

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597282>

FTIR Monitoring of Chemical Changes in Softwood During Heating

Risto A. Kotilainen^a; Timo-Jaakko Toivanen^a; Raimo J. Alén^a

^a Department of Chemistry, Laboratory of Applied Chemistry, University of Jyväskylä, Finland

To cite this Article Kotilainen, Risto A. , Toivanen, Timo-Jaakko and Alén, Raimo J.(2000) 'FTIR Monitoring of Chemical Changes in Softwood During Heating', *Journal of Wood Chemistry and Technology*, 20: 3, 307 – 320

To link to this Article: DOI: 10.1080/02773810009349638

URL: <http://dx.doi.org/10.1080/02773810009349638>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

FTIR MONITORING OF CHEMICAL CHANGES IN SOFTWOOD DURING HEATING

Risto A. Kotilainen, Timo-Jaakko Toivanen, Raimo J. Alén
University of Jyväskylä, Department of Chemistry,
Laboratory of Applied Chemistry, P.O. Box 35, FIN-40351,
Finland

ABSTRACT

A multivariate chemometric method for monitoring the mass loss of Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) by IR spectroscopic determination of chemical changes occurring during the heat treatment (160 - 260 °C, 2 - 8 h) of these wood materials was developed. The method was based on the handling of FTIR data on treated and untreated wood powder samples by the partial least squares (PLS) method. In addition, unknown samples (treated and untreated pine and spruce) were classified into separate groups by the principal component analysis (PCA) method. The chemical changes occurring in the wood samples during heating were also briefly discussed.

INTRODUCTION

It has been established^{1,2} that heating of wood at low temperatures (160 - 260°C) enhances its ability to resist biological stress caused by fungi. In addition, the dimensional stability of wood increases in the course of heat processing. The commercial production of heat-treated wood, carried out mainly in several small-

volume production units, has gradually increased during the last decade in Finland. As a result of this trend an increasing need for developing suitable ways of monitoring the heat-treatment process has also emerged. One potential method would be to observe the chemical changes that take place in wood material during treatment. Since there exists a clear correlation between the mass loss of the dry matter of wood feedstock and the beneficial properties (*e.g.*, an increased stability of wood against fungal attacks and dimensional changes) of the heat-treated product,² it was further concluded that the correlations between mass loss and easily detectable chemical changes in wood present the interesting possibility of developing a proper control method. Such an approach would also avoid the difficulty of measuring the accurate mass loss in feedstock (often with varying moisture content) under process conditions, thus revealing the simultaneous possibility of controlling product quality.

The main constituents of wood consist of carbohydrates (cellulose and hemicelluloses) and lignin together with a minor proportion of extractives and inorganics.^{3,4} When subjecting wood to heating, a multitude of chemical reactions in the individual wood constituents take place. Our earlier studies⁵⁻⁷ have focused on the thermochemical degradation of the chemical components of Norway spruce (*Picea abies*), Scots pine (*Pinus sylvestris*), and silver birch (*Betula pendula*) under conditions relevant to the technical processes of introducing suitable properties into these wood feedstocks.

Vibrational spectroscopy has been shown to be a rapid method for indicating different chemical bonds and thus different functional groups. On the basis of this fact, many FTIR and Raman studies on lignocellulosic materials (wood, pulp, MWL, etc.) have been published.⁸⁻¹²

On the other hand, multivariate analysis has been used to handle the spectral data on wood samples.¹³⁻¹⁶ Methods such as multiple linear regression (MLR), partial least squares (PLS), and principal component analysis (PCA) have proved to be useful for this purpose.

The purpose of this study was to develop a rapid and reliable method of determining the mass loss of heat-treated wood on the basis of the FTIR reflectance spectra from wood powder. A prerequisite for the use of this kind of method is the adequate calibration of the statistical model by previously well-characterized samples.

EXPERIMENTAL

Wood samples and heat treatments

The wood feedstocks used were boards (approximate dimensions (4 cm x 4 cm x 20 cm) of moisture-stabilized (65 % RH) and bark-free Scots pine (*Pinus sylvestris*) (14 samples) and Norway spruce (*Picea abies*) (23 samples).

The heat treatments were carried out at the Technical Research Centre of Finland (VTT), Sections of Building Technology and Energy. The treatment systems consisted of a temperature-controlled furnace in which the wood boards were disposed such that each board had a sufficient space around it and held under a steam (pine boards, 160 - 230 °C) or nitrogen (spruce boards, 160 - 260 °C) atmosphere for 2-8 h. Each feedstock sample was treated separately. As judged by the naked eye without any optical aids the brownish color was in each case evenly distributed within the feedstock material. The mass losses of the treated samples (12 pine samples and 22 spruce samples) are presented in TABLE 1.

For the chemical analysis, all samples were ground in a Cyclotec 1093 sample mill (Tecator, Inc.) and the < 1 mm fraction was used.

Analytical determinations

The FTIR(Fourier transform infrared)/DRIFT(diffuse reflectance infrared Fourier transform) measurements were performed in each case from a homogenized mixture

TABLE 1
Mass Loss of the Heat-Treated Wood Samples (% of the Sample Dry Solids)*

Pine (P)		
5.5	9.5	12.5
7.6	10.1	13.1
8.3	11.1	13.5
9.4	11.9	14.4
Spruce (S)		
1.0	3.7	10.2
1.7	4.9	12.0
2.4	5.4	12.5
2.6	6.2	13.9
3.0	6.3	19.7
3.0	7.5	27.5
3.1	7.9	
3.2	8.3	

* Symbols for the untreated samples were P0 (two samples) and S0 (one sample).

of wood powder and KBr, the corresponding mass proportion being 1:9. The analysis was carried out with a Nicolet Magna-IR 550 Series II FTIR spectrometer in the wavenumber range 400 - 4000 cm^{-1} . In each measurement 128 scans were accumulated at 4 cm^{-1} resolution and analyzed with a cosine function prior to the Fourier transformation. The interferograms were Happ-Genzel apodized and the resulting spectra were stored in the absorbance scale (Fig. 1). To obtain the background contribution, the KBr spectrum was measured for automatic background subtraction.

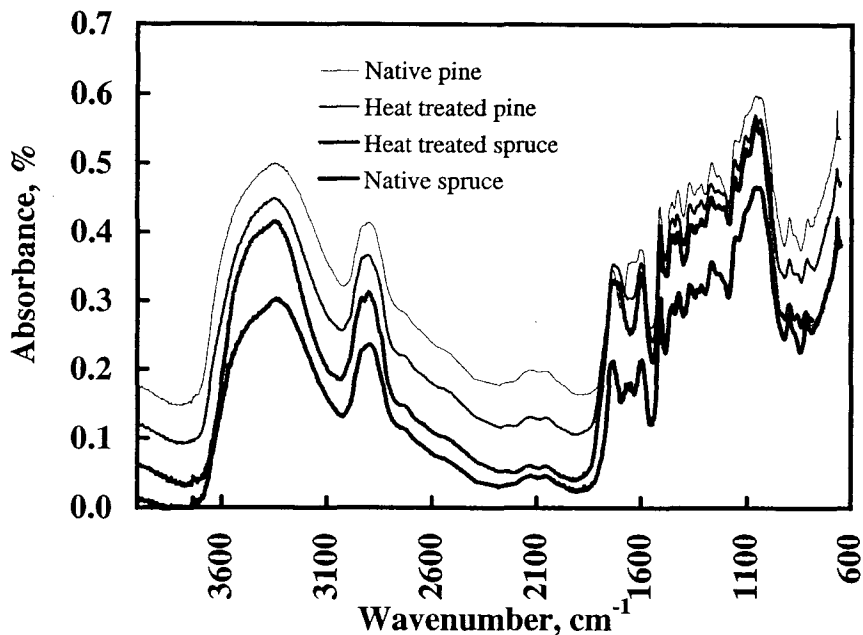


FIGURE 1. Examples of FTIR spectra of the treated and untreated samples.

In addition, the absorbance peaks of water (*i.e.*, air humidity) were eliminated by measuring first the DRIFT spectrum of the empty sample chamber and then subtracting this spectrum from that of the sample mixture. An OMNIC software program by Nicolet was used to determine the peak positions and intensities.

Multivariate data analysis was carried out by using Matlab for Windows 4.2c.1 software (Mathworks, Inc.) and data analysis toolbox (ProfMath Inc). For PLS analysis, 37 samples consisting of pine and spruce were divided into a calibration set (19) and a validation set (18). The spectra were Kubelka-Munk-transformed (Equation 1), centered, and scaled to unit variance before the PLS analysis. Selection of the spectral variables for PLS calibration was performed by calculating squared correlation coefficients (R^2) between the measured mass losses and the spectral

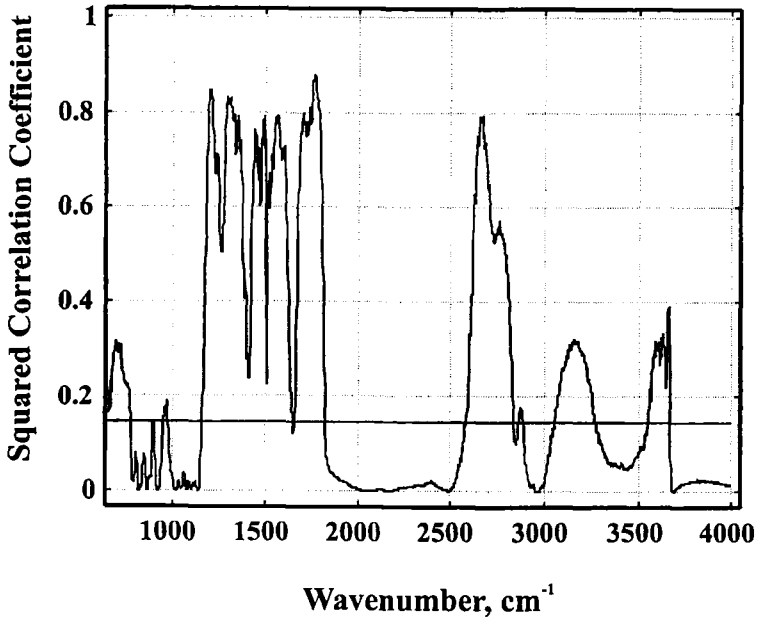


FIGURE 2. Squared correlation coefficient between the spectral intensities and the mass losses of the samples. Spectra were Kubelka-Munk-transformed and normalized before analysis. Best PLS calibration was obtained by selecting spectral variables with correlation coefficients over 0.145.

intensities (Fig. 2). The best PLS calibration was obtained by selecting spectral variables with correlation coefficients greater than 0.145. The prediction ability was tested with the independent validation set.

$$F(R_{\infty}) = \frac{K}{S} = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \quad [1]$$

where $F(R_{\infty})$ is intensity in Kubelka-Munk units, s scattering coefficient, k absorption coefficient, and R_{∞} percentage of reflectance.

RESULTS AND DISCUSSION

General changes in spectral data

TABLE 2 shows the assignments of various absorption bands in the region 800 - 4000 cm^{-1} for the wood samples. The straightforward interpretation of the spectral data was not easy due to the complex nature of wood and the multitude of chemical reactions taking place in the individual wood constituents (cellulose, hemicelluloses, lignin, and extractives) during heating. In addition, in IR spectroscopy one chemical component may absorb at several frequencies and, on the other hand, two or more components may contribute to the same absorption band.

Carbohydrates

The opening of pyranose rings of cellulose and hemicelluloses was seen as a decrease in absorption at 895 cm^{-1} (TABLE 2).¹⁷ The increase in absorption at 1060 cm^{-1} indicated the formation of aliphatic alcohols during heating.⁸ The band observed at around 1700-1730 cm^{-1} has earlier been reported¹⁹ to be the absorption of carbonyl stretching of ester and carboxyl groups which are the most abundant in wood hemicelluloses. In spite of earlier findings⁸, in this study no straightforward explanation for the increase in absorbance (with an increasing mass loss) at 1730 cm^{-1} could be given. The same phenomenon has been reported in several studies (*cf.*, refs.^{20,21}). In wood the source of carboxyl groups are the primary hydroxyl group of the pyranose ring in carbohydrates and the primary hydroxyl and aldehyde groups in lignin.⁸

Lignin

The absorption at 855 cm^{-1} originated from aromatic C-H out-of-plane deformation in guaiacyl-type lignin. A small increase in the absorption band at 1030

TABLE 2
Assignment of Diffuse Reflectance Infrared Fourier Transform Absorption Bands
in the Region 809 - 3600 cm^{-1} for the Heat-Treated Samples

Wavenumber, cm^{-1}	General trend, with an increasing mass loss	Remarks*
809	decreases	mainly vibration of mannan and C-H out-of-plane bending vibration in lignin. ²²
855	decreases	aromatic C-H out-of-plane deformation (guaiaacyl-type lignin) ¹⁸
895	decreases	C ₁ -carbon in hemicelluloses and in cellulose (pyranoid ring) ¹⁷
1030	increases	C-O deformation in aliphatic alcohols and ethers, symmetric C-O-C stretching of dialkyl ethers, aromatic C-H deformation in plane ²³
1060	increases	C-O deformation in aliphatic alcohols and ethers (carbohydrates) ¹⁸
1110	increases	OH association (cellulose) ¹⁷
1160	increases	C-O-C symmetric stretching ^{17,24}
1205-1210	increases	OH-bending (cellulose), aryl aldehyde, α - and β -unsaturated aldehyde, lactones, phenols, diarylethers ²⁵
1234	increases	alkyl-aryl-ether bonds, lactones ^{23,25}
1268	increases	esters, phenols ²³
1330	increases	phenol group ^{23,26}
1370	increases	C-H bending, -CH ₃ (lignin), -CH ₂ (carbohydrates), LCC(lignin carbohydrate complexes) bonds ^{17,27}
1426	increases	aromatic skeletal vibrations (lignin) and C-H deformation in plane (cellulose) ^{17,24,28}
1450	increases	C-H bond, extractives, O-H in plane deformation(cellulose) ²⁸
1510	increases	aromatic skeletal vibrations (lignin) ²⁹
1600	increases	aromatic skeletal vibrations, affected by aromatic C-O stretching mode and by conjugation with α -carbonyl groups ^{17,24}
1650	decreases	conjugated double bonds, ⁹ Adsorbed water. ²⁸
1700-1730	increases and the peak broadens to lower wavenumbers	carboxyl- and ester groups, nonconjugated aldehyde ^{8,22}
2000-2150	decreases	overtone of fundamental C-OH stretchings at 1000-1070 cm^{-1} (cellulose) ²⁵
2800-2910	decreases	C-H stretching ²³
3340-3375	decreases	O-H stretching, hydrogen bonded OH-groups ³⁰
3600	decreases	stretching of free OH-groups ²³

* Literature reference was included only in the cases typical for wood constituents.

cm^{-1} was probably caused by the pronounced aromatic nature of the heat-treated product⁵, since this absorption band also indicates aromatic C-H deformation in plane.¹⁸ Two absorption maxima detected at 1268 cm^{-1} and 1234 cm^{-1} originated from the $\text{C}_{\text{aryl}}\text{-O}$ structures in guaiacyl-type lignin.³¹ As an overall trend these peaks seemed to rise slightly during treatment. The increasing peak at 1330 cm^{-1} has been reported²⁶ to originate from phenolic hydroxy groups, which were the main functional groups formed from lignin in the temperature range used. The absorption bands at 1426 cm^{-1} , 1510 cm^{-1} , and 1600 cm^{-1} indicated aromatic skeletal vibrations.¹⁸ The increase in absorption at these wavenumbers was mainly due to the increase in relative lignin content in the heat-treated samples.⁵ Various explanations are offered in the literature for the absorption at about 1650 cm^{-1} . Morohoshi²⁸ reported that the absorption bands at 1630 cm^{-1} , 1650 cm^{-1} , and 1720 cm^{-1} were caused by the adsorbed water molecules on cellulose. Furthermore, an absorption band at 1650 cm^{-1} also indicated the amount of conjugated double bonds. A further possible explanation for the decrease in this absorption was the formation of diphenylmethane structures by the condensation of lignin during heating.⁹

PCA method and PLS calibration

As can be seen from Figs. 3 and 4 the mass loss of pine and spruce samples during heating were predicted with reasonable accuracy by the PLS calibration model. The correlation coefficient (R^2) for the calibration set was 0.960 and the correlation coefficient (R^2) for the validation set was 0.894 (6 dimensions included). Although the present results were promising, further work remains to be done with different wood species and under different processing conditions.

It was possible to identify the two wood species by the PCA method on the basis of the spectral data. It was also possible to classify wood samples into typical subgroups by the PCA method on the basis of FTIR data. When the second principal component (PC2) was plotted against the third principal component (PC3), the

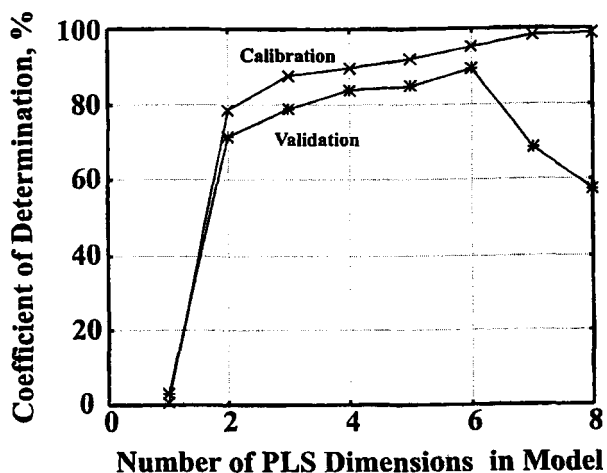


FIGURE 3. Coefficients of determination in different PLS dimensions for calibration and validation sets.

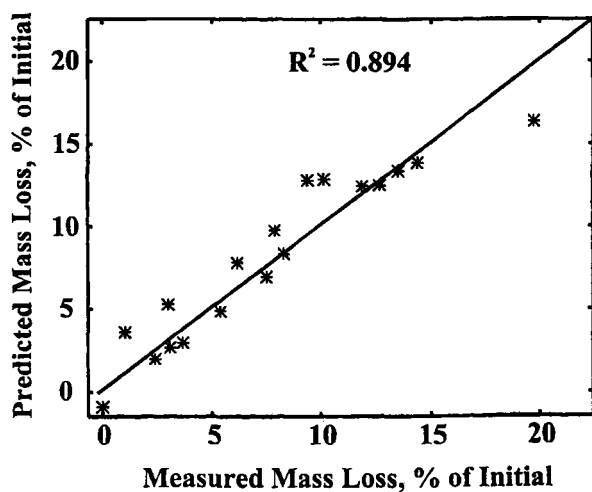


FIGURE 4. Measured mass loss vs. predicted mass loss.

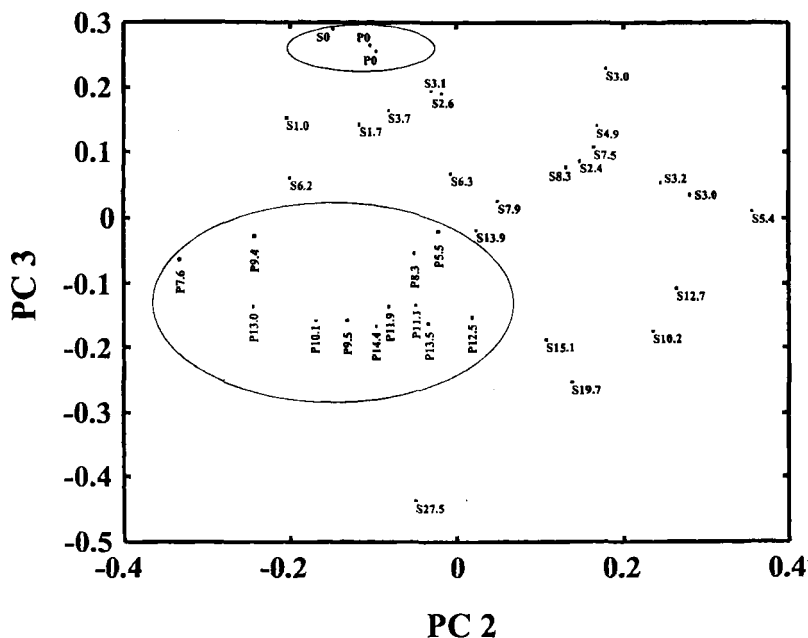


FIGURE 5. Classification of the pine and spruce samples according to the PCA model. For abbreviations, see TABLE 1.

samples were classified into i) feedstock, ii) heat-treated pine, and iii) heat-treated spruce subgroups (Fig. 5).

CONCLUSIONS

The FTIR spectroscopic method used here seems to have a potential for determining rapidly and accurately the mass loss of wood feedstock during heat treatment at temperatures of 160 - 260 °C. In the method the mass loss is obtained from the PLS calibration on the basis of the spectral data. The prerequisite for

constructing a suitable model in each case is the representative samples of heat-treated wood with a known mass loss and IR spectral data.

ACKNOWLEDGEMENTS

Financial support from The Foundation of Natural Resources in Finland (Suomen Luonnonvarain Tutkimussäätiö) is gratefully acknowledged. The authors wish to thank research professor Pertti Viitaniemi and research scientist Saira Jämsä, both from the Technical Research Centre of Finland (VTT), Building Technology, and research scientist Vesa Arpiainen from VTT, Section of Energy for kindly providing the heat-treated wood samples. Special thanks are due to Mrs. Marja Salo for her skillful assistance with the elemental analysis.

REFERENCES

- 1 D. Dirol and R. Guyonnet 1993, the International Research Group on Wood Preservation, Section 4 - Process. Proc. 24 Annual Meeting in May 16 - 21, 1993, Orlando, USA, 1.
- 2 P. Viitaniemi and S. Jämsä, Modification of Wood With Heat Treatment, 57 p., VTT Research Report Publications 814, Espoo, Finland, 1996 (In Finnish).
- 3 D. Fengel and G. Wegener, Wood: Chemistry, Ultrastructure, Reactions, p. 26 - 344, Walter de Gruyter, Berlin, Germany, 1989.
- 4 E. Sjöström, Wood Chemistry - Fundamentals and Applications, 2. edn., p. 1-113, Academic Press, San Diego, USA, 1993.
- 5 R. Alén, R. Kotilainen and A. Zaman, Wood Sci. Technol. (In press).
- 6 A. Zaman, R. Alén and R. Kotilainen, Wood Fib. Sci. (In press, 2000).
- 7 R. Kotilainen, R. Alén and V. Arpiainen, Pap. Puu., 81, 384(1999).
- 8 S.-Z. Chow, Wood Sci. Technol., 2, 27 (1971).

- 9 M. Funaoka, T. Kako and I. Abe, *Wood Sci. Technol.*, **24**, 277 (1990).
- 10 S. Backa and A. Brolin, *Tappi J.*, **74**, 218 (1991).
- 11 A.J. Michell, *Appita*, **47**, 29 (1994).
- 12 U.P. Agarwal, R.H. Atalla and I. Forsskåhl, *Holzforschung*, **49**, 300 (1995).
- 13 T. Schultz, M. Templeton and G. McGinnis, *Anal. Chem.*, **57**, 2867 (1985).
- 14 T. Schultz and D. Burns, *Tappi J.*, **73**, 209 (1990).
- 15 L. Wallbäcks, U. Edlund, B. Nordén and I. Berglund, *Tappi J.*, **74**, 201 (1991).
- 16 L. Schimleck, P. Wright, A. Michell and A. Wallis, *Appita*, **50**, 40 (1997).
- 17 M.-L. Kuo, J.F. McClelland, S. Luo, P.L. Chien and R.D. Walker, *Wood Fiber Sci.*, **20**, 132 (1986).
- 18 O. Faix, In *Methods in Lignin Chemistry*, Chap. 4.1, S.Y. Lin and C.W. Dence (eds.), Springer-Verlag, Berlin, Germany, 1992.
- 19 T.E. Timell, In *Advances in Carbohydrate Chemistry and Biochemistry*, Vol. 20, p. 409-483, M.L. Wolfrom (ed), Academic Press, New York, 1965.
- 20 M.M. Tang and R. Bacon, *Carbon* **2**, 211 (1964).
- 21 F. Teratani and K. Miyazaki, *J. Japan Wood Res. Soc.*, **14**, 91 (1968).
- 22 K.J. Harrington, H.G. Higgins and A.J. Michell, *Holzforschung*, **18**, 108 (1964).
- 23 N.B. Colthup, L.H. Daly and N.B. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3. edn., 547 p., Academic Press, San Diego, USA, 1990.
- 24 H.L. Hergert, In *Lignins - Occurrence, Formation and Reactions*, p. 267-297, K.V. Sarkanen and C.H. Ludwig (eds.), Wiley Interscience, New York, USA, 1971.
- 25 W. Kemp, *Organic Spectroscopy*, 393 p., Macmillan Education Ltd., Hong Kong, 1991.
- 26 K.V. Sarkanen, H-M. Chang and E. Bernt, *Tappi*, **50**, 572 (1967).
- 27 A. Nagaty, O.H. El-Samyr, S.T. Ibrahim and O.Y. Mansour, *Holzforschung*, **36**, 29 (1982).

- 28 N. Morohoshi, In Wood and Cellulosic Chemistry, p. 331-392, D.N.-S. Hon and N. Shiraishi (eds.), Marcel Dekker, New York, USA, 1991.
- 29 O. Faix, R. Patt and O. Beinhoff, Das Papier., 41, 657 (1987).
- 30 T. Kondo, Cellulose, 4, 281 (1997).
- 31 W.E. Collier, T.P. Schultz and V.F. Kalasinsky, Holzforschung, 46, 523 (1992).