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UV-laser inducted photodegradation of lignin impregnated into cellulose plate

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Summary

Excimer UV-laser was used to investigate the photodegradation of lignin. The effect of irradiation was examined by DRIFT method. The results show that the aromatic part of the lignin units did not suffer changes by UV-laser irradiation. Some C-O linkages between the lignin units and the polysaccharides were destroyed and others were rebuilt.

Introduction

Our best knowledge this is the first occasion when this type of UV-laser used to study the photodegradation of lignin. In our method exactly one wavelength is emitted by the laser in contrast the traditional methods where beside the wide range of UV light considerable amount of visible light and infrared radiation are also emitted. So the result of irradiation by UV-laser must be more identical than the other irradiations, where the results are influenced by other different effects.

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 eight wood species by using of Excimer UV-laser. 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 caused by UV-laser. This method is useful to

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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, Tolvaj and Faix 1995, Pandey and Theagarajan 1997, Kosikova and Tolvaj 1998).

This paper is a preliminary report about the special UV photodegradation of lignin impregnated into cellulose plate.

Further research including also characterisation of structure changes is necessary for elucidation of lignin and cellulose photodegradation during UV-laser irradiation.

Materials and methods

The examined lignin samples were isolated from water prehydrolyzate of beech wood, than it was impregnated into a cellulose plate.

For irradiation a Krypton fluoride Excimer laser was used. The wavelength of the laser beam was 248.5 nm and 15 nanosecond impulse time. The samples were chuffed by 5000 impulse, 10 impulse per second and the energy of the impulse were 20 mJ. The effect of irradiation was examined by DRIFT method. Diffuse reflectance spectra were recorded before and after irradiation using Bio- Rad Digilab FTIR- spectrophotometer. With 4 cm^{-1} resolution 164 interferogramms were collected. 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}.For difference spectroscopy the spectrum of the untreated sample was subtracted from the spectrum of the irradiated one.

Results and discussion

The difference spectra of lignin caused by UV-laser irradiation are plotted in Fig. 1.and Fig. 2. The greatest positive change (absorption increase) was observed in the 3100-3600 cm^{-1} region. This is the absorption area of the hydroxyl groups being in different position. There was a small increase in number of CH_n groups absorbing around 2900 cm^{-1}.

The greatest surprise was that no change was observed at 1510 cm^{-1}, which is the characteristic band of the skeletal vibrations of aromatic ring of lignin. Using traditional UV

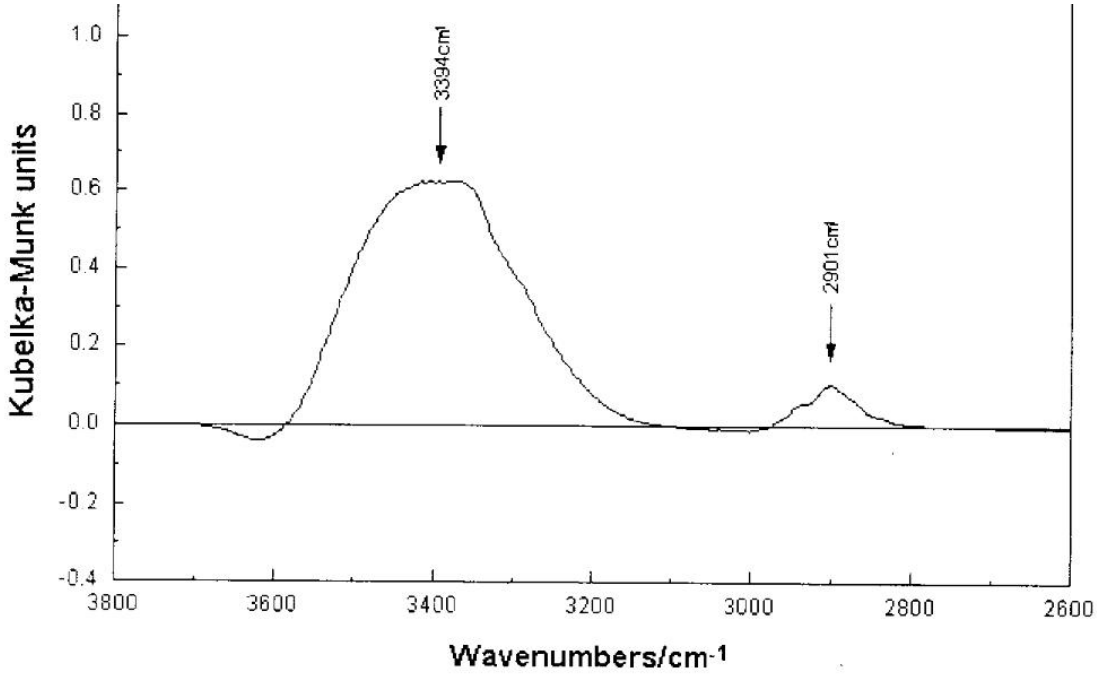

Fig.1. Difference spectrum of the type "irradiated lignin minus blank" in O-H and C-H region

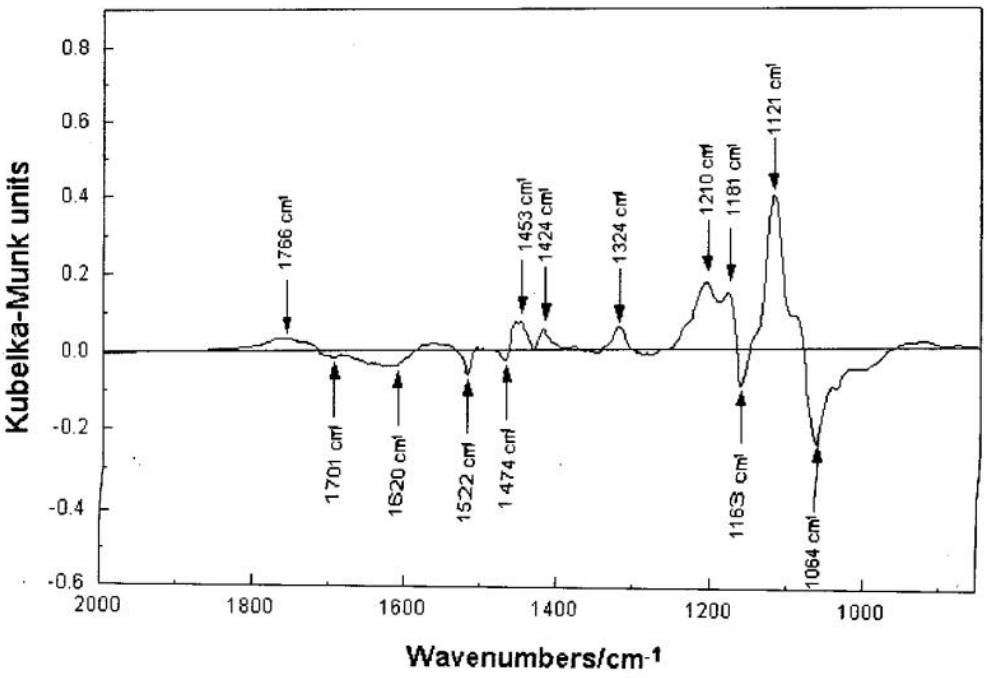

Fig.2. Difference spectrum of the type "irradiated lignin minus blank" in fingerprint region

irradiators the decrease of this peak was always reported in the case of wood, pulp and lignin as well. In contrast we found three characteristic absorption decreases which were observed at UV-laser treatment of solid wood samples too (Barta et al. 1998).These peaks were in that case at 1539, 1465 and 1396 cm^{-1} In Fig. 2 can also observe these negative peeks but the last two are overlapped by an absorption increase. Because of this superposition the maximums are shifted.

In the absorption region of C-O groups it is visible an increase of three absorption bands at 1210, 1181 and 1121 cm^{-1} and two decreases at 1163 and 1064 cm^{-1}. The absorption decrease at 1163 cm^{-1} is overlapped by the both neighbours positive peaks at 1181 and 1121 cm^{-1}. This phenomena could shift the maxima of all three peaks considerably.

The results show that the aromatic part of the lignin units did not suffer changes by UV-laser irradiation. Some C-O linkages between the lignin units and the polysaccharides were destroyed and others were rebuilt. To clear up this changes further chemical investigations are needed which can clarify the change of the number of OH groups as well. The basic material the cellulose also could have suffered changes which will be seen after the irradiation of the pour cellulose by UV-laser. This will be the subject of further investigation.

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Fotodegradation von in Zellstoffplatten getränken Lignin, verursacht durch UV-Laser

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Zusammenfassung

Bei der Untersuchung der Fotodegradation von Lignin wurde Eximer UV-Laser verwendet. Untersucht wurde die Wirkung der Einstrahlung mit der DRIFT-Methode. Die Ergebnisse zeigten, daß der aromatische Teil des Lignins durch die UV-Laser-Behandlung sich nicht veränderte. Einige C-O-Verbindungen zwischen dem Lignin und den Polysacchariden haben sich gelöst, während einige neue Verbindungen entstanden.