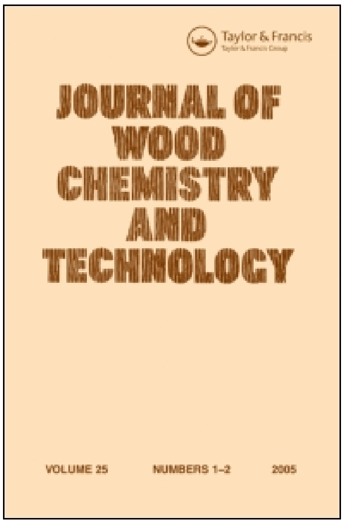
This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Ftir Spectra of Milled Wood Lignins and Lignin Polymer Models (DHP's) with Enhanced Resolution Obtained by Deconvolution

O. Faix[a]; O. Beinhoff[a]
[a] Federal Research Center for Forestry and Forest Product. Institute for Wood Chemistry and Chemical Technology of Wood Leuschnerstrasse 91, Hamburg 80, Federal Republic of Germany

To cite this Article Faix, O. and Beinhoff, O.(1988) 'Ftir Spectra of Milled Wood Lignins and Lignin Polymer Models (DHP's) with Enhanced Resolution Obtained by Deconvolution', Journal of Wood Chemistry and Technology, 8: 4, 505 — 522

To link to this Article: DOI: 10.1080/02773818808070698

URL: http://dx.doi.org/10.1080/02773818808070698

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.

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 8(4), 505-522 (1988)

FTIR SPECTRA OF MILLED WOOD LIGNINS AND LIGNIN POLYMER MODELS (DHP's) WITH ENHANCED RESOLUTION OBTAINED BY DECONVOLUTION

O. Faix and O. Beinhoff
Federal Research Center for Forestry and Forest Product. Institute for Wood Chemistry and Chemical Technology of Wood
Leuschnerstrasse 91, D-2050 Hamburg 80,
Federal Republic of Germany

Downloaded At: 13:17 25 January 2011

ABSTRACT

FTIR spectra of spruce, beech, and bamboo MWL's, representing G, GS and HGS lignins, were recorded and examined in the wavenumber range of 1800 to 700 cm^{-1}. The spectra were then submitted to a mathematical self-deconvolution technique in order to resolve the intrinsically overlapped bands. The same procedure was carried out with the IR spectra from two G and two GS dehydrogenation polymers (DHP's) prepared by the "zutropf" (ZT) and "zulauf" (ZL) polymerization method. Thus, approx. 30 bands typical for lignins and lignin-like polymer models were detected in contrast to standard spectroscopic conditions, which render visible 15 to 17 broad bands. Hidden bands, usually visible as shoulders, came to light, i.e. the apparent resolution was increased considerably by deconvolution. The deconvolved spectra are standardized and depicted in the absorption mode together with the original spectra. The wavenumbers and intensities of 54 bands apparent after deconvolution are compiled in a Table to render possible a direct comparison of the IR characteristics of lignins and DHP's. A difference spectrum obtained by subtraction of a G ZT DHP spectrum from a spruce MWL spectrum illustrates the differences between these polymers.

Copyright © 1988 by Marcel Dekker, Inc.

INTRODUCTION

IR spectroscopy is a useful method for a rapid and convenient characterization of small wood samples and its major components. Using micro-methods the sample weight can be reduced below 0.1 mg. The importance of IR spectroscopy in the field of lignin chemistry was already recognized in the fifties. Early efforts and the pioneering publications of Kawamura and Higuchi on lignin classification by IR-spectroscopy[1], and of Sarkanen et al. on quantification of IR-spectroscopic data[2,3,4] in the sixties were reviewed by Hergert[5], who wrote without knowing of the renaissance of IR spectroscopy[6] a few years later: "..., infrared spectroscopy is a relatively old technique, but it is also a dynamic one that offers much promise for the future." Indeed, the advent of FTIR spectroscopy in the seventies and the possibility of post-spectroscopic standardization and "manipulation" of IR widened the perspectives for classical IR spectroscopy: The quantitative evaluation of IR data is more reliable with equipment of the new FTIR generation than with dispersive IR spectrometers, and now it is routine to use IR libraries with automatic search programs. Therefore, it is amazing that quantitative evaluation of FTIR spectroscopic data of wood[7], lignins[7,8,10], lignin polymer models[9], and pulp and papers[12-14] was not reported until 1985. A more comprehensive study was finished recently on quantitative FTIR spectroscopy on lignins and lignin polymer models using the multiple linear regression approach[11].

When interpreting IR spectra of lignins, one should recall an important comment of Hergert[5]: "..., the most common error is to conclude that two or more lignin products are "identical" because their infrared spectra are "similar". Rather, the opposite must be true, i.e., if the spectra are not precisely identical, it must be concluded that the products are not identical." As a matter of fact, small details are very important in the interpretation of IR-spectra of lignins.

Downloaded At: 13:17 25 January 2011

To visualize small details in band shapes and "hidden" unresolved band components two methods can be applied: differentiation and deconvolution[15-17]. Both permit the user to reduce computationally broad spectral bandwidths and are frequently referred to as resolution enhancement techniques. Mathematical backgrounds and practical consequences of differentiation and deconvolution were explained in the literature quoted above. It was pointed out by these authors that the sensitivity to noise is identical in both methods. The original band position is equally retained, whereas the integrated band intensity is retained only in the case of deconvolution. Peak heights are changed in both techniques. Bandwidths are also lost after deconvolution but the relative bandwidths are retained using mathematic derivation. However, the interpretation of the first derivation of lignin IR spectra is difficult because they do not resemble the original. Higher derivation spectra are distorted by large lobes.

On the other hand, deconvolved spectra are very clear and similar to the original. Deconvolution allows the spectroscopist to determine the number of individual components contributing to a superimposed band. This technique works in the interferogram as well as in the spectral domain and should not be confused with spectral simulation, which works only in the spectral domain. (Spectral simulation tries to detect the individual lines as parts of a superimposed band by optimization.) Only small lobes and undesirable artifacts can be observed when appropriate spectra with low noise and, if necessary, smoothing techniques are used. (In the case of low signal to noise ratio deconvolution will also increase the noise, a fact which makes the interpretation of spectra difficult.) Therefore, this paper deals exemplarily with deconvolved FTIR spectra. Derivative IR spectroscopy will be the subject of another publication. Three MWL's, which represents G, GS, and HGS lignins, are the focus of this paper. (The abbreviations H, G, and S refer to 4-hydroxy-phenylpropane,

Downloaded At: 13:17 25 January 2011

guaiacylpropane, and syringylpropane units of lignins.) Lignin polymer models (dehydrogenation polymers = DHP's)[18] were also included in this study because such preparations play an important role in understanding of lignin structures and of the polymerization of lignin precursors. Spectra of two G and GS DHP's, prepared each by "zutropf" (ZT) and "zulauf" (ZL) polymerization methods, will be discussed. (ZT is synonym for continuous and ZL for discontinuous polymerization methods.)

EXPERIMENTAL

MWL's from Picea abies L. (spruce), Fagus sylvatica L. (beech) and Bambus sp. (bamboo) were isolated by standard procedures according to Björkman's method[19]. Molecular weight determination were done by HPLC[20] using polystyrene standards for calibration. ZT and ZL DHP's were prepared[9] in phosphate buffer at pH 6.8 using the system "horseradish peroxidase/H_2O_2" for dehydrogenation; polymerization time 6 d. Experimental details for these procedures and those for preparative fractionation of DHP's on a Sephadex LH 60 column by methylcellosolv as solvent are described in the literature[21]. The samples described here were taken from batches of preparative fractionation with identical retention volumes. Consequently, the DHP's have similar molecular weights. The analytical and IR spectroscopic data from the G DHP's were already described[9], but the formula are repeated in Table 1 together with those of GS DHP's and the MWL's.

The standard KBr technique (0.7mg lignin/300mg KBr) was applied for spectroscopy. A BioRad Digilab FTS40 FTIR spectrometer was used for collecting the interferograms and BioRad software was used for deconvolution. Detector: DTGS/KBr; Resolution: 4 cm^{-1}; Number of scans: 64; Apodization: triangular; Bandwidth for deconvolution: 15 cm^{-1}. Spectra and deconvolved spectra were standardized in such a way that the absorption of the highest band was equal to 1.0.

Downloaded At: 13:17 25 January 2011

TABLE 1

Analytical Data of the Samples Investigated

	C_{900} formula								mol %		
	H	O	OMe	$\bar{M}_w$	$\bar{M}_n$	Disp.	DBE*	Degr. of Dehyd.▪	H	G	S
SPRUCE MWL	821	276	97	6750	3000	2.25	442	- 82	06	92	<02
BEECH MWL	779	277	146	9400	4800	1.69	439	- 75	00	54	46
BAMBOO MWL	778	279	103	2200	1000	2.20	461	-119	20	67	13
DHP G ZT	736	260	103	1100	810	1.36	481	-161	00	100	00
DHP G ZL	749	239	101	1000	760	1.30	476	-150	00	100	00
DHP GS ZT	785	260	175	1170	1035	1.13	421	-40	00	25	75
DHP GS ZL	737	253	174	1160	1065	1.10	446	-89	00	26	74

• DBE: Double Bound Equivalent ((Number of C*2 + 2)-Number of H)÷2

▪ Degree of Dehydrogenation = 1000 - (H/C_{900} + OMe/C_{900})
Calculations, see Lit.[11]

Downloaded At: 13:17 25 January 2011

RESULTS AND DISCUSSION

Effect of deconvolution

In Fig. 1 the IR spectra of the MWL's are shown before and after deconvolution. Fig. 2 displays the spectra of G and GS DHP's in the same way, comprising the ZT and ZL variants of these polymers. The deconvolved spectra (hatched area) display more fine structure and demonstrate the effects of this technique. Narrow bands sharpen up, and shoulders or points of inflection become peaks. The broader the line, the less the effect of deconvolution. Many superimposed bands were separated, although some of them to a minor extent. One gets the impression of an essentially higher spectral resolution. The operator is able to influence the grade of deconvolution by the parameter "bandwidth": the higher the bandwidth setting the better the artificial enhancement of resolution. On the other hand, there are limits for increasing the beneficial effects of this method. Noisy spectra leads to artifacts when the parameter "band-width"

Downloaded At: 13:17 25 January 2011

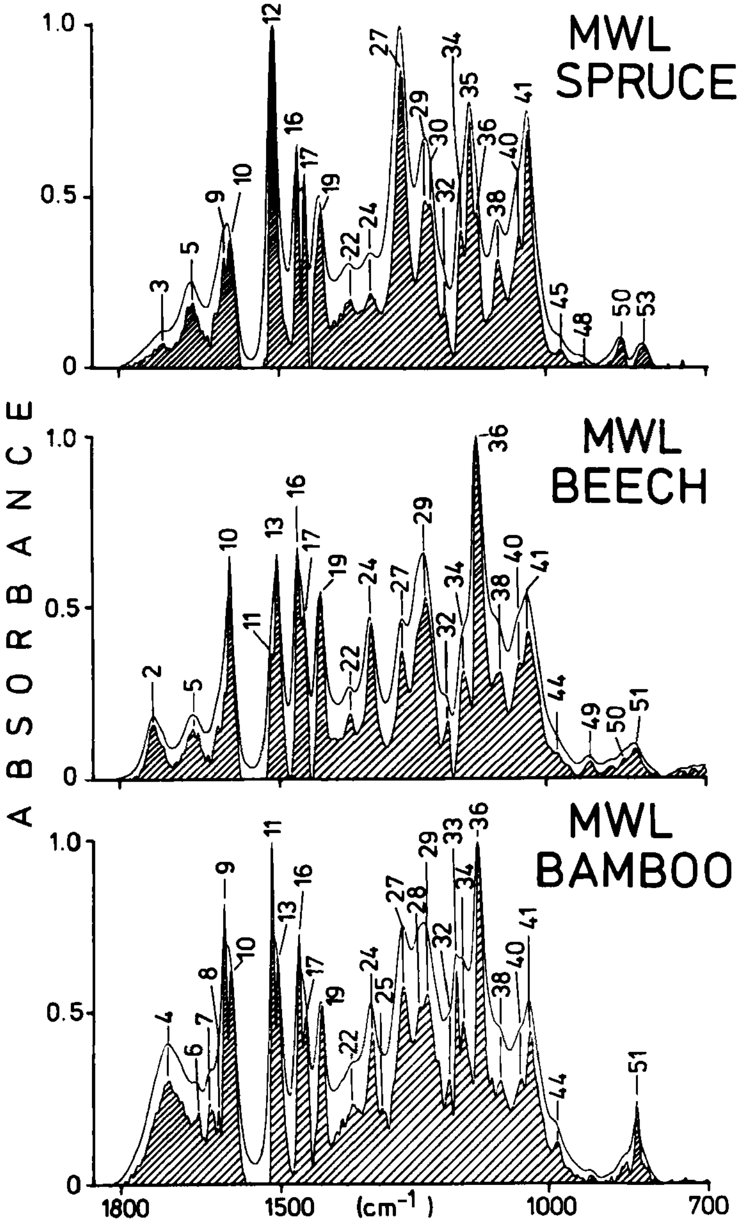


FIGURE 1. FTIR spectra from 3 MWL's before and after deconvolution. (Hatched area: deconvolved spectra.)

Downloaded At: 13:17 25 January 2011

is to high. Besides, deconvolution is achieved in any case by sacrificing the signal to noise ratio. Spectral artifacts, positive and negative sidelobes can also be enhanced. In Figs. 1 and 2 some noise can be seen in the range of carbonyl bands between 1750 and 1660 cm^{-1}, probably due to residual vapor present in the equipment. The vapor lines, increased by deconvolution, appear as noise after deconvolution. However, this effect is very small. Thus, the vapor was succesfully eliminated and the bandwith setting (15 cm^{-1}) was approximatelly right. (The maximal possible value is 21.) No smoothing, neither before nor after deconvolution, was necessary.

As the Figures demonstrate, there are approx. 54 bands in the 1800 - 700 cm^{-1} region for the seven polymers (most of them are common) after deconvolution, instead of 15 to 17 bands visible under standard spectroscopic conditions. Bamboo MWL and the GS DHP's display the most complex spectra with ca. 27 deconvolved bands. (For comparison: monomeric and dimeric lignin model compounds show in general 20 to 30 spectral bands with 4 cm^{-1} resolution.) Table 2 is a compilation of quantitative IR spectroscopic data derived from deconvolved spectra. To each "true" band (marked with a *) the exact wavenumber and the band intensity from the standardized spectrum is given. In special cases of broad bands the intensities from the shoulders are also reported to render possible comparisons between samples, even if they do not have common maxima in the same wavelength range. On the right side of Table 2 the average wavenumbers are listed. These values are reported in the discussion below of the positions of the bands.

Comparison of the MWL spectra before deconvolution

It is beyond the scope of this paper to give a detailed review on spectral characteristics of G, GS, and HGS lignins. Only the most remarkable differences between the original spectra in Fig. 1 are briefly noted, in order to make understandable the

Downloaded At: 13:17 25 January 2011

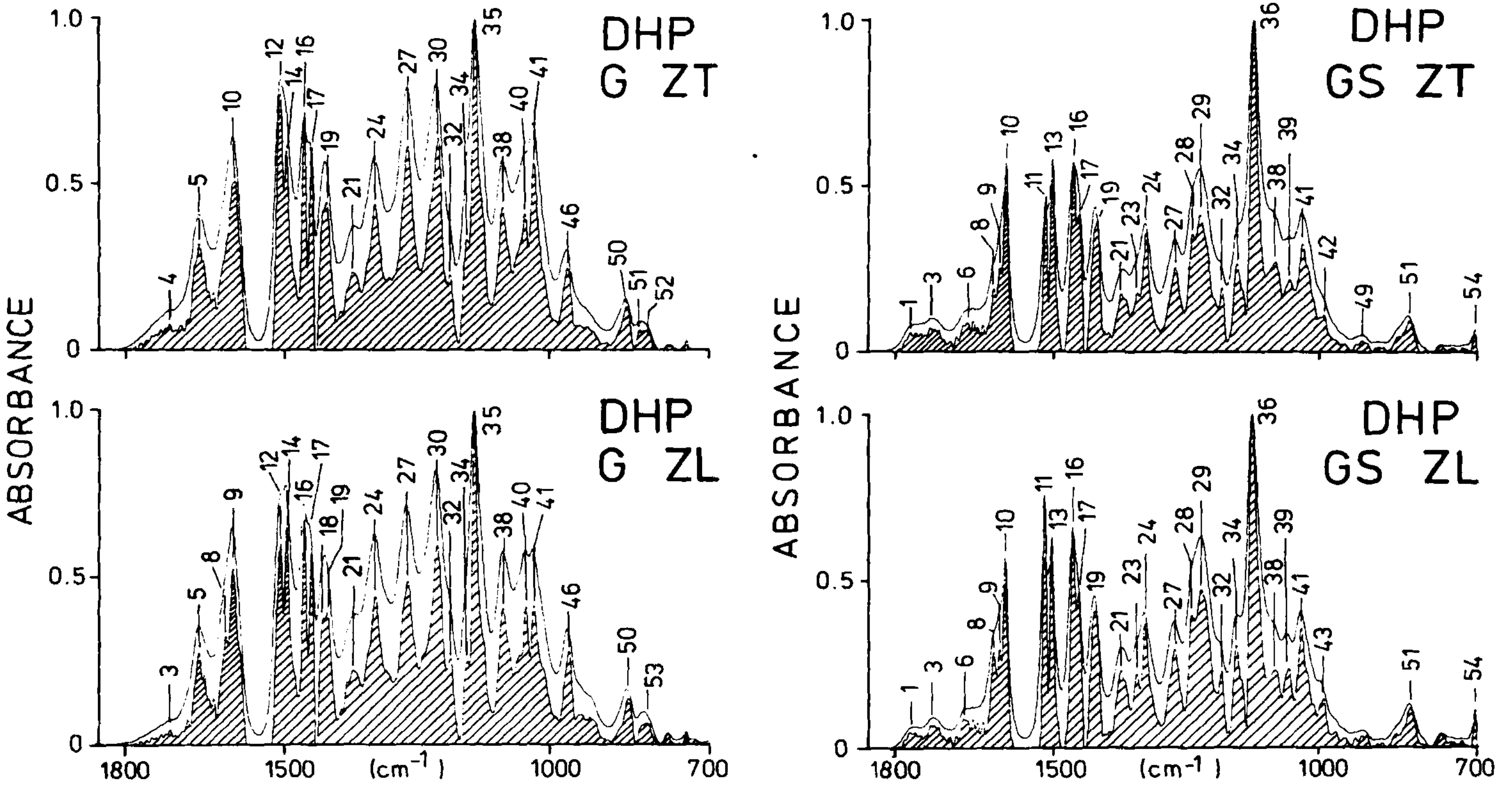


FIGURE 2. FTIR spectra from G and GS DHP's prepared by the "zutropf" (ZT) and the "zulauf" (ZL) dehydrogenation method. (Hatched area:. deconvolved spectra.)

Downloaded At: 13:17 25 January 2011

TABLE 2

Intensities and wavenumbers taken from MWL and DHP FTIR spectra after deconvolution. Bands marked with • are maxima. The band numbers left side refer to the bands numbered in Fig. 1 and 2.

	M W L's						D H P's								
	SPRUCE		BEECH		BAMBOO		G ZT		G ZL		GS ZT		GS ZL		x
#	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}
1											1771	6*	1771	5*	1771
2	1737	4	1737	17*	1737	18	1737	2	1737	2	1737	6	1737	5	1737
3	1718	7*	1718	10	1718	25	1720	7	1720	4*	1720	7*	1720	6*	1720
4	1710	5	1710	5	1710	30*	1710	7*	1710	4	1710	3	1710	2	1710
5	1664	19*	1664	16*	1664	19	1663	32*	1664	29*	1664	8	1664	9*	1664
6					1655	21*	1655	27*	1654	22*	1653	9*	1653	7	1654
7					1634	24*									1634
8	1616	16	1617	16	1616	21*	1616	25	1613	34*	1614	19*	1614	29*	1614
9	1604	33*	1604	26	1605	82*	1605	46	1600	53*	1604	25*	1603	30*	1604
10	1593	37*	1592	67*	1593	62*	1595	51*	1591	28	1592	56*	1592	57*	1593
11			1515	38*	1515	100*					1517	47*	1518	76*	1516
12	1511	100*					1511	78*	1510	61*					1511
13			1504	67*	1504	65*					1505	58*	1505	63*	1505
14							1499	60*	1498	66*					1498
15	1493	12					1493	27	1493	25			1493	9	1493
16	1465	66*	1465	69*	1465	73*	1465	72*	1465	69*	1465	58*	1465	67*	1465
17	1451	58*	1455	48*	1453	49*	1451	60*	1451	58*	1454	40*	1454	46*	1453
18	1427	28			1428	15	1431	41	1428	39*	1428	35			1428
19	1421	46*	1421	56*	1422	52*	1422	44*	1422	41*	1420	40*	1423	41*	1422
20	1384	16			1384	19*			1383	23*					1384
21							1372	23*	1373	23*	1374	18*	1374	23*	1373
22	1366	20*	1368	18*	1365	23*			1368	22	1368	15	1368	20	1367
23							1344	28	1344	27	1343	18*	1344	22*	1344
24	1328	22*	1328	46*	1329	44*	1331	44*	1331	45*	1328	36*	1329	37*	1329
25					1311	21*			1311	21					1311
26					1290	29									1290
27	1269	87*	1270	38*	1269	58*	1269	61*	1268	49*	1272	26*	1273	29*	1270
28			1240	47	1237	52*			1237	27	1240	35*	1240	40*	1239
29	1224	49*	1224	54*	1225	56*	1225	49			1226	41*	1223	48*	1225
30	1215	48*					1212	63*	1214	60*	1214	31	1214	43	1214
31					1204	37*									1204
32	1189	18*	1185	17*	1184	31*	1189	22*	1189	25*	1184	19*	1184	23*	1186
33					1170	63*									1170
34	1158	41*	1154	32*	1158	48*	1157	33*	1157	25*	1156	27*	1157	30*	1157
35	1141	72*					1143	100*	1144	100*	1143	18	1143	20	1143
36	1128	46*	1128	100*	1127	100*	1128	42	1128	33	1126	100*	1126	100*	1128
37					1104	31*									1104
38	1089	33*	1086	32*	1088	30*	1090	43*	1090	40*	1084	27*	1085	23*	1086
39							1057	30	1057	27	1057	22*	1058	23*	1057
40	1048	39*	1048	34*	1048	31*	1048	41*	1046	42*					1048
41	1031	70*	1032	44*	1031	45*	1031	56*	1032	42*	1033	28*	1033	37*	1032
42	1020	24	1020	34	1020	24	1020	28	1020	23	1020	25	1020	22	1020
43											991	11*	991	15*	991
44			981	8*	984	12*									982
45	972	6*													972
46							966	25*	966	28*					966
47									945	9*					945
48	927	2*							926	8*					926
49			918	6*	922	2*					919	4*			920
50	856	10*	854	7*	854	7*	856	13*	855	14*	851	5*	853	5*	854
51			834	9*	834	24*	831	6*	831	5*	828	9*	827	12*	831
52							822	6*							822
53	816	7*			815	5*			818	6*					816
54											704	7*	704	12*	704

deconvolved spectra. Band assignments were done according to the literature[5,22,24].

1) Spruce. The band at 1511 cm^{-1} (aromatic skeletal vibration) and at 1269 cm^{-1} (guaiacyl ring breathing with carbonyl stretching) dominates. The intensities of the bands at 1596 cm^{-1} (aromatic skeletal vibr. breathing with C=O stretching, also influenced by "condensed" aromatic rings) and at 1463 cm^{-1} (C-H deform. asym.) are much lower than that of the 1510 cm^{-1} band. The pronounced 1140 cm^{-1} band (C-H in plane deform. of guaiacyl ring), 1031 cm^{-1} band (C-H in-plane deform. guaiacyl ring and C-O deform. primary alcohols, influence of non-conjugated C=O groups is also probable) and the two smaller maxima at 856 and 816 cm^{-1} (aromatic C-H out-of-plane deform.) are prominent.

2) Beech. The band at 1128 cm^{-1} (C-H in-plane deform. of syringyl rings) dominates. Moreover, the presence of syringyl units is also evident from the bands at 1593 cm^{-1} and 1463 cm^{-1}. Their intensities are in the same order of magnitude as that of the 1504 cm^{-1} band. In contrast to the spectrum of spruce MWL the band at 1328 cm^{-1} (syringyl ring breathing with C=O stretching, also influenced by "condensed" aromatic rings) is large and the band at 1270 cm^{-1} is small. The same is true for the 1032 cm^{-1} band. It is remarkable that in the range of aromatic C-H out-of-plane deform. vibrations (at 835 cm^{-1}) only one band appears.

3) Bamboo. The 1127 cm^{-1} band dominates, as in the case of the beech MWL spectrum, but the bandwidth is much smaller. The pronounced maximum at 1170 cm^{-1} is an infallible proof for HGS lignins. This band is not visible in all other lignin spectra without deconvolution. Because alkaline hydrolysis and borohydride reduction decreases the intensity of this band, it is probable that a close relation exists between this band and the numerous carbonyl (ester) bands of bamboo lignin. Also, the broad carbonyl stretching band around 1710 cm^{-1} (unconjugated ketone

Downloaded At: 13:17 25 January 2011

and carbonyl groups) is very characteristic for bamboo (and for other Gramineae). The bands at 1604 cm^{-1} and 1269 cm^{-1} are intense, too. This can partly be explained by the contribution of the carbonyl bands to aromatic skeletal vibrations and to the guaiacyl C-H in-plane deformations, respectively. In many respects, bamboo MWL show characteristics both of G and GS lignins. For example the presence of syringyl units is unequivocally demonstrated by the pronounced 1329 cm^{-1} band. In the spectra of Gramineae the band is typical at 834 cm^{-1} with higher intensity than in the case of GS lignins. DHP's prepared from p-coumaryl alcohol also show this spectral feature[9], so that high intensities at 834 cm^{-1} are indicative for H units.

Downloaded At: 13:17 25 January 2011

Comparison of the deconvolved spectra

It was already demonstrated that the borders are fluid between typical G, GS and HGS lignins[8,11] and that linear regression equations describe well the correlation between IR spectroscopic and lignin analytical data[9,11]. The question arises, however, what may be the contribution of deconvolved IR spectra to lignin chemistry? What is the advantage to observe bands with apparently better resolution?

As mentioned above, the advantage of deconvolution is less obvious in the case of the broad carbonyl band region, but interesting details are revealed in four other regions of the IR spectra: On the bands around 1600 cm^{-1}, at 1510 cm^{-1}, at 1463 cm^{-1}, and between 1170 and 1104 cm^{-1}.

The 1600 cm^{-1} band is composed of 3 lines at 1614, 1604 and 1593 cm^{-1} (band no. 8, 9, and 10). Their relative intensities differ in the samples investigated. The first one is best visible and most intense in the case of G ZT, GS ZT and GS ZL DHP's, but it is also present in the spectrum of bamboo MWL. Band no. 9 at 1604 cm^{-1} is usually well discernible in samples rich in G units. In polymers with more S units, band no. 10 is much higher than band no. 9. The contribution of the carbonyl stretching vibrations to the aromatic skeletal vibrations occurs probably around 1605 cm^{-1}. At least in the case of bamboo MWL the coincidence between the high intensities of the carbonyl bands and band no. 9 is striking. For comparisons it is of interest that model compounds containing carboxylic acid functional groups also display splitting in the 1600 cm^{-1} region. Ferulic acid ($\underline{1620}$+1600 cm^{-1}), p-coumaric acid (1628+$\underline{1602}$+1593 cm^{-1}) - both important components of bamboo lignin - show the splitting patterns as given in parenthesis, wherein the underlined band dominates. This observation is not a convincing corroboration for the assumption that the intense 1605 cm^{-1} line of bamboo is influenced by the carbonyl bands of the acids mentioned above (or their esters) but is not in contradiction to it. Band no. 10 dominates in G ZT polymer, whereas in the corresponding ZL polymer band no. 9 has the preponderance. ZT polymers are supposed to have more alkyl-aryl ether linkages than ZL polymers[22], therefore, one could conclude that the ratio of bands no. 9 and 10 is also related to the ratio of β-O-4 alkyl-aryl ether linkages to the linkages derived from β-5, β-β or 4-O-5 coupling modes of the basic units. Accordingly, the line at 1593 cm^{-1} is more intense than the line at 1604 cm^{-1} when more alkyl-aryl ether linkages are present in the molecule, or when more S units are present, or - generally speaking - when the ZT character of a polymer is more pronounced.

The band of the basic aromatic skeletal vibration around 1510 cm^{-1} is also a multiple band. Maxima appear for all samples at least at four wavelengths after deconvolution: 1516, 1511, 1505, and 1498 cm^{-1} (band numbers 11 - 14). Each polymer, with the exception of spruce MWL, displays a resolution pattern with two distinct maxima. Four samples (spruce MWL, G ZT and ZL DHP's and GS ZL DHP) show an additional shoulder at 1493 cm^{-1}, so that

Downloaded At: 13:17 25 January 2011

Downloaded At: 13:17 25 January 2011

altogether five lines contribute to the overall absorbance in this region. It is worthwhile to mention that the aromatic skeletal vibrations of β-5 dimers also show a 1518 + 1497 cm^{-1} splitting pattern (without deconvolution). Some β-O-4 dimers with benzylic OH groups display 1515 + 1500 or 1525 + 1506 cm^{-1} resolution patterns. Bands no. 11 and 13 at 1516 and 1505 cm^{-1} are visible only in co-polymers with participation of S units (including bamboo), whereas band no. 12 at 1511 cm^{-1} is typical for pure G polymers, such as spruce MWL and G ZT and ZL DHP's. This observation explains the findings that in spectra without deconvolution G lignins show maxima at 1510 cm^{-1} and typical GS lignins at 1505 cm^{-1}. It was observed[25] that the wavenumbers of the maxima move continuously from 1510 to 1504 cm^{-1} when the S content in GS lignins increases. Explanation: With increasing S content the band component at 1505 cm^{-1} dominates more and more and superimposes the component band at 1516 cm^{-1} . An apparent shift results from higher to lower wavenumbers due to the limited resolution under standard spectroscopic conditions.

The high intensity of band no. 11 of bamboo MWL is remarkable. The reason for this is not obvious. It cannot be explained neither exclusively by the presence of S units nor by H units in this lignin. (Beech MWL, and GS co-polymerisates possess more S units and the intensity of this band is still lower. H DHP's display 1510+1491 cm^{-1} (intensities, 1:1) splitting pattern in this region[9,11], which differs of that of bamboo MWL.) Band no. 11 is also intense in GS ZT and especially in GS ZL DHP and in organosolv lignins. However, this band cannot be observed in acetylated samples. This band reflects, accordingly, the structural peculiarites of S units but the influence of phenolic OH groups and of ester carbonyl groups is also probable. Moreover, it is of interest that in contrast to spruce MWL, in G ZT and ZL DHP's the component band no. 14 at 1498 cm^{-1} is present. In the spectrum of G MWL's this short wavenumber component does not appear as a clear maximum. This subtle difference is a further proof for structural differences between DHP's and lignins. As the intensity of band no. 14 is higher in the spectrum of G ZL DHP than in the spectrum of the corresponding ZT DHP, this part of the aromatic skeletal vibration band is probably indicative for "condensed" aromatic rings, such as in β-5, 5-5 or 4-O-5 units.

The 1463 cm^{-1} band (C-H deform. asym.) is split very uniformly by deconvolution into two bands at 1465 cm^{-1} and 1453 cm^{-1} in all spectra. The composed character of this band is frequently visible in IR spectra of softwood lignins even under standard spectroscopic conditions as already pointed out in the sixties[24]. Consequently, the effect of enhanced resolution is best visible in the case of spruce MWL followed by the two G DHP's. In GS polymers - including the bamboo MWL - the 1453 cm^{-1} component is less intense and not so well separated from the 1465 cm^{-1} line. It seems that S units are more represented by the 1465 cm^{-1} moiety of this band.

Between the wavenumbers 1170 and 1104 cm^{-1} details become visible, which are not so clear without enhanced resolution. G, GS, or HGS lignins can easily be recognized by the relative intensities of the bands at 1170, 1157, 1143, 1128, and 1104 cm^{-1} (band no. 33 - 37). As is well known, the band no. 35 at 1143 cm^{-1} is typical for polymers with G units if its relative abundance is 90 mol %, or more. In the presence of a few mol % S units the band no. 36 at 1128 cm^{-1} dominates over the band no. 35 at 1143 cm^{-1} in such a way, that this band cannot be detected even as a shoulder after deconvolution. Therefore, G and GS lignins can be distinguished unequivocally by dominance of band no. 35 (G lignins only) or band no. 36 (GS lignins, even if a few mol % S units are present). Bamboo MWL (Gramineae, HGS lignin) also show the dominant band no. 36, but the width is smaller than in the spectrum of beech MWL. Moreover, band no. 33 at 1170 cm^{-1}

Downloaded At: 13:17 25 January 2011

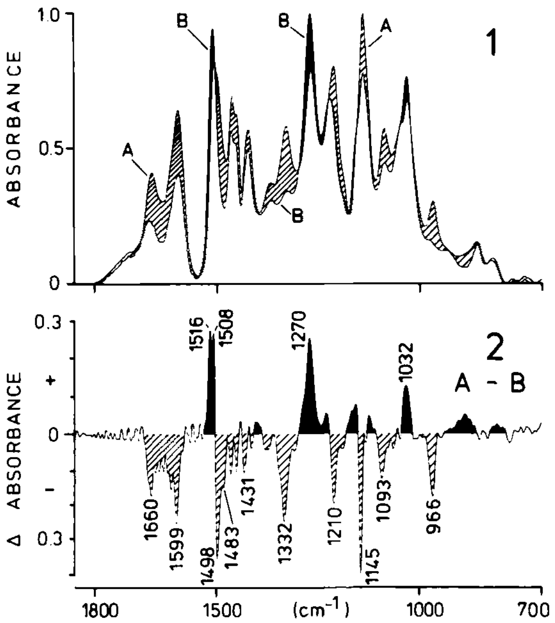


FIGURE 3. 1) Standardized FTIR spectra without deconvolution from spruce MWL (A) and G ZT DHP (B). 2) Difference spectrum "A minus B" from spectra after deconvolution

Downloaded At: 13:17 25 January 2011

is very typical for Gramineae, as already indicated above. p-Coumaric acid and ferulic acid display maxima in this region at 1172 and 1177 cm^{-1}, respectively, although the intensities are not very pronounced. This is a further indication that the 1170 cm^{-1} band is associated with carboxyl, or ester groups. The line at 1157 cm^{-1} (band no. 34) is very pronounced in all spectra of lignins but has not yet been interpreted in terms of structural significance.

Structural differences between MWL's and DHP's[27-31] and between ZT and ZL DHP's[22,23,27], respectively, were frequently discussed taking into account theoretical considerations and spectroscopic/analytical data. There is a consensus about the findings that ZT DHP's are more similar to lignins than ZL DHP's; but in any case there are differences between lignins and their polymer models. In order to demonstrate the analytical possibilities (and limits) of the FTIR spectroscopy a difference spectrum is depicted in Fig. 3. This spectrum was created by subtraction of the deconvolved spectrum of G ZT DHP from that of spruce MWL. Positive and negative bands indicate the distinctions between these samples, which can be interpreted to a great extent with the help of the band assignments of the literature[5] and the results described above. The difference spectrum "beech MWL minus GS ZT DHP" and difference spectra of ZT and ZL DHP's also display interesting details, which will be described elsewhere. The results in this paper are in agreement with data in the literature with reference to similarities and differences between G DHP's and G lignins[26-30] and between ZT and ZL dehydrogenation polymers[21,22,26], respectively. There are only gradual deviations from the results of Lai and Sarkanen[22] on IR spectra from ZT and ZL DHP's. These can be attributed to the different techniques used for DHP preparation, purification, and fractionation.

CONCLUSIONS

There are numerous advantages of increasing the apparent resolution by using deconvolution techniques. Small differences in band shapes become visible and hidden bands in the spectra come to light. The comparison of spectra of different origin yield information with more details, and small differences can more easily be detected. Nevertheless, many details uncovered can be interpreted in terms of lignin structure when more analytical and more quantitative ^{13}C NMR spectroscopic data become available for the polymers in question. Hence, this paper is mainly a description and comparative presentation of the results of deconvolution. Once "calibrated" with other methods, IR spectra will give much information conveniently. Therefore, the intent of this paper is to give impetus for more research work on understan-

Downloaded At: 13:17 25 January 2011

ding the relations between lignin structures and IR spectroscopic data.

REFERENCES

1. L. Kawamura and T. Higuchi, p. 439 - 456 in: "Grenoble Symposium", Chimie et biochimie de la lignine, de la cellulose et des hemicelluloses; Les Imprimeries Reunies de Chambery, 1964

2. K. V.Sarkanen, H.-m. Chang and B. Ericsson, Tappi, 50, 572 (1967)

3. K. V. Sarkanen, H.-m. Chang and G. G. Allan, Tappi, 50, 583 (1967)

4. K. V. Sarkanen, H.-m. Chang and G. G. Allan, Tappi, 50, 587 (1967)

5. H. L. Hergert, p. 267 - 293 in: Lignins, K. V. Sarkanen and C. H. Ludwig (Eds.) Wiley-Interscience, N. Y., 1971

6. W. Herres, Chimia No. 2 - 3, 64 (1985)

7. T. P. Schultz, M. C. Templeton and G. D. McGinnis, Anal. Chem., 57, 2867 (1985)

8. O. Faix, p. 133 - 134 in: Proceedings, Int. Symp. on Pulp and Pap. Chem., Vancouver Can., 1985

9. O. Faix, Holzforschung, 40, 273 (1986)

10. T. P. Schultz and W. G. Glasser, Holzforschung, 40, Suppl. 37 (1986)

11. O. Faix, Quantitative FTIR-spektroskopische Untersuchungen Ligninen und Ligninmodellsubstanzen, Habilitation Thesis, Vol. I and Vol. II, University of Hamburg, Fachb. Biology, 1987

12. R. Patt, O. Faix und U. Welkener, Das Papier, 41, (10A) V7 (1987)

13. S. A. Berben, J. P. Rademacher, L. O. Sell, and D. B. Easty Tappi, 70, 129 (1987)

14. O. Faix, R. Patt und O. Beinhoff, Das Papier, 41, 657 (1987)

15. J. K. Kauppinen, D. J. Moffatt, H. H. Mantsch, and D. G. Cameron, Appl. Spec., 35, 35 (1981)

16. J. Gronholz and W. Herres, Instruments & Computers, No. 3, 13 (1985)

17. D. G. Cameron and D. J. Moffatt, Journal of Testing and Evaluation, 12, (2), 76 (1984)

18. K. Freudenberg, in: The Constitution and Biosynthesis of Lignin, p. 47 - 129, K. Freudenberg and A.C. Neish, Springer-Verlag, Heidelberg, 1968

19. A. Björkman, Svensk. Papperstidn., 59, 477 (1956)

Downloaded At: 13:17 25 January 2011

20. O. Faix, W. Lange and O. Beinhoff, Holzforschung, 34 174 (1980)

21. O. Faix, M. D. Mozuch and K. Kirk, Holzforschung, 39, 203 (1985)

22. Y. Z. Lai and K. V. Sarkanen, in: Lignins, p. 165 - 240, K. V. Sarkanen and C. H. Ludwig (Eds.), Wiley-Interscience, New York, 1971

23. Y. Z. Lai and K. V. Sarkanen, Cellul. Chem. Technol., 9, 239 (1975)

24. H. I. Bolker and N. G. Sommerville, Pulp Paper Mag. Can. 64, T 187 (1963)

25. O. Faix, to be published

26. H. H. Nimz, D. Robert, O. Faix and M. Nemr, Holzforschung, 35, 16 (1981)

27. H. H. Nimz, J. Mogharab and H.-D. Lüdemann, Makrom. Chem., 175, 2563 (1974)

28. T. K. Kirk, W. J. Connors, R. D. Bleam, W. F. Hackett and J. G. Zeikus, Proc. Nat. Acad. Sci., 72, 2515 (1975)

29. H. H. Nimz and H.-D. Lüdemann, Holzforschung, 30, 33 (1976)

30. G. Brunow and K. Lundquist, Paperi Ja Puu, 62, 669 (1980)

31. D. Robert and G. Brunow, Holzforschung, 38, 85 (1984)

Downloaded At: 13:17 25 January 2011