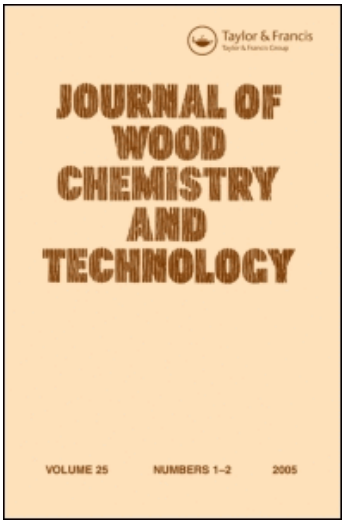

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FRACTIONATION OF ALCELL® LIGNIN BY SEQUENTIAL SOLVENT EXTRACTION

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ABSTRACT

A prototype solvolytic lignin has been fractionated into three fractions by successive extraction with organic solvents of increasing hydrogen-bonding capacity. A comparison between the fractions and the starting lignin has been made in terms of methoxyl group content, fractionation yields, molecular weight distribution, alkaline nitrobenzene oxidation, and ^{1}H and ^{13}C NMR spectroscopy. The fractionation procedure was found to isolate fractions having distinct group functionalities and molecular weight distributions. In particular, the heterogeneity of ALCELL® lignin is demonstrated from the data. A significant portion of this lignin, 27%, was found to be comprised of a very low molecular weight (M_w = 714 g/mol) fraction soluble in ether. This fraction had a lower polydispersity but a higher content of guaiacyl structures with saturated side chains than the higher molecular weight fractions.

Keywords: ALCELL® lignin, fractionation, functionality, nitrobenzene oxidation, molecular weight distribution, NMR spectroscopy.

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INTRODUCTION

Increasing interest is being paid towards the utilization of lignins produced by "newer" pulping methods as a raw materials source for production of higher value-added products such as useful low-molecular weight chemicals[1] and polymeric materials[2]. Among the important advantages of these lignins often mentioned are their high reactivity, solubility, and lower molecular weight when compared to technical lignins from conventional kraft pulping. The lignins are isolated as major by-products when using these novel pulping techniques which render the woody biomass susceptible to solvent penetration, in the case of organosolv pulping, or to a base solution, as in the case of "steam explosion" pulping, and therefore solubilize the lignin between the fibers. A major advantage of these schemes is that they afford the recovery of the three major polymeric wood constituents in high yield and purity[3]. Thus, each wood fraction can potentially be utilized as a feedstock source using an appropriate strategy for production of high value-added products, and therefore afford the highest potential return on investment.

When compared to the conventional kraft pulping process, organosolv pulping reportedly offers a number of advantages such as economical pulping on a smaller scale, and a sulphur-free, and, therefore, an environmentally benign process. However, it is only recently that these attractive features of solvent pulping have been proven beyond the pilot plant scale with the construction and operation of demonstration-scale plants both in West Germany[4] and in Canada[5].

In Canada, a semi-commercial scale plant based on a proprietary ethanol-water based pulping technology, the Alcell process, has been in operation since 1989. The 30 ton/day mill has operated routinely since start up. It has proven its capability of producing fully bleachable pulps with physical and optical properties similar to those of kraft pulp[5]. A major lignin fraction, known as ALCELL® lignin, is precipitated from the spent black liquor after alcohol evaporation and concentration. This lignin, which is the major by-product of the process and recovered as a free flowing powder, is dried and bagged for sale.

The objective of this paper is to elucidate the heterogeneity of ALCELL® lignin by subjecting it to a sequential solvent fractionation scheme. The characteristics

of the fractions in terms of molecular weight distribution, group functionality, alkaline nitrobenzene oxidation, and NMR spectroscopy, are discussed here. Separation methods such as gel chromatography or ultrafiltration are not practical for economically fractionating lignins on a large scale. Thus in this investigation, ALCELL® lignin was fractionated by successive extraction with solvents of increasing dissolving power for lignin.

EXPERIMENTAL

(a) Materials

ALCELL® lignin from a mixed hardwood (15% poplar, 50% maple and 35% birch) furnish was produced by Alcell Technologies Inc., a subsidiary of Repap Enterprises Ltd. (Montreal, QU., Canada) at its semi-commercial facility in Newcastle, N.B., Canada.

(b) Analytical Techniques

Methoxyl Group Determination: The methoxyl group content was quantified using the TAPPI method T209-WD-79[6].

High Pressure Solvent Elution Chromatography (HPSEC): A Waters liquid chromatograph connected to a Waters NEC 80486 data system was used. Three stainless steel columns (300 x 7.5 mm) connected in series and packed with ultrastyragel spherical particles of porosity 10^4, 500, and 100 Å were used. A UV monitor (277 nm) was used for detection. A constant flowrate through the system was maintained by a single piston, reciprocating pump. The following operating conditions were employed: eluent, degassed tetrahydrofuran (purged with N_2); temperature, 25°C; injection volume, 100 µL; flow rate, 1 mL/min.

A relative calibration curve was obtained using monodisperse polystyrene standards (Polymer Laboratories, England, UK). A third-order polynomial of the form $y = ax^3 + bx^2 + cx + d$ best describes the relation between the log of the actual molecular weights of polystyrene standards (y) and their retention times (x). The following coefficients were calculated: a = -0.00021, b = 0.0283, c = -1.279, d = 20.64. These gave a fit with a correlation coefficient of 0.99. The size exclusion volume (V_o) for the column system was 6.4.

Fractionation Scheme: ALCELL® lignin was fractionated by sequential solvent extraction. This approach is based on the work of Schuerch[7] who discovered that lower molecular weight lignin fractions are soluble in organic solvents with weak or moderate hydrogen-bonding capacity with a wider range of Hildebrand solubility parameters than are the higher molecular weight fractions. Our solvent selection was based on preliminary solubility tests conducted on ALCELL® lignin at room temperature. The results are shown in Table 1. The sequence of fractionation was as follows. Ether was added to a 250 mL volumetric flask containing a weighed quantity of lignin. The contents were agitated for 20 minutes using a magnetic stirrer at room temperature. The suspension is then allowed to stand for another 10 minutes to allow any suspended lignin particles to settle before decanting the supernatant into a collection flask. The same procedure is repeated several times until it was considered that the majority of the ether solubles were removed from the starting lignin. Evidence for this was the resulting light yellowish color of the supernatant after the last extraction. The remaining solvent in the residue was evaporated under reduced pressure. Methanol was next used in the sequence. However, the contents of the flask were now agitated using an ultrasonic cold water bath for 10 minutes instead of a stirrer. The reason for using this mode of agitation was because the remaining residue, after the first extraction with methanol, was a highly viscous but flowing black liquid. After repeating the extraction several times, the methanol solubles were considered sufficiently removed by the very light colored supernatant after the last extraction. The remaining residue in the extraction flask, after evaporation of the solvent, constituted the third fraction.

The combined supernatant liquid for each of the two fractions was evaporated under reduced pressure in a 150 mL evaporation flask in aliquots of about 100 mL until a viscous residue remained at the bottom of the flask. To ensure removal of the rest of the solvent, all three fractions were kept in a desiccator under vacuum for two days.

Each fraction was then removed from the flask and stored in bottles under a nitrogen blanket in the dark until further use.

TABLE 1. Solubility of ALCELL® Lignin in Various Solvents.

Solvent	*σ(H)	Solubility
Hexane	7.3	Insoluble
Carbon tetrachloride	8.6	Insoluble
Ethylacetate	8.9	Highly soluble but some residue remaining
Toluene	8.9	Virtually insoluble - solvent slightly colored
Tetrahydrofuran	9.1	Completely soluble
Benzene	9.2	Virtually insoluble but solvent slightly colored
Chloroform	9.3	Highly soluble
Water	23.4	Insoluble
Acetone	9.9	Highly soluble with a slight amount of residue remaining
Dioxane	10.0	Completely soluble
Iso-propylalcohol	10.0	Highly soluble with some residue remaining
Ethanol	10.0	Somewhat soluble with a moderate amount of residue remaining
n-propanol	10.5	Only slightly soluble
Ethylene glycol	10.7	Somewhat soluble with a moderate amount of residue remaining
Methanol	14.5	Somewhat soluble with a moderate amount of residue remaining
Ethylether	7.4	Slightly soluble
Methylene chloride	9.7	Moderately soluble but some residue remaining
1-Butanol	13.6	Moderately soluble
2-Octanol		Only slightly soluble (light brown supernatant)
Nonanol	8.4	Only slightly soluble (light brown supernatant)
Hexanol	10.7	Moderately soluble (better than nonanol and 2-octanol)

Note: * Values of solubility parameters (σ) were taken from Barton[20].
Solubility Tests: ~0.05 g of lignin was shaken at room temperature in 4-5 mL of solvent and observed for depth of color of solvent and presence of undissolved material.

In this manner, a fraction for each solvent extraction sequence was obtained from ALCELL® lignin. All three fractions were black, viscous and sticky polymers with no visible granular particles. The lignin, on the other hand, is a free running powder and light brown in color.

Nitrobenzene Oxidation: ALCELL® lignin and its fractions were each subjected to oxidative treatment in an alkaline medium using a 500 mL capacity batch reactor equipped with a magnetic stirrer. Amounts of initial sample and reactants used per run were as follows: 10 g of dry lignin; 240 mL of water; 20 g of NaOH; 30 mL of nitrobenzene. Conditions for reaction were 180 °C held for 2 h, 300 rpm agitation. After reaction, the combined washings and product liquids were stored in 500 mL bottles at -15°C prior to work-up using the following procedure. After pre-equilibrating to room temperature, the solution was initially extracted with (5X) with 100 mL of ether to remove the excess nitrobenzene. The aqueous layer was then acidified with 10% (v/v) hydrochloric acid to a pH of 1-1.5, filtered, and the filtrate extracted with ether until the last ether extract was judged to be colorless. The combined ether extracts were evaporated to constant weight under reduced pressure at room temperature, leaving an oily yellowish fraction as residue.

A portion of the ether-soluble fraction was derivatized by the acetic anhydride-pyridine procedure and directly analysed by gas chromatography[8]. A 30 m DB-5 capillary column was employed. Compounds were identified by comparing their peak retention times to those of authentic samples. Response factors were determined for each compound to be quantified using resorcinol as the internal standard. Tests on a standard blend showed the deviation to be within 5% for the aldehydes considered, namely, vanillin and syringaldehyde. The following oven programmation was found to produce good product separation: initial temperature, 40°C; rate, 6°C/min; held constant at 140°C for 10 minutes; rate, 4°C/min; held constant at 220°C for 10 min; cool to 40°C.

Quantitative Acetylation: The high solubility of the lignin and its fractions in the acetylating agents warranted the following procedure to be employed. Approximately 4g of sample was dissolved in 60 mL of a 1:1 mixture of pyridine/acetic anhydride

in a 125 mL glass vial. The mixture was agitated for 2 days at room temperature using a rotary shaker. The product was recovered by pouring the mixture into an ice-water mixture. The resulting aqueous phase was then extracted (2X) with methylene chloride, and the organic phase, consisting of the dissolved acetylated lignin and pyridine in CH_2Cl_2, was then evaporated under reduced pressure to remove the methylene chloride solvent. The pyridine in the remaining sample was removed by azeotropic evaporation with toluene under reduced pressure (3X). Residual toluene was then removed by evaporation with methanol under reduced pressure (2X). The resulting product was dried under vacuum for 20-24 h and stored under nitrogen in a vial until further use.

^{13}C NMR: Alcell® lignin and its fractions were acetylated and analyzed using a Brüker 400 WD spectrometer. Samples were prepared by dissolving *ca.* 800 mg of lignin in 2 g of DMSO-d_6 at room temperature and placing the solution in 10 mm i.d. glass tubes. The instrument was set in proton inverse gated decoupled mode, with a scan delay of 2 sec. All samples were run at a temperature of 50 °C.

RESULTS AND DISCUSSION

Yields: Similar fractional yields (within 3%) were obtained from three 50 g and two 100 g initial lignin samples tested, demonstrating the reproducibilty of the fractionation procedure. The data in Table 2, for a 50 g sample, demonstrates the heterogeneity of ALCELL® lignin. Fr-1 represents 27% of the initial lignin; the major fraction is the methanol-soluble fraction (Fr-2) which comprises approximately 53% of ALCELL® lignin; the unsolubilized portion (Fr-3) makes up 18% of the initial lignin. Using this extraction procedure, losses were calculated by difference and consistently amounted to 2% or less.

HPSEC: Owing to differences in chemical structure between the calibration polystyrene standards and the lignin, all data on molecular weight distribution of the lignin and fractions in this work should only be taken as relative values of molar mass. The method can, however, be used to compare the molecular weights of the lignin and its fractions.

TABLE 2. Fractionation Yields, Methoxyl Content, and Molecular Weight Averages (Polystyrene Equivalent) of ALCELL® Lignin and Fractions.

Fraction No.	Yield (%)	Methoxyl (%)	M_w (g/mol)	M_n (g/mol)	d
1 (Ether)	27	13.2	720	480	1.5
2 (MeOH)	53	15.4	2410	1040	2.3
3 (Insol.)	. 18	17.5	6950	2400	2.9
Losses	2	--	--	--	--
Original Lignin	100	16.5	3300	900	3.7

Figure 1 shows the molecular weight distribution patterns of the unfractionated ALCELL® lignin and the three fractions after acetylation. Important observations in the chromatograms are as follows. The starting lignin exhibits a multimodal distribution pattern, with a relatively prominent high molecular weight peak whose maximum corresponds to 3079 g/mol (polystyrene-weight equivalent). The presence of one or more distinct peaks in the elution profile seems to be a typical feature of acetylated organosolv lignins[3,9].

The weight average (M_w) molecular weight, number average (M_n) molecular weight and polydispersity (d), are listed in Table 2. A steady increase is observed in both molecular weight and polydispersity from Fr-1 to Fr-3. This suggests that Fr-1 contains materials of essentially similar molecular weight whereas Fr-3 is comprised more of a mixture of medium and high molecular weight materials. There is a significant amount (27%) of low molecular material (M_w = 714 g/mol) in ALCELL® lignin that can be extracted with ethyl ether. As seen in Table 2, the polydispersity (d) values of the fractions are all rather low (<3), increasing from Fr-1 to Fr-3.

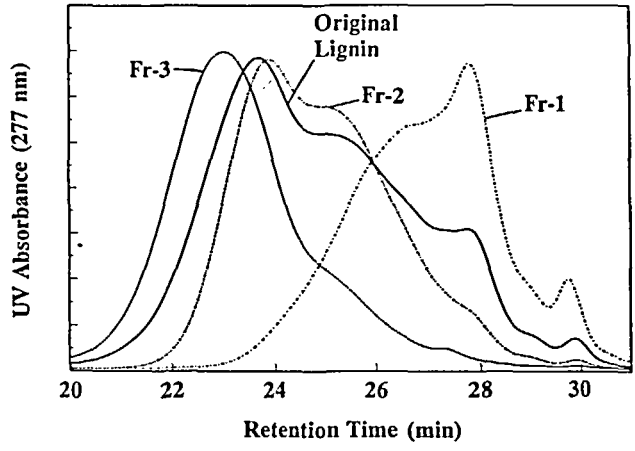

FIGURE 1. Molecular weight distribution (polystyrene weight equivalent) of acetylated ALCELL® lignin and its fractions.

The starting lignin, on the other hand, has the broadest distribution (highest d value). Fr-2 may therefore be considered as a medium molecular weight fraction, essentially deplete of high and low molecular weight material. Thus, the solvents used in the present work are very selective for fractionating ALCELL® lignin, as demonstrated by the rather distinct molecular weight distribution patterns.

Nitrobenzene Oxidation: The technique has been widely used for characterizing protolignin as well as isolated lignins to deduce their structural features, and, especially in the case of the latter, their degree of condensation[10,11]. In the present work, the method is applied to determine whether significant structural differences exist between isolated ALCELL® lignin and its fractions.

As seen in Table 3, the yields of aldehydes strongly suggest that indeed, moderate to significant structural differences exist between the starting lignin and fractions. For both aldehydes, the yields obtained are highest from the initial lignin than from any of the fractions. The yields of both aldehydes are similar from Fr-1 and Fr-2, but distinctly lower in Fr-3. This indicates that Fr-3 is comprised of the highest

TABLE 3. Yields of aldehydes (wt% initial lignin) identified from the alkaline nitrobenzene oxidation of ALCELL® lignin and its fractions.

Monomeric Products	Initial Lignin	Fr-1	Fr-2	Fr-3
Vanillin (V)	8.2	7.2	7.0	4.6
Syringaldehyde (S)	11.0	8.5	9.4	6.4
S/V (g/g)	1.34	1.18	1.34	1.40
(S+V)	19.2	15.7	16.4	11.0
Methylene chloride Solubles	20.7	22.3	17.7	16.3

amount of condensed structures, causing it to be the least amenable to oxidative degradation. The low aldehyde yield in this fraction may also be due to the incorporation of non-lignin materials such as carbohydrate products[11]. Klemola and Nyman[12] have postulated that a more condensed, stable material may also arise from the reaction of furfural and its precursors with lignin to form new carbon-carbon linkages.

It has been reported that the syringaldehyde/vanillin (S/V) ratio is an important criterion for assessing the degree of condensation of a lignin[11]. As seen in Table 3, the S/V values increase with increasing fraction number, indicative of the syringyl character from Fr-1 to Fr-3. This trend is verified in Table 2 where the methoxyl group content of the fractions is also increasing with molecular weight. It is apparent that the character of ALCELL® lignin as a hardwood lignin is most obvious in the higher molecular weight fractions. A similar trend was also obtained in the case of fractions of ethanol-water lignins from birch [13]. However, it should be noted that the yields of both aldehydes from Fr-3 were substantially lower than in the starting ALCELL® lignin but less so for Fr-1 and Fr-2.

^{1}H NMR: The proton NMR spectra of ALCELL® lignin and its fractions are shown in Figure 2. Peak assignments are in accordance with those of other workers[14,15].

Fr-1 exhibits the highest intensity of signals at 0.9-1.4 ppm (due to methyl and methylene protons) indicating that this fraction contains the most aliphatic saturated structures. The strong sharp signal at about 2 ppm in the starting lignin is absent in all the fractions. The cause of this signal is not known by the authors.

The intensity of the signal of acetates due to aromatic (2.20-2.50 ppm) and aliphatic (1.60-2.20 ppm) hydroxyl protons steadily decreases from Fr-1 to Fr-3, indicative of the decrease in catechol bearing units with increasing fraction number. The intensities of the signals at about 4.2-6.0 ppm (except for the peak at 6.0 ppm), attributed to protons attached to γ-carbons in several types of structures (mostly β-O-4 and β-5), are highest in Fr-1 but lower or even absent in Fr-2 and Fr-3. This suggests that Fr-1 contains a higher proportion of structures linked by β-O-4 and β-5 interlinkages than the other two fractions. The peak at 5.5 ppm, assigned to protons attached to α-carbons in β-5 structures, has the highest intensity in Fr-1. The presence of the signal at 6.0 ppm (due to H-α in β-aryl ether bonds) in Fr-2 and Fr-3, and its absence in Fr-1, suggests the former fractions contain more structures linked by β-aryl ether linkages than the latter fraction. This is indeed confirmed by the results from ^{13}C NMR spectroscopy and alkaline nitrobenzene oxidation.

All the spectra of the fractions display marked differences in the 6.4-8.0 ppm region, attributed to protons attached to aromatic carbons. This strongly suggests that the aromatic character of each fraction is distinct from the others as well as from the starting lignin. The signals between 8 and 9 ppm, attributed to protons of carboxylic acid groups, are more intense in Fr-2 and Fr-3 but very weak in Fr-1 and the initial lignin.

^{13}C NMR: Figure 3 shows the ^{13}C NMR spectra of acetylated ALCELL® lignin and its fractions. The peak assignments are based on previous works[14,16,17].

Important differences exist between the signal intensities in the 166-170 ppm region. The higher intensity of the signal at 168 ppm (phenolic hydroxyl groups) in all the spectra than the signal at 170 ppm (primary aliphatic hydroxyl groups)

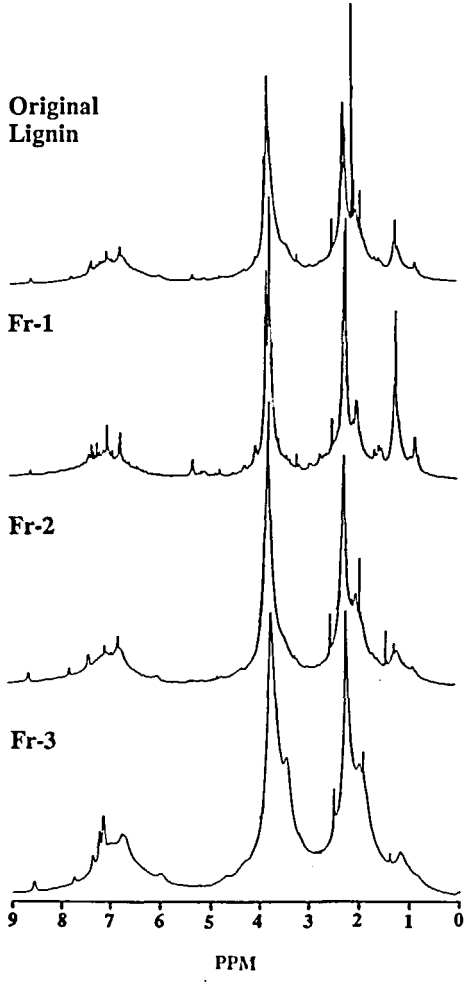

FIGURE 2. ^{1}H NMR spectra of acetylated ALCELL® lignin and its fractions; solvent, DMSO-d_6.

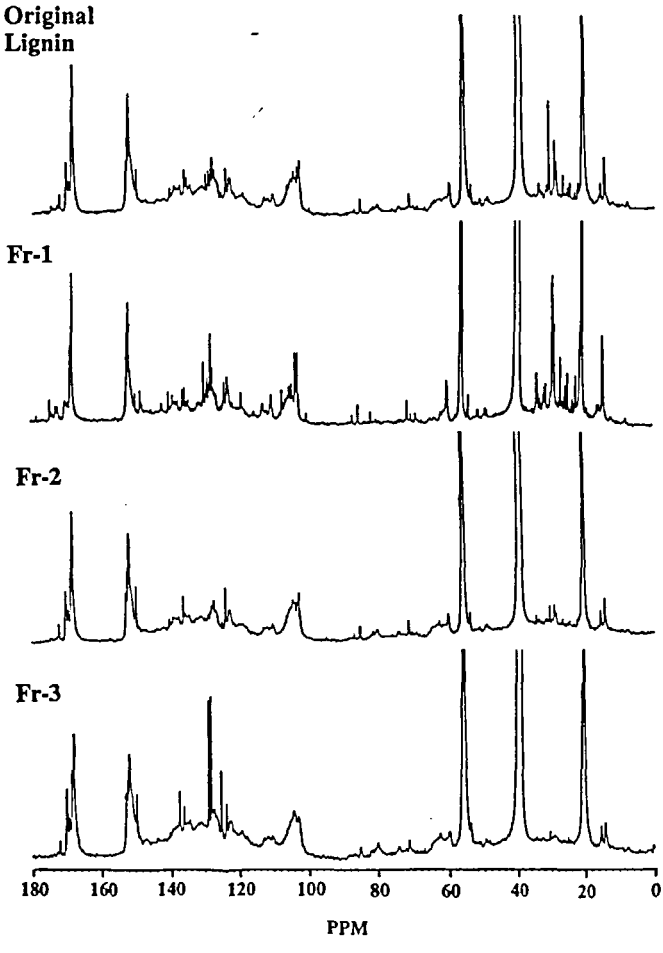

FIGURE 3. ^{13}C NMR spectra of acetylated ALCELL® lignin and its fractions; solvent, DMSO-d_6.

suggests the former contributes more to the total hydroxyl group content than the latter in both the starting lignin and fractions. Fr-1 is seen to be almost devoid of primary aliphatic hydroxyl groups; the signal at 170 ppm is all but absent. On the other hand, the intensity of this signal is the highest in Fr-3. The lack of terminal

hydroxyl groups (primary and secondary) on the side-chain, especially in Fr-1, suggests that these have probably been removed by a water-elimination reaction and/or bond rupture between the β- and α- carbons (Sudo et al.[18]) during Alcell pulping. The intensity of the signal at 169 ppm, attributed to secondary aliphatic hydroxyl groups, is of very low intensity in all the spectra indicating that these groups are virtually absent in ALCELL® lignin. Also, the high intensity of the signal due to phenolic hydroxyl groups suggests that this lignin is demethoxylated during Alcell pulping. However, demethoxylation is not extensive as evidenced by the very high intensity of the signal at 55 ppm attributed to methoxyl groups. Demethoxylation reactions occurring in lignins during pulping have been known to increase the content of phenolic hydroxyl groups.

In the aromatic region (153-104 ppm), the signal at 150 ppm, due to C-3/C-4 in etherified guaiacyl units, is highest in intensity, demonstrating that ALCELL® lignin contains a rather high proportion of guaiacyl moieties. Indeed, this is confirmed by the results from nitrobenzene oxidation. The sharp signals at 129-128 ppm are very significant in Fr-3. These signals are due to a toluene impurity from the acetylation workup. This is confirmed by the presence of two other toluene signals at about 125 ppm and 137 ppm. The methyl signal in toluene at about 20 ppm is masked by the large acetate methyl signal from the acetylated sample.

Signals in the 86-50 region are attributed to oxygenated and non-oxygenated interunit linkages in lignin. As observed, these signals in all the spectra are low in intensity, except for the signal at 62 ppm (due to γ- and β- carbons in dilignols). Extractives such as resin acids also would appear in this region. Signals in the 34-12 ppm region are assigned to saturated hydrocarbon structures in the aliphatic side-chains (C atoms in n-alkyl moieties or in $CH_3CH_2CH(CH_3)C$ groups). A distinct difference in this region between the spectra is the high abundance and intensity of signals in Fr-1 and their almost complete absence from the higher molecular weight fractions, especially in Fr-3. In the starting lignin, these signals are present but lower in intensity. As in the case of kraft pulping (Mörck and Kringstad[19]), some of these saturated hydrocarbon structures can be introduced into the side chains of the lignin

during the cooking stage of the pulping process. It may be concluded then that Fr-1 is mostly composed of material containing saturated aliphatic residues. Also, it must be noted that since the initial wood used in the Alcell process is not extractives-free, these saturated structures may partly arise from fatty acids or other non-volatile extractives.

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