^{1}H NMR Spectroscopy for Lignin Analysis.

Recently it has been demonstrated that 1H-NMR spectroscopy of lignins offers another valuable way to analyze and quantify phenolic hydroxyl groups in lignins. Lundquist performed an extensive study on the use of ^{1}H-NMR spectroscopy to analyze phenolic groups in underivatized lignin samples, i.e. non-acetylated lignins in dry DMSO-d_6. DMSO–d_6 is an excellent lignin solvent and the chemical shift of hydroxyl protons in this solvent is characteristic and proton exchange is slow. Li and Lundquist have stated that ^{1}H–NMR spectrometric analysis of lignin–phenolic groups in DMSO–d_6 solvent is possible if the following conditions are maintained: the amount of water present is minimized, no acid is present except for the small number of lignin–carboxylic acid groups, and no base is present. The T_1 relaxation parameter for lignin in DMSO–d_6 solution has been found to be < 1 second and a pulse delay of 7 seconds has been used.

Model compounds were used to make signal assignments for the various types of phenolic groups present in lignins. Figure 1 spectrum contains several resolved signals arising from protons on specific lignin structures.

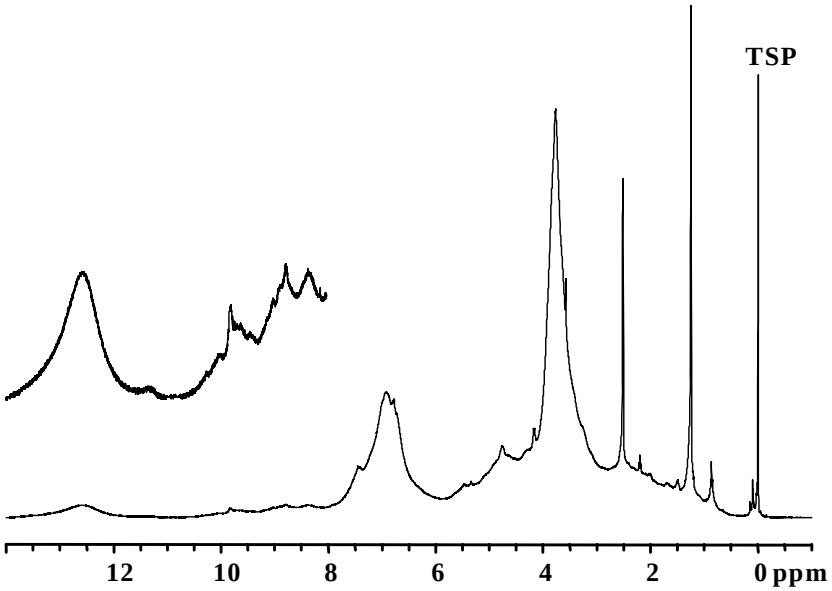

Figure 1. Quantitative ^{1}H–NMR spectrum of a residual isolated from an oxygen delignified softwood kraft pulp (brownstock, kappa = 47, prepared in this study).

. The peaks in the range of δ 9.4-10.0 are mainly due to formyl groups yet some phenolic hydroxyl groups may also be present in this region. Model compound studies found that phenolic groups with carbonyl groups conjugated with the aromatic ring had signals in this region. The more predominate phenolic groups, i.e. not conjugated with carbonyl groups, can be found in the δ 8.0-9.4 range. The model compound study showed that the large signals at δ 8.99 and 8.76 belong to phenolic groups in phenylcoumaran and arylgylcerol β-O-4 structures, respectively. Such structures are known to be predominant in wood lignin. Another region of interest is from δ 8.5-8.0 in which C5 substituted or

'condensed' type phenolic hydroxyl groups can be found, such as biphenyl structures. The analysis of underivatized lignins also allows for the quantification of carboxylic acid groups which have a well separated signal at approximately δ 12. Integrating this signal has been found to yield valuable data on the quantity of carboxylic acid groups in lignins. A major advantages of ^{1}H–NMR are no modification of the residual lignin are required and the high intrinsic sensitivity allows for the use of a small sample size and a short acquisition time.

Integration regions for ^{1}H–NMR analysis of isolated lignins.

Structure	δ ^{1}H–NMR (ppm)
Carboxylic acid	14.0 – 11.0
Aldehyde	11.0 – 9.4
Unsubstituted phenolic	9.4 – 8.5
Substituted phenolic	8.5 – 7.9
Aromatic and vinylic	7.9 – 6.3
Aliphatic (H_α and H_β)	6.3 – 4.0
Methoxy and H_γ	4.0 – 3.5
H_β in β–1	2.9 – 2.8
Internal standard, TSP	0.08 – (-0.08)

Summary of ^{1}H–NMR Determined Functional Group Data (mmol/g Lignin) for Oxygen and Peracetic Acid Bleached Kappa 24 Softwood Kraft Pulps.

Structure	BS [a]	O	O*	PaO*
Carboxylic acid	0.85	1.33	2.31	2.57
Aldehyde	1.05	1.22	1.06	0.90
Unsub.phenolic	2.68	1.65	1.34	1.28
Substituted phenolic	1.39	1.24	1.14	1.08
Total Phenolic	4.06	2.89	2.48	2.36
Aromatic and vinylic	15.91	13.79	12.86	15.40
Aliphatic (Hβ & Hα)	10.99	14.24	13.44	16.16
Methoxy (Hγ & OH)	20.04	17.79	15.95	20.12
Hβ in β–1	8.57	7.27	7.81	13.21

BS: brownstock, O delignified, O* extended oxygen delignified, PaO* peraectic acid, and then extended oxygen delignification

Reference: Li, S. and Lundquist, K., "A New Method for the Analysis of Phenolic Groups in Lignins by ^{1}H-NMR", *Nordic Pulp and Paper Research Journal*, 3, 191, (1994).