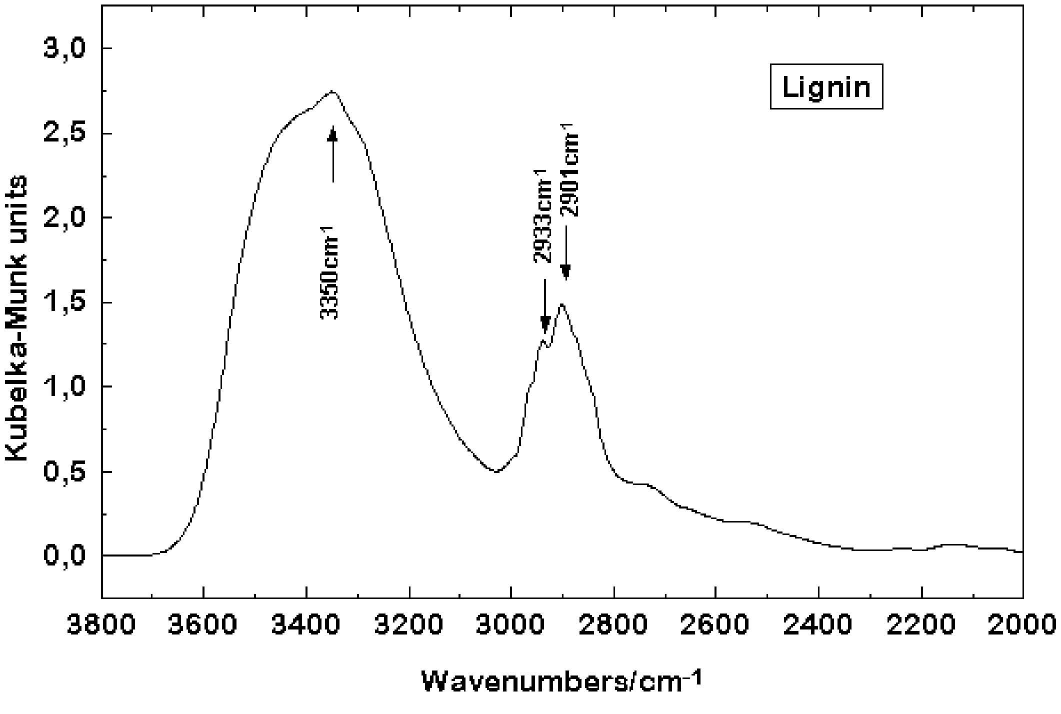

Figure 1a: DRIFT spectra of lignin (the range is shown by the horizontal axes).

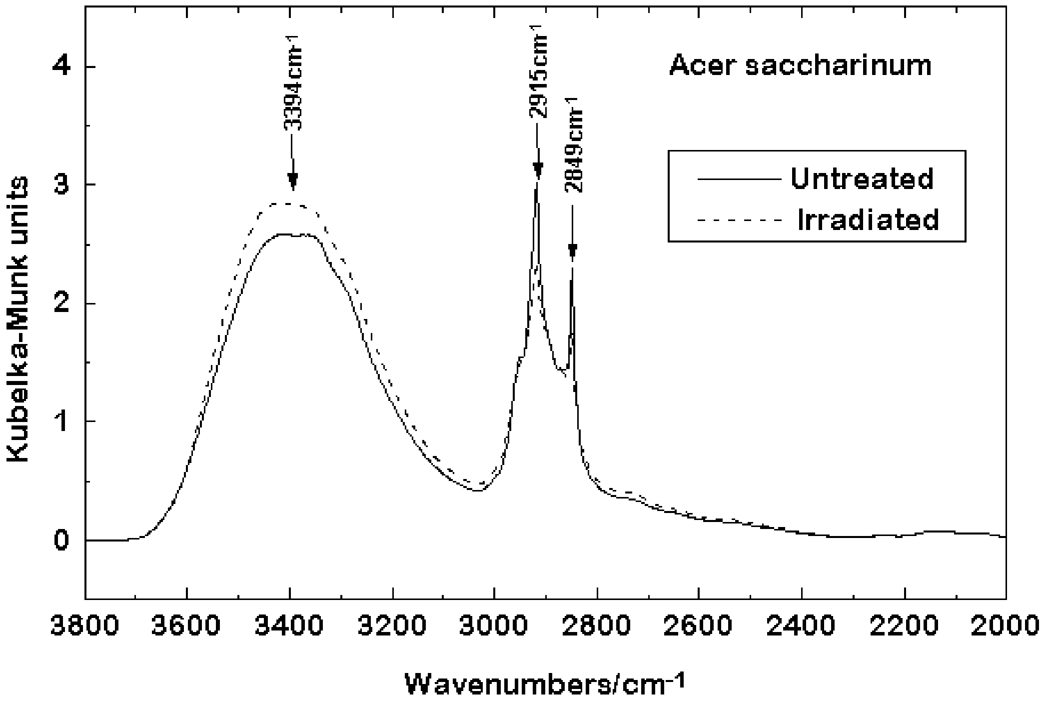

Figure 1b : Untreated and irradiated DRIFT spectra of silver maple.

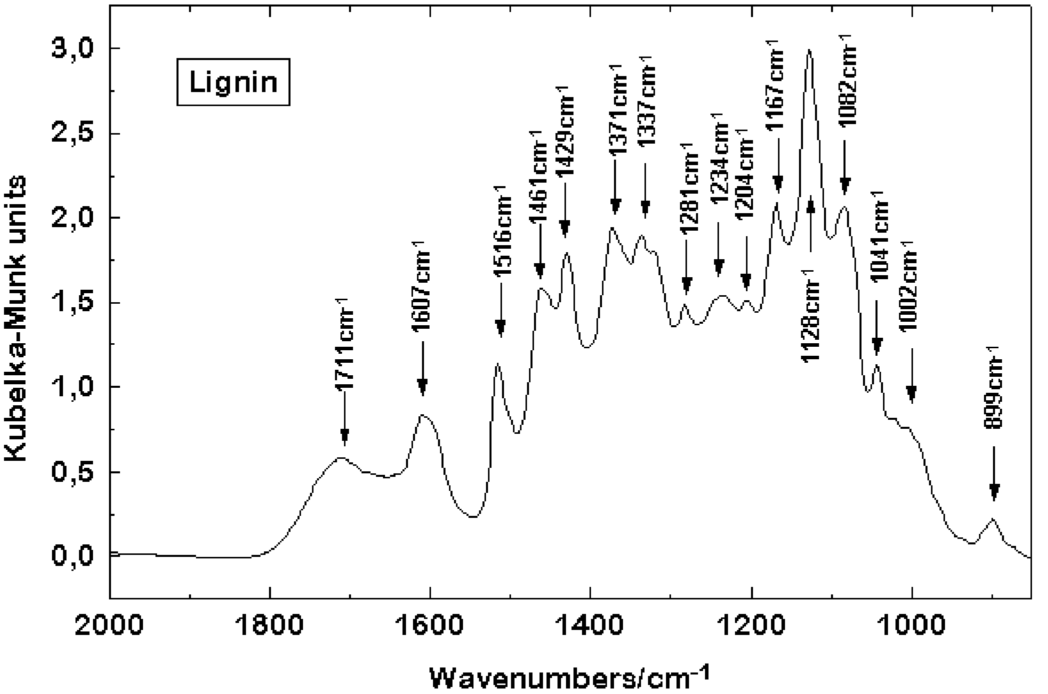

Figure 2a: DRIFT spectra in region 2000-850 cm^{-1} of lignin.

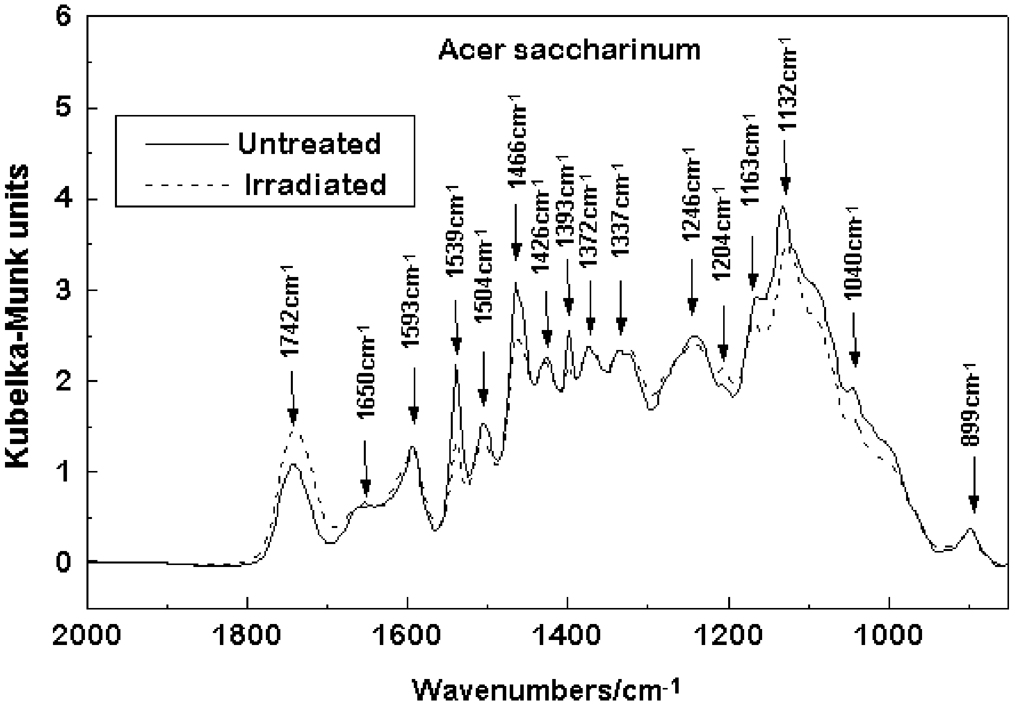

Figure 2b: DRIFT spectra in region 2000-850 cm^{-1} of silver maple.

The IR spectra of D-glucono-1,5-lactone, D-gluconic-acid and the alkali metal D-gluconate-salts has been studied by Tajmir-Riahi et al.1993, where the C=O stretching vibration of the free lactone was observed at 1728cm^{-1} whereas in free D-gluconic-acid it appeared at 1716cm^{-1}. Similarly, the carbonyl-stretching vibration of D-glucurono-1,4-lactone occurred at 1758cm^{-1}, whereas in free D-glucurono-acid it was observed at 1707cm^{-1}. These types of constituents result the broad band around 1711cm^{-1} in lignin, and around 1742cm^{-1} in wood, respectively (see Fig. 2a, Fig. 2b). The presence of a moderate band at 1650cm^{-1} in the wood (absent in lignin) was attributed to the H_2O bending mode. The conjugated carbonyl groups have an absorption maximum at 1596cm^{-1} and this band can be attributed to the aromatic skeletal vibration. In the lignin this results a broad band around 1607cm^{-1}, whereas in the wood it appeared at 1593cm^{-1}. The aromatic skeletal vibration of lignin at 1516cm^{-1} split into two components at 1539 cm^{-1} and 1504cm^{-1} in wood. The C-H, C-OH, C-O and C-O-C vibration modes were observed as several sharp bands at ~1460-898cm^{-1} in the IR spectrum (there are marked similarities between them) of lignin and wood. Fig. 1b and Fig. 2b demonstrate how the spectra of wood is influenced by UV-laser irradiation. However, to obtain additional information from DRIFT spectra of wood and lignin we have done the difference spectra „spectra after irradiation minus spectra of untreated material”. Several spectral changes can be observed from the difference spectra in Fig. 3a and Fig. 3b. The OH bands are increased both for lignin and wood. It is completely different from that results what were obtained by Tolvaj and Faix (1995) where the effect of UV irradiation up to 200hrs was monitored on five wood species by spectro colorimetry and DRIFT spectrometry, using traditional UV-sources. There the OH bands are decreased at 3500cm^{-1} and, to a less extent, at 3200cm^{-1}. Their interpretation were, that the results are the manifestations of the loss of OH groups followed by dehydration upon UV irradiation. It means, that in our cases the number of OH groups increased with the 248.5nm UV light irradiation. The results should preferably be interpreted that the OH band region in the IR spectra of woods is dominated by the OH groups of lactone. X-ray structural data have shown (Nawata et al. 1981) that there are four distinct H bounded OH groups in the crystal structure of free D-glucono-1,5-lactone. A tentative assignment of the lactone OH stretching vibrations has been made on the basis of the intermolecular O...O and O...H distances. A sharp, intense band at 3462cm^{-1} is assigned to 6-OH...O-2, a strong band at 3387cm^{-1} is related to 4-OH...O-1, a broad band with medium intensity at 3277cm^{-1} is assigned to 2-OH...O-3 and a strong band at 3225cm^{-1} is due to the strongly H-bonded 3-OH...O-6 stretching vibrations. The increase of intensity around 3476cm-1 and 3279cm-1 can be attributed to formation of lactone both for woods and lignin. In the case of lignin the „lignin1" and „lignin2" were irradiated by 5000 and 10000 pulses, respectively.

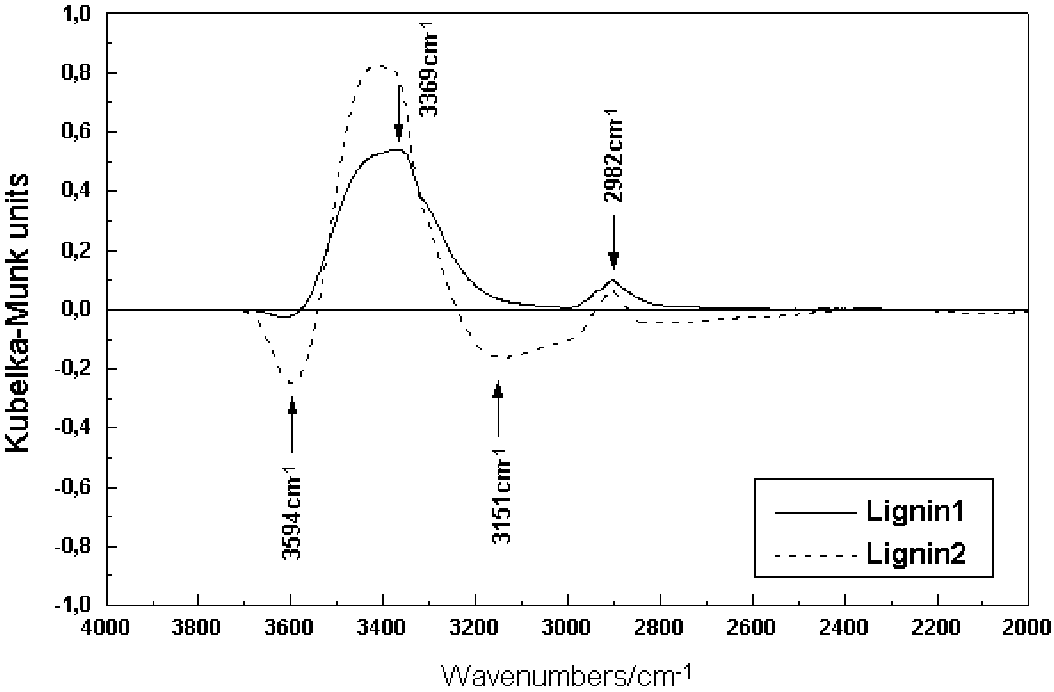

Figure 3a: DRIFT difference spectra of lignin (the range is shown by the horizontal axes).

The results explicitly show that the higher energy has increased the OH band content of lignin. The CH$_n$ valence vibrations are supposed to be stable upon photoirradiation (Forsskahl and Janson 1992). However, we obtained intensity loss at 2915cm^{-1} and 2849cm^{-1} in the spectra of silver maple and not so meaningful increase of intensity at 2982cm^{-1} in lignin (Fig. 3a and Fig. 3b). The later one could be an artifact, which is related to the low resolution in this range, because the CH$_n$ band is not well separated of the increasing OH band. But, in the case of wood it could be due to elimination of CH$_2$OH groups from polysaccharides, and formation of new C=C bonds in photocyclized ring systems (Tolvaj and Faix 1995). The difference spectra for the range of 850-2000cm^{-1} (the „finger print range" of wood and lignin) are shown by Figure 4 for lignin and for silver maple it can be seen from Fig. 2a. The most characteristic differences are, that independently on the energy dose there is no intensity changes in lignin spectra for carbonyl bands, while for the wood the absorption is considerably increased in the range of 1700-1800 cm^{-1}, which means that the number of C=O groups have risen up. Also, the aromatic part did not suffer changes in the lignin, but in the wood a decrease of absorption at 1539cm^{-1} and 1504cm^{-1} appeared, which is attributed to split off the aromatic rings.

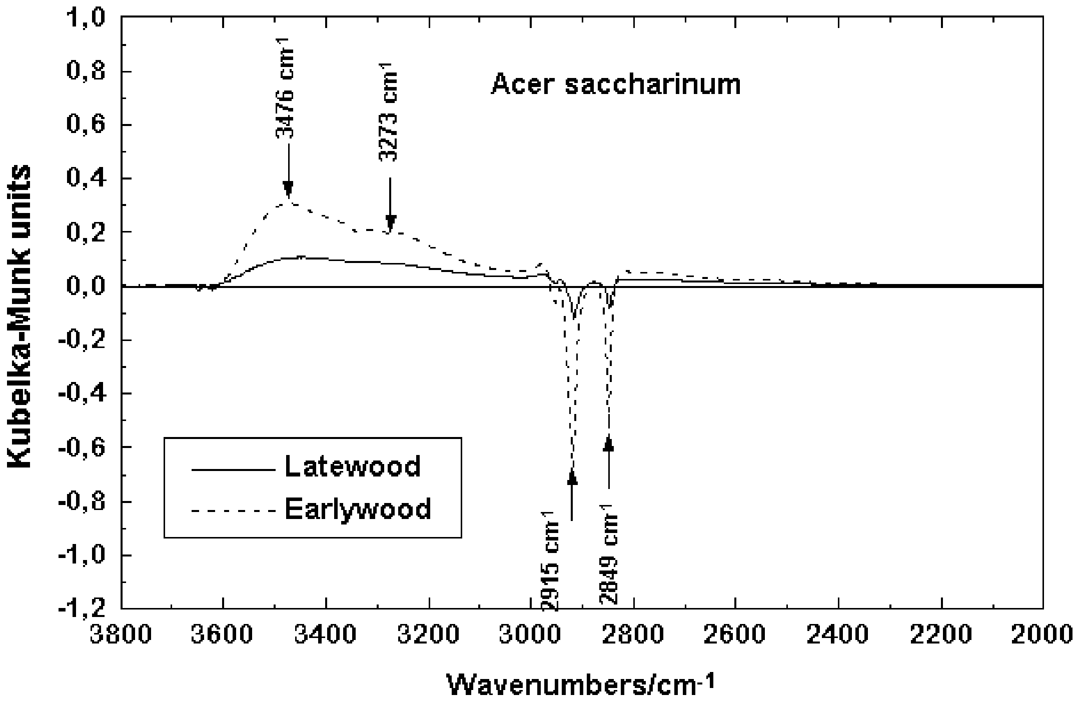

Figure 3b: DRIFT difference spectra of wood (the range is shown by the horizontal axes).

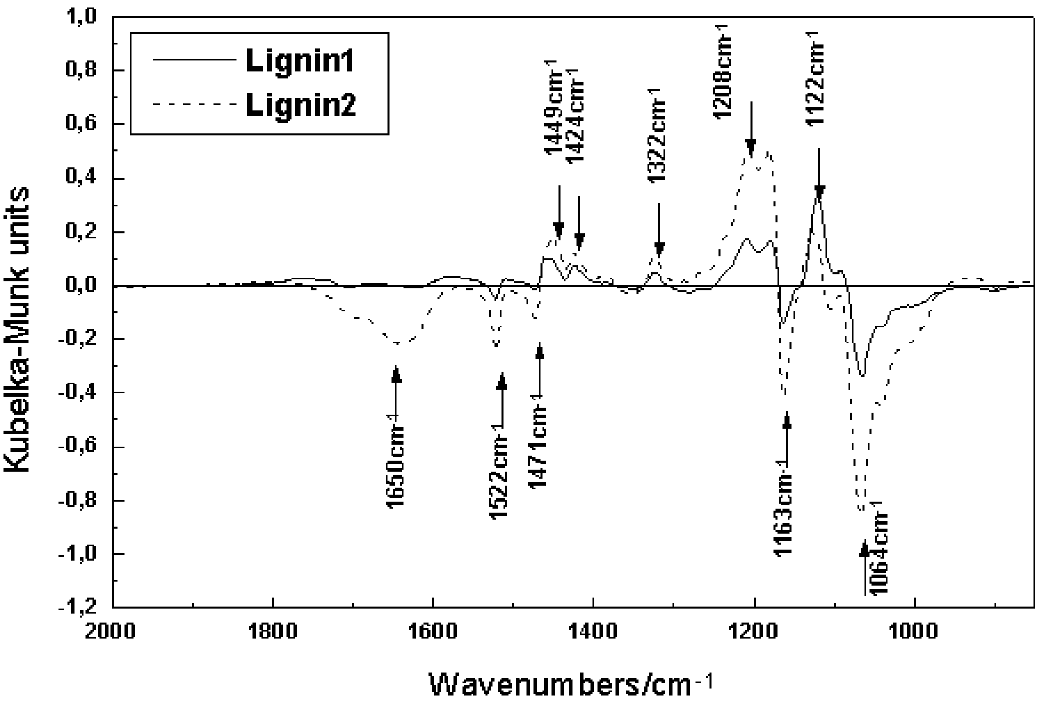

Figure 4a: DRIFT difference spectra of lignin in the „finger print” range.

Changes, which can be compared to wood only in the range of 1000-1300cm^{-1} can be found.

CONCLUSIONS

REFERENCES

Backa, S and A. Brolin. 1991. Determination of pulp characteristics by diffuse reflectance FTIR. Tappi Journal 5. 218-226.

Barta, E.; Tolvaj, L.; Nagy, T.; Szatmáry, S.; Berkesi, O.; Papp, G. 1998a: Wood degradation caused by UV-laser of 248.5 nm wavelength. Holz als Roh- und Werkstoff (accepted)

Barta, E.; Tolvaj, L.; Nagy, T.; Szatmáry, S.; Berkesi, O.; Papp, G. 1998b: Hardwood degradation caused by UV-laser of 248.5 nm wavelength. Wood Structure and Properties '98 3rd International Symposium, Zvolen

Dirckx, O.G.; Masson, D.M.; Deglise, X.M. 1987: Photodegradation du boise, de la cellulose et de la lignine. Wood and Pulping Chemistry Symposium, Paris

Kimura, F., T. Kimura, D.G. Gray. 1994. FT-IR Study of the Effect of Irradiation Wavelength on the Colour Reversion of Thermomechanical Pulps. Holzforschung *48.* 343-348.

Kosikova, B and L. Tolvaj. 1998. Structural changes of lignin-polysaccharide complex during photodegradation of Populus grandis. Wood Research *43*. (1). 37-46.

Nawata,Y, Ochi, K., Shiba, M., Morita, K., Itaka, Y. (1981) Acta Crystallogr., Sect. B, 37. 246-249.

Németh, K.; Faix, O. 1994: Beobachtung der Photodegradation des Holzes durch quantitative DRIFT-Spectroskopie. Holz als Roh- und Werkstoff 52: 261-266.

Stehr, M.; Seltman, J.; Johansson, I. 1998: UV Laser Ablation - An Improved Method of Sample Preparation for Microscopy. Holzforschung 52: 1-6.

Tajmir-Riahi, H.-A.,Agbevavi, J.T. 1993. Carbohydrate interaction with monovalent ions. Carbohydr. Res. 241. 25-35.

Tolvaj, L.; Faix, O. 1995: Artificial Ageing of Wood Monitored by DRIFT Spectroscopy and CIEL*a*b* Colour Measurements. Holzforschung 49: 397-404.