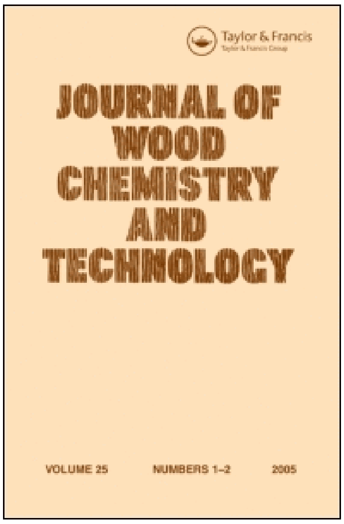

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PHENOLIC OH GROUP ESTIMATION BY FTIR AND UV SPECTROSCOPY. APPLICATION TO ORGANOSOLV LIGNINS

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ABSTRACT

The phenolic hydroxyl group content of 34 acetylated organosolv lignins, obtained by ethanol or methanol autocatalyzed pulping of *Eucalyptus globulus* was measured by FTIR spectroscopy. The absorbance of aromatic IR ester bands of acetylated lignins at 1765 cm^{-1} was employed to estimate the lignin phenolic hydroxyl group content. To compare different samples the spectra recorded were baseline corrected and normalized with the bands around 1500, 1600 and 1423 cm^{-1}. Partial least-squares (PLS) and multiple linear

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regression (MLR) calibrations were carried out to establish a mathematical correlation between UV data sets and FTIR spectra. The best results were shown by the models obtained by PLS regression. In these models the band at 1766 cm^{-1} was normalized using the band at 1744 cm^{-1} and the baseline corrections were performed with the bands at 1423 cm^{-1} (ethanol lignin) and 1507 cm^{-1} (methanol lignin).

INTRODUCTION

The phenolic hydroxyl group content is crucial for lignin characterization when evaluating the extent of change and it is one of the most important functionalities affecting the physical and chemical properties of lignin polymers. The chemical reactivity of lignin in various modification processes is also profoundly influenced by its phenolic hydroxyl content (e.g. in the reaction with formaldehyde for the production of lignin adhesives[2]). Therefore, reliable and rapid techniques are required for its determination.

Among the analysis techniques described in the literature, FTIR spectroscopy shows interesting characteristics such as high sensivity and selectivity, high signal-to-noise ratio, accuracy, data handling facility, mechanical simplicity and the short time and small amount of sample required for the analysis.[3] Besides, the spectrum of a lignin sample gives an overall view of its chemical structure.[4]

In former papers FTIR spectroscopy was employed to determine the phenolic hydroxyl group content in milled wood (MWL), Organocell, Kraft, steam explosion, Alcell and ball milled enzyme lignins from bagasse, aspen, poplar, cottonwood, etc.[3,5–7] The calibration was usually carried out by simple linear regression analyses using phenolic hydroxyl group content data obtained by methods based on titration, UV, ^{13}C NMR, ^{1}H NMR, periodate oxidation and aminolysis. The correlation obtained was used to asses the feasibility of the method. To achieve reliable comparisons between different lignin samples baseline correction and normalization were recommended.

In all the studies mentioned above FTIR spectra were obtained using acetylated lignin samples. Upon acetylation, the hydroxyl band at 3410–3460 cm^{-1} disappears, acetoxy bands appear at 1766 cm^{-1} (aromatic), 1744 cm^{-1} (aliphatic) and 1371 cm^{-1}, as do peaks in a cluster with maxima at 1217, 1225–1227, and 1198 cm^{-1} bands.[3,6,7] The ratio of the acetoxy absorbance bands (A_{1766}/A_{1744}) can be used to estimate the ratio of phenolic/aliphatic hydroxyl groups.[3] In the case of organosolv lignins, which are removed from wood through partial splitting of interunit ether linkages such as α-aryl and arylglycerol-β-aryl ether, the FTIR spectra shows additional maxima at 1600 , 1131, and 1044 cm^{-1}.

Although FTIR spectroscopy has been used to estimate the phenolic OH group content of a variety of lignins,[3,5–7] no information is available on the application of this technique to Organosolv lignins from *E. globulus*. The aim of this study was the FTIR determination of the phenolic OH group content of lignin samples obtained in the autocatalyzed ethanol-water or methanol–water pulping of *E. globulus* wood.

RESULTS AND DISCUSSION

A representative FTIR spectrum of the lignins studied (sample M-2) before and after acetylation can be seen in Figure 1. According to the lignin classification rules, the spectra belong to a GS type lignin.[8–12] Thus, the relatively high intensity of the band at 1330 cm^{-1} (syringyl ring vibrations) and the 1128 cm^{-1} band (aromatic C-H plane deformation, syringyl type) indicates a high syringyl content.

The aromatic skeletal vibration absorption band (around 1500 cm^{-1} for syringyl and 1515 cm^{-1} for guaiacyl) was evident at 1500 cm^{-1} for ethanol lignin and at 1507 cm^{-1} for methanol lignin. As mentioned above, the broad hydroxyl band decreases upon acetylation and two bands arise at 1744 cm^{-1} (C=O stretching of aliphatic acetoxy groups) and 1766 cm^{-1} (C=O stretching of aromatic acetoxy groups). The absorbances at these bands were taken as measures of the aliphatic and aromatic acetoxy group content, respectively.

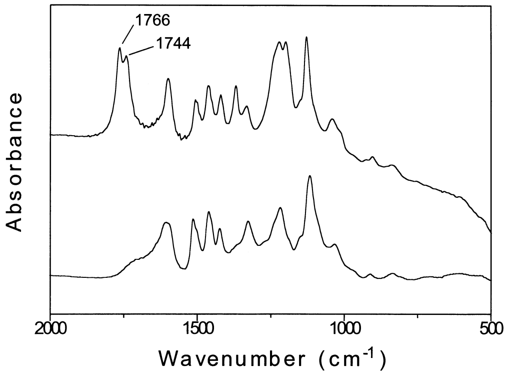

Figure 1. FTIR spectrum of sample M-2 before (bottom) and after acetylation (top).

The absorbance of the samples studied at the relevant IR bands is shown in Tables 1 and 2. The bands around 1423, 1500, and 1600 cm^{-1} correspond to aromatic skeletal vibrations and are usually employed to carry out baseline corrections.[5,10,13–19]

In Tables 1 and 2 the phenolic OH content of the samples studied can also be seen. The values obtained are between 1 and 3% (w/w). These values are in agreement with those obtained by others for the autocatalyzed pulping of hardwoods in alcohol–water medium.[20] The values around 1% are rather low for technical lignins, however these values correspond to lignins obtained at very mild cooking conditions, where the cleavage of interunit linkages takes place in a low extent.[21,22] As the intensity of the cooking conditions increases an increase in the amount of phenolic hydroxyl group content can be obtained.[20–22] The lignins with higher phenolic hydroxyl group content are in the range reported for kraft lignin and lignosulfonates.[23,24]

The normalized absorbances proposed were regressed both with partial least-squares regression (PLS) and multiple linear regression (MLR) against the phenolic hydroxyl group content. In the PLS models the absorbance at 1766 cm^{-1} was normalized using the absorbance at 1744 cm^{-1} and is shown by $(A_{1766}/A_{1744})_x$, where x is the band employed in baseline correction.

Table 1. Methanol Lignin Analysis. Phenolic Hydroxyl Content and Band Absorbance

Sample	Phenolic OH (% w)	A_{1744}	A_{1766}	A_{1600}	A_{1507}	A_{1423}
M-1	1.80	1.304	1.261	1.187	1.131	1.116
M-2	2.50	0.557	0.571	0.513	0.470	0.481
M-3	1.98	0.501	0.487	0.45	0.421	0.431
M-4	2.96	0.413	0.448	0.382	0.353	0.374
M-5	2.04	1.279	1.257	1.152	1.09	1.095
M-6	1.65	1.018	0.996	0.945	0.926	0.902
M-7	1.80	1.192	1.170	1.090	1.048	1.020
M-8	1.42	1.179	1.147	1.060	1.106	0.960
M-9	1.65	0.657	0.626	0.571	0.548	0.539
M-10	2.56	0.884	0.904	0.844	0.803	0.786
M-11	1.63	0.766	0.730	0.702	0.665	0.662
M-12	2.00	1.183	1.184	1.121	1.072	1.062
M-13	2.54	1.313	1.335	1.251	1.203	1.181
M-14	1.93	0.901	0.882	0.806	0.774	0.752
M-15	1.94	1.066	1.052	1.002	0.972	0.960
M-16	1.90	0.485	0.474	0.429	0.400	0.390
M-17	1.92	1.854	1.847	1.784	1.708	1.677

Table 2. Ethanol Lignin Analysis. Phenolic Hydroxyl Content and Band Absorbance

Sample	Phenolic OH (% w)	A_{1744}	A_{1766}	A_{1600}	A_{1500}	A_{1423}
E-1	1.35	0.512	0.491	0.446	0.427	0.467
E-2	2.36	0.596	0.606	0.555	0.503	0.507
E-3	2.30	0.680	0.689	0.609	0.577	0.580
E-4	2.78	0.620	0.651	0.600	0.564	0.560
E-5	1.34	0.732	0.671	0.612	0.598	0.596
E-6	1.86	0.543	0.528	0.486	0.466	0.462
E-7	1.78	0.550	0.523	0.479	0.456	0.451
E-8	1.92	0.874	0.868	0.791	0.741	0.730
E-9	2.02	0.959	0.943	0.851	0.816	0.799
E-10	2.39	0.733	0.777	0.702	0.669	0.556
E-11	1.33	0.838	0.799	0.749	0.718	0.759
E-12	1.92	0.860	0.853	0.793	0.747	0.735
E-13	2.22	1.390	1.411	1.324	1.253	1.240
E-14	2.04	1.158	1.142	1.039	0.986	0.947
E-15	1.97	0.754	0.737	0.719	0.661	0.659
E-16	1.89	0.829	0.813	0.746	0.697	0.685
E-17	1.84	0.896	0.876	0.835	0.764	0.760

Table 3. Results of PLS Correlation

Sample Set	Baseline Correction Band (cm^{-1})	Regression Coefficient, r	Sum of Squares Residuals, SQR
M1–M17	1507	0.97	0.1539
	1600	0.94	0.3283
	1423	0.89	0.5449
E1–E17	1423	0.980	0.1059
	1500	0.86	0.6156
	1600	0.81	0.8537

Three PLS correlations (those corresponding to the baseline correction with the bands around 1423 , 1500 and 1600 cm^{-1} bands) were carried out for both ethanol and methanol lignins. The results obtained can be seen in Table 3.

According to the correlation coefficient (r) and the sum of squares residuals (SQR) values, the PLS models selected were that corresponding to baseline correction with the band at 1507 cm^{-1} for methanol lignins and that at 1423 cm^{-1} for ethanol lignins. The expressions of the models are as follows,

- Methanol lignin:

$$\mathrm{PhOH} = 1.557\left(\frac{A_{1766}}{A_{1744}}\right)_{1507} + 0.534 \quad (r = 0.97; \mathrm{SQR} = 0.1539)$$

- Ethanol lignin:

$$\mathrm{PhOH} = 1.453\left(\frac{A_{1766}}{A_{1744}}\right)_{1423} + 0.632 \quad (r = 0.98; \mathrm{SQR} = 0.1059)$$

In the case of MLR models, several normalizations were tested: (A_{1766}/A_{1744}), (A_{1766}/A_{1423}), (A_{1766}/A_{1500}) and (A_{1766}/A_{1600}). The baseline corrections were carried out with the bands at 1423, 1500 and 1600 cm^{-1}. The terms $(A_{1766}/A_{1744})_{1744}$, $(A_{1766}/A_{1423})_{1723}$, $(A_{1766}/A_{1500})_{1500}$ and $(A_{1766}/A_{1600})_{1600}$ were excluded to avoid indeterminations. Therefore, the MLR models included a total of 9 terms. The analysis of variance of the regression models was used to identify the significant terms. In the model for methanol lignin the significant terms were $(A_{1766}/A_{1423})_{1600}$, $(A_{1766}/A_{1507})_{1600}$, $(A_{1766}/A_{1600})_{1507}$ and $(A_{1766}/A_{1600})_{1423}$. The ethanol lignin data set did not provide a satisfactory regression since none of the terms was found to be significant. The SQR values obtained were 3.555 and 11.376 for methanol and ethanol lignin, respectively, remarkably higher than those calculated for the PLS models.

Therefore, the PLS models were selected. The suitability of the models can be seen in Figure 2, where the correlation plot of experimental phenolic hydroxyl contents vs. the results predicted by the models are shown. A good agreement can be found between both values. The average prediction error is 4.0 and 3.8% for methanol and ethanol lignins, respectively. With regard to the absolute error or the method, it depends on the calibration method. UV spectroscopy is a convenient technique for analyzing phenolic hydroxyl lignin content because of its fingerprinting capability.[24] However, if more accuracy is needed, the use of another primary analysis such as NMR or oximation advisable.

The suitability of PLS calibration have also been reported by other authors,[5,6] who correlated data sets of FTIR spectra and aminolysis. The equations obtained by PLS are more robust that developed by MLR.[6] Besides, under unfavorable circumstances MLR generates too large models.

It must be pointed out that no acceptable correlation was obtained when ethanol lignins and methanol lignins were considered as a single set,

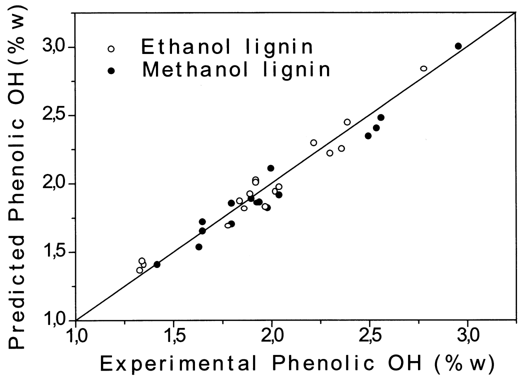

Figure 2. Experimental phenolic OH group contents vs. values calculated from FTIR spectra by the PLS models.

which indicates that in spite of the fact the lignin source was the same (*E. globulus*) and the cooking medium was similar, the structural differences between ethanol and methanol lignins are of importance. The different properties of ethanol and methanol lignin have been reported in previous works.[21,22] It was shown that ethanol lignin has, on average, a higher molecular weight, a lower phenolic OH content and a higher carbonyl group content than methanol lignin.

EXPERIMENTAL

Lignin samples were precipitated from black liquors obtained by autocatalyzed pulping of *E. globulus* in ethanol-water or methanol water. A total of 34 pulping runs were carried out at different conditions. The detailed pulping conditions and procedure were described in former papers.[25,26] The pulping variables studied were pulping temperature (170–200°C), time at maximum temperature (40–120 min) and alcohol concentration (30–70%, w). In these conditions the phenolic OH content was found to increase as the cooking temperature and time were increased and the concentration of ethanol in the pulping liquor was reduced.[21,22] These conditions lead to a more extensive cleavage of the bonds between lignin units and the occurrence of functional groups due to the longer treatment, higher temperature and increased acidity of the pulping liquor. To separate lignin black liquor aliquots of 100 mL were diluted with 300 mL of water and the pH of the mixture adjusted to 2 with 0.1 M sulfuric acid. The sample was filtered, washed with distilled water and dried at 40°C in a vacuum oven.

To carry out calibration the phenolic hydroxyl content of lignin samples was determined by UV spectroscopy as it was described by Goldsmith[27] and Lin.[24] The method is based on the difference absorption at 300 nm between phenolic units in neutral and alkaline solutions. Data are shown in Tables 1 and 2.

To acetylate lignins 100 mg of sample and 2 mL of acetic anhydride-pyridine reagent (1 : 1, v/v) were placed in a 50 mL beaker. The beaker was shaken, covered and kept for 48 h under a nitrogen atmosphere. Then, 10 mL of ice-cold methanol–dichloromethane (1 : 8, v/v) were added to the reaction mixture. The resulting solution was washed with 2 M hydrochloric acid and water, filtered and dried under reduced pressure.

FTIR spectroscopy was performed on a Mattson Satellite 5000 spectrometer by the KBr pellet technique (ca. 0.7 mg acetylated sample with 300 mg KBr; resolution 4 cm^{-1}, 64 scans). The resulting spectra were baseline corrected and normalized with the bands around 1500, 1600 and 1423 cm^{-1}.

CONCLUSIONS

Partial least-squares regression (PLS) was found to be the most adequate technique for calibration of FTIR data sets with phenolic hydroxyl group contents of autocatalyzed alcohol pulping lignins which had been acetylated.

The best results were achieved when the ratio between the absorbances for aromatic acetoxy bands and aliphatic acetoxy bands (A_{1766}/A_{1744}) was employed. The baseline corrections were carried out at 1507 and 1423 cm^{-1} for methanol and ethanol lignins, respectively. The average absolute prediction errors are around 4%.

The estimation method involves the following steps: lignin acetylation, band intensity measurement at the corresponding wave number and phenolic OH calculation with the calibration equation.

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