Cateto, C.A., Barreiro, M.F., Rodrigues, A.E., Brochier-Salon, M.C., Thielemans, W., Belgacem, M.N., **"FTIR and NMR studies on lignin acetylation"** 9th European Workshop on Lignocellulosics and Pulp – EWLP 2006, Vienna, Austria, 27-30 August (2006) (*poster*).

POSTER PRESENTATIONS

FTIR AND NMR STUDIES ON LIGNIN ACETYLATION

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Introduction

Acetylation is a widely used technique for lignin characterization. Total hydroxyl content, structural analysis by ^{1}H and ^{13}C NMR spectroscopy, and molecular weight determination using SEC, are usually based on acetylation procedures. Acetylation of lignin introduces some structural features in the molecule that could be detected both by FTIR and ^{13}C NMR spectroscopy. The direct quantification of the total hydroxyl content using FTIR spectroscopy is not a current practice but ^{13}C NMR spectroscopy is a widely used technique for that purpose. However both techniques, are useful to monitor the acetylation process.

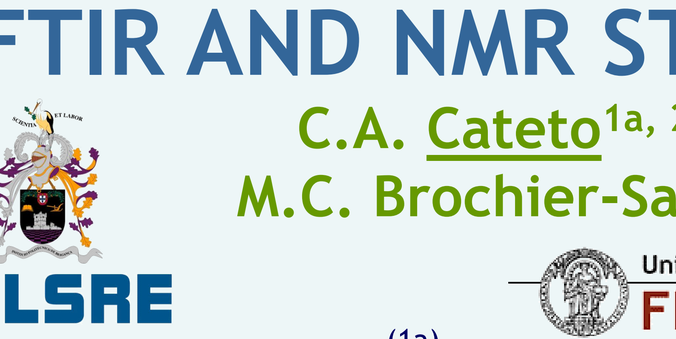

Figure 1. Lignin structural model: (i) original sample and (ii) partially acetylated sample.

Objectives

- Study of the reliability of an acetylation procedure by FTIR and ^{13}C NMR spectroscopy through the examination of samples subjected to the acetylation process during 1 and 2 hours;
- Determination of the total hydroxyl content using the standard titration procedure and ^{13}C NMR results.

Four technical lignin samples, representing guaiacyl and guaiacyl-syringyl type, and two pulp processes, Kraft and Organosolv, were used: Alcell, Indulin AT, Sarkanda and Curan 27-11P.

Experimental

Elemental analysis: Elemental analysis was carried out by CNRS (Vernaison, France). The content of C, H, N, S and O (by difference) was determined.

Acetylation procedure: The general procedure followed the method described in the international standard ISO 14900:2001.

Lignin recovery procedure: The procedure to recover the acetylated lignin samples to perform FTIR and NMR analysis was adapted from the procedure described by Glasser et al. (1993).

FTIR analysis: FTIR measurements were taken on a FTIR Bomen model MB 104 working in transmittance mode using KBr pellets. Forty eight scans per spectrum were taken in the range from 4000 to 650 cm^{-1} with a resolution of 4 cm^{-1}. KBr pellets were prepared with a lignin concentration of 1% (w/w) using a Specac hydraulic press.

^{13}C NMR analysis: ^{13}C NMR spectra were recorded on a MERCURY Varian spectrometer, equipped with a 10-mm BB probe operating at 100.624 MHz. Experiments were conducted at 50ºC in DMSO-d6 99.8% (SDS). ^{13}C chemical shifts are given relative to tetramethylsilane (TMS). The positions of the peaks were referenced to the residual solvent peak DMSO-d6 (δ=39.5 ppm). Spectra were quantitative (proton broad band decoupling only during the acquisition time. ^{13}C spectra were obtained using a 23 kHz (228ppm) spectral width, 32K data points, 11s relaxation delay, and 12ms for a 75° pulse, zero-filling and 10Hz line broadening.

Results and Discussion

FTIR Analysis:

In order to correct for concentration fluctuations, the spectra were corrected according to the area of the band assigned at 1507 cm^{-1} in the original sample. This vibration was not affected by the acetylation procedure. This procedure was tested with success for the Indulin AT in a previous work (Cateto et al., 2005). For the other samples analysed in this work, some difficulties were encountered and the method is being reviewed and improved.

13C Analysis:

The following approximate integration limits were used:

- Primary hydroxyls from 170.4 to 169.4 ppm;
- Secondary hydroxyls from 169.4 to 168.5 ppm;
- Phenolic hydroxyl from 168.5 to 165.8 ppm.

For all the samples, except for Sarkanda lignin, the original spectrum is free of of contributions in the analysed region. A correction was made.

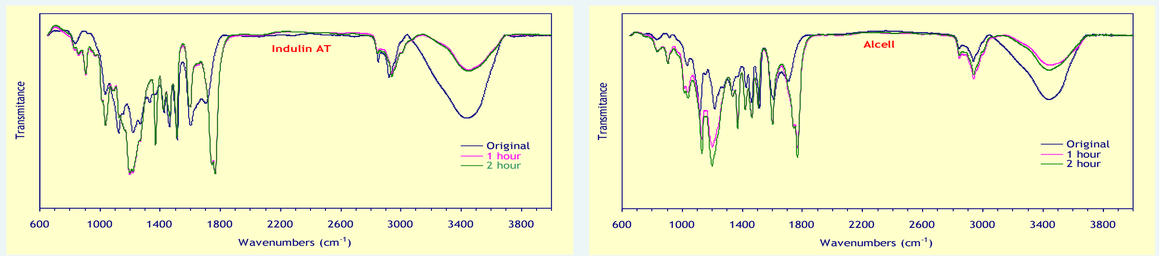

Figure 2. FTIR spectra of lignin samples (Indulin AT, Curan 27 11P, Alcell and Sarkanda) before and after acetylation (acetylation time of 1 hour and 2 hours).

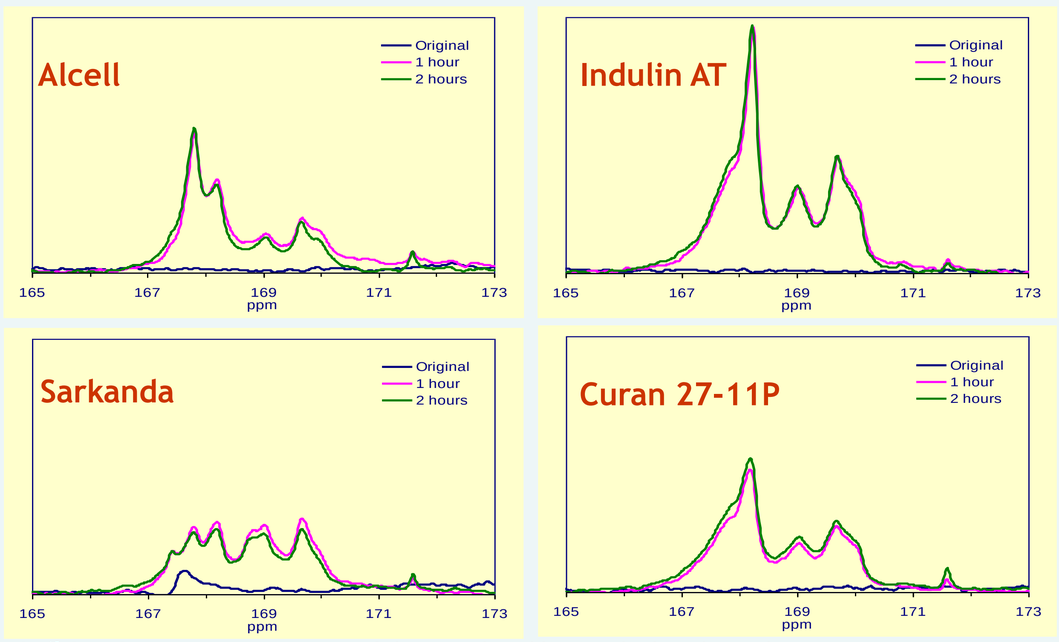

Figure 3. ^{13}C NMR spectroscopy spectra of the acetylated lignins, hydroxyl signals.

Total OH content using 13C NMR results:

The C9 empirical formula was determined based on the results achieved by elemental analysis (content of C, H and O) and ^{13}C NMR (content of OCH_3) according to Pasquini (2000). Based on this empirical formula, the molecular weight of the C9 unit was determined and thus, allows for the calculation of the of the total OH content (mmol/g) using the ^{13}C NMR results (OH/C9 unit).

Table 1. Number of C atoms associated with OH groups per C9 unit (acetylated lignins).

	Reaction time = 1 hr				Reaction time = 2 hr			
	OH (I)	OH (II)	OH (ϕ)	**OH (total)**	OH (I)	OH (II)	OH (ϕ)	**OH (total)**
Indulin AT	0.33	0.22	0.72	**1.27**	0.28	0.20	0.67	**1.15**
Curan 27 11P	0.29	0.19	0.69	**1.17**	0.27	0.18	0.67	**1.12**
Alcell	0.16	0.10	0.70	**0.96**	0.19	0.12	0.68	**0.99**
Sarkanda	0.25	0.32	0.54	**1.11**	0.24	0.33	0.58	**1.15**

Table 2. Comparison of the total OH content (mmol/g) determined based on ^{13}C NMR and titration results.

Lignin	Empirical formula	M (g/mol)	NMR results (reaction time = 1 h)		Titration results (reaction time = 1 h)
			Total OH/C9	Total OH (mmol/g)	Total OH(mmol/g)
Indulin AT	$C_9H_{8.7}O_{2.81}(OCH_3)_{0.77}$	185.53	1.27	6.85	7.10
Alcell	$C_9H_{7.22}O_{2.06}(OCH_3)_{1.11}$	182.59	0.96	5.26	5.04
Curan 27-11P	$C_9H_{9.31}O_{4.33}(OCH_3)_{0.83}$	212.32	1.17	5.51	5.42 (*)
Sarkanda	$C_9H_{9.20}O_{3.31}(OCH_3)_{0.98}$	236.54	1.05	4.44	4.30

(*) obtained after alcalinity correction

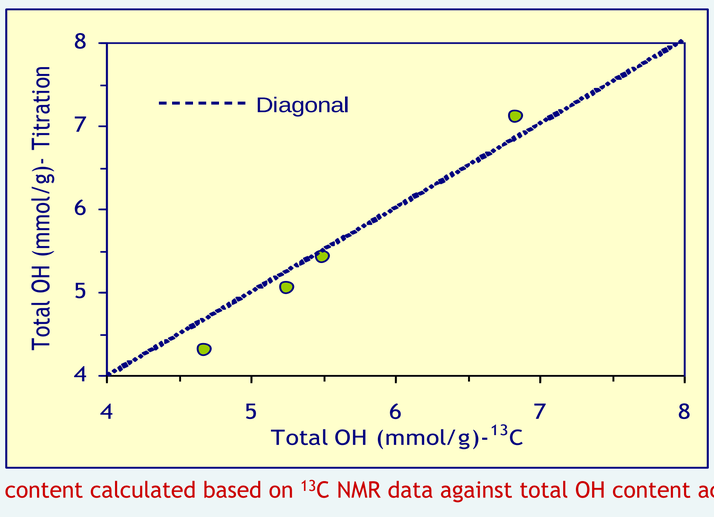

Figure 4. Total OH content calculated based on ^{13}C NMR data against total OH content achieved by titration.

Conclusions

- For all the cases studied, an incomplete acetylation yield was achieved as verified by the presence of a residual OH band in the FTIR spectra;
- The maximum reaction yield was reached for reaction time of 1 hour as was indicated by the FTIR experiments and confirmed by the ^{13}C NMR results;
- Total OH content was determined both by titration and using the ^{13}C NMR results and found to be in close agreement.

Acknowledgements:

We thank the French-Portuguese Scientific Cooperation Programme and FCT for financial support within action F-13/06 and grant SFRH/BD/18415/2004, respectively; to MeadWestvaco for supplying us the Indulin AT samples and BooregaardLignoTech for supplying us the Curan 27-11 P samples.

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