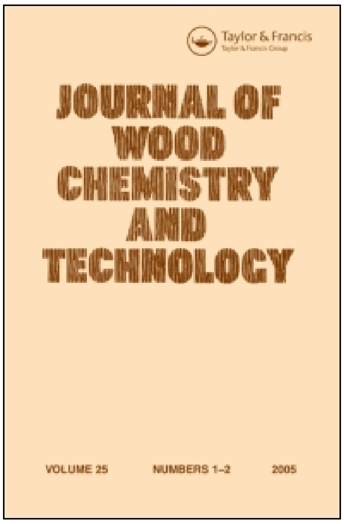

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Froass, Peter M. , Ragauskas, Arthur J. and Jiang, Jian-er(1996) 'Chemical Structure of Residual Lignin from Kraft Pulp', Journal of Wood Chemistry and Technology, 16: 4, 347 — 365

To link to this Article: DOI: 10.1080/02773819608545820

URL: http://dx.doi.org/10.1080/02773819608545820

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 16(4), 347-365 (1996)

CHEMICAL STRUCTURE OF RESIDUAL LIGNIN FROM KRAFT PULP

Peter M. Froass and Arthur J. Ragauskas
Institute of Paper Science and Technology
Atlanta, GA 30318

and

Jian-er Jiang
R&D Laboratory
Ahlstrom Machinery
Glens Falls, NY 12801

ABSTRACT

Structural characteristics of wood lignin and residual lignin in conventional and modified kraft pulps were examined employing elemental and methoxyl analysis and ^{13}C, ^{1}H, and ^{31}P-NMR. The structural analysis revealed that kraft residual lignin differs significantly from wood lignin while differences between residual lignins in conventional and EMCC® pulps have similar structural characteristics at kappa numbers corresponding to the point where the selectivity of the cook becomes poor. NMR analysis suggested that residual lignin, compared to the wood lignin, is much less reactive towards pulping chemicals due to the low content of aryl ether linkages and the prevalence of condensed type structures.

INTRODUCTION

The manufacturing of bleached kraft pulp has changed dramatically over the past decade in response to a variety of environmental concerns. Of the many technological advances being developed to improve bleached chemical pulp production one of the most promising has been extending delignification during kraft pulping. Due to the slow final phase of kraft delignification, when pulping selectivity becomes poor, extending delignification (i.e., modified kraft) is not as straightforward as increasing the cooking time or alkali charge. Instead process changes must be made to the pulping system that improves the selectivity during the final phase of delignification.

During the late 1970's and early 1980's investigations into kraft pulping revealed four principles that would permit the production of low lignin content pulps with acceptable pulp strength.[1,2,3] These principles include leveling out the alkali concentration throughout the cook, maintaining a high hydrosulfide concentration particularly at the beginning of the bulk delignification stage, keeping the dissolved lignin and sodium ion concentration low particularly towards the end of the cook, and employing low cooking temperatures.

Despite these advances in pulping technologies the fundamental principles which contribute to the success of extended kraft pulping remain poorly understood. The nature of the dissolved and residual lignins produced during conventional kraft pulping procedures have been analyzed by Gellerstedt[4-10] and others.[11-19] These studies have established the general chemical structure of dissolved and residual lignins produced from conventional kraft pulping procedures and have highlighted many of the chemical pathways by which lignin is removed during pulping. Of particular importance, results from Gellerstedt's group have shown that noticeable changes occur in the relative frequency of structural subunits of lignin during kraft pulping. Compared to native wood lignin, dissolved and residual kraft lignins contain a greater content of free phenolic groups (with dissolved lignins having a significantly greater amount of such groups), a reduced amount of β-O-4 aryl ether linkages, and an increased amount of carbon-carbon linkages. These structural changes hinder additional fragmentation reactions causing the residual lignin to be unreactive towards the pulping chemicals. Experimental evidence supporting the formation of lignin carbohydrates complexes (LCC's) during kraft pulping has been reported.[20,21] Such linkages may also hinder the lignin's dissolution during pulping.

Recent studies by Gellerstedt have found that the dissolved lignin in a modified kraft cook has a lower phenolic content compared to the dissolved lignin of a conventional kraft cook.[9] Hortling et al. have examined the chemical nature of residual lignin isolated from MCC® and Super-Batch® pulping technologies.[14] The lignin isolated from these pulps was compared against an overcooked conventional kraft pulp. The results suggest that compared to the residual lignin in conventional kraft pulp the residual lignins in extensively delignified kraft pulps have a lower content of β-O-4 linkages, a higher content of C-5 condensed structures, and a similar content of phenolic groups except for the overcooked conventional which has a slightly higher content of phenolic groups.

For the studies reported in this paper three pulps were prepared from a single wood source. The three pulps were a conventional kraft, an EMCC® kraft and an EMCC® cook terminated prior the counter-current cooking stage. Lignin isolated from each of the kraft cooks and the starting wood chips were characterized by elemental and methoxyl analysis and by advanced NMR techniques.

TABLE 1.
Pulping Conditions and Pulp Properties for the Conventional, Interrupted EMCC®, and EMCC® Kraft Pulps.

Kraft Pulp	Conventional	Interrupted EMCC®	EMCC®
WL Sulfidity, %	34.6	34.6	34.6
Total EA, % NaOH	19.7	20.0	20.0
Impregnation	19.7	13.0	13.0
Co-current	-	5.0	5.0
Max Temperature,°C	170	165	165
Time at Temp., min	95	60	300
Kappa No.	27.4	98.4	17.9
Visc., mPa.s	39.9	-	38.9
V/K	1.46	-	2.17
Screened Yield, %	46.9	56.9	44.3

EXPERIMENTAL

Kraft Pulping

The pulping experiments were performed at Ahlstrom Machinery's pilot facilities in Glens Falls, NY. Literature procedures were used to simulate conventional and EMCC® pulping.[22] Southern pine wood chips were employed as the wood source for the pulps. Table 1 lists some relevant pulping conditions and properties of the pulps.

Chemicals

All chemicals employed in this study were purchased from Aldrich and used without further purification.

Residual Lignin Isolation from Kraft Pulps

The pulps were first extracted with acetone for 24 hours in a Soxhlet extractor and then washed thoroughly with deionized water and air dried.

The residual lignin was isolated from the kraft pulps following Gellerstedt's dioxane/water acid hydrolysis procedure which basically involves refluxing the pulp for two hours in a 0.1 N HCl 4:1 dioxane:water solution.[9,10] The yield of isolated lignin ranged from 55-65% based on the kappa number of the pulp before and after the acid hydrolysis.

Wood Lignin Isolation Procedure

The lignin from the wood was isolated in the same manner as the residual lignin was isolated from the pulp. Prior to the acid hydrolysis, the wood was milled in a Willy mill with a 1 mm mesh screen and extracted for 24 hours with acetone in a Soxhlet extractor.

Lignin Acetylation Procedure

Prior to ^{1}H-NMR analysis, the lignins were acetylated following literature procedures.[23] A dry lignin sample (~100mg) was first dissolved in 1 ml of anhydrous pyridine and then treated with an equal volume of acetic anhydride. The mixture was stirred for 24 hours at room temperature. Ethanol was repeatedly added and removed under reduced pressure several times until all the pyridine and acetic acid was removed. The acetylated lignin was purified by dissolving in chloroform and precipitating in ether. The acetate was dried at 40°C under vacuum.

Elemental and Methoxyl Analysis of Isolated Lignin

All lignins were analyzed for elemental composition and methoxyl content (see Table 2) by E + R Microanalytical Laboratory Inc. in Corona, NY.

Qualitative ^{13}C-NMR Spectroscopy

Qualitative ^{13}C-NMR spectra were recorded on all lignins in dimethylsulfoxide-d_6 using a Varian 400 MHz spectrometer operating at 100.57 MHz. The concentration of these samples ranged from 300 - 500 mg/3.0ml. Standard waltz decoupling was employed. A 45° pulse angle was used along with a one second pulse delay. A minimum of 30,000 scans were collected for each sample.

Quantitative ^{1}H-NMR Spectroscopy

Quantitative ^{1}H-NMR were recorded on all acetylated lignins in $CDCl_3$ using a Varian 300 MHz spectrometer. All proton NMR spectra were recorded employing ~25 mg sample/0.7 ml solvent using tetramethylsilane as an internal reference.

Quantitative ^{31}P-NMR Spectroscopy

The procedure used for the ^{31}P-NMR analysis in this study was followed as described in the literature.[24,25] The dry lignin samples were dissolved in a 1.6:1 mixture of pyridine and $CDCl_3$ and phosphitlated with 1,3,2-dioxaphospholanyl chloride. 4,4'-Isopropylidenediphenol was employed as an internal standard. The ^{31}P-NMR spectra were recorded on a Bruker DMX 400 MHz spectrometer employing an inverse gated pulse sequence with a 2s pulse delay. In all, eight spectra (200 transients each) were recorded for each lignin sample. The integral regions used for the quantitative estimates of the various hydroxyl groups were the same as the regions published for kraft lignin.[25]

TABLE 2.
Elemental and Methoxyl Analysis with Calculated Molecular Formulas of the Wood and Residual Lignins.

Lignin Sample	%C	%H	%O	%S	%OMe	Molecular formula
Wood	59.0	6.0	31.0	-	13.0	$C_{100}H_{105.5}O_{33.7}(OCH_3)_{9.3}$
Int. EMCC®	61.0	5.9	32.2	0.9	12.4	$C_{100}H_{98.5}O_{34.5}S_{0.6}(OCH_3)_{8.5}$
Conv.	59.8	5.3	33.7	1.2	11.6	$C_{100}H_{90.2}O_{37.6}S_{0.8}\,(OCH_3)_{8.1}$
EMCC®	61.9	5.6	31.2	1.3	12.0	$C_{100}H_{92.6}O_{32.8}S_{0.8}\,(OCH_3)_{8.1}$

RESULTS AND DISCUSSION

The kraft pulps used in this study were prepared in laboratory pilot scale digesters. Table 1 summarizes the kraft pulping conditions employed to prepare the conventional (kappa # 27.4), EMCC® (kappa # 17.9) and interrupted EMCC® (kappa # 66) kraft pulps. The lignin isolated from the conventional and EMCC® kraft pulps were produced near the point at which the slow delignification phase begins. Additionally, lignin from the wood chips and an EMCC® cook terminated at the end of the co-current stage were isolated and characterized.

After pulping, fiber samples were exhaustively washed with distilled water and extracted with acetone. The pulps were then refluxed for two hours in a solution of 0.10 N HCl dioxane:water (4:1).[9] The extracts were filtered and concentrated under reduced pressure. The precipitated lignins were collected, freeze dried, and analyzed by elemental and methoxyl analysis as summarized in Table 2. All acid hydrolysis experiments were performed under identical conditions and control experiments verified that the lignin isolation procedure was reproducible. Differences in lignin structure isolated from different pulps could therefore be attributed to differences in residual lignin structure.

The acidic isolation conditions employed for the lignin extraction process are believed to result in the hydrolysis of LCC linkages allowing for the release of lignin fragments into the aqueous dioxane solution. Repeating the acid hydrolysis procedure in the absence of an acid catalyst failed to release any lignin into solution which supports the proposed LCC acid hydrolysis mechanism. The acid hydrolysis conditions can be expected to cause some structural modifications to the lignins including the cleavage of some alpha aryl and alkyl ethers as well as beta aryl ethers in benzyl alcohol units.[26] The cleavage of the aryl ethers would result in the creation of phenolic hydroxyl groups causing the content of this functional group to be higher than the actual amount present in the wood or pulp. Lignin condensation reactions under acidic conditions are also possible but believed not to occur during the isolation, at least for residual lignin in kraft pulp.[10]

Elemental and Methoxyl Analysis

Table 2 summarizes the results from the elemental and methoxyl analysis of the wood and residual lignins. The residual lignins from the three kraft pulps exhibited lower methoxyl contents than the lignin isolated from wood suggesting that the kraft lignin samples have undergone some demethylation during pulping. The residual kraft lignins have also been sulfidized, as to be expected during kraft pulping. The interrupted EMCC® lignin has methoxyl and sulfur contents that lie in between the wood lignin and residual lignin. Interestingly, the conventional and EMCC® residual lignin samples have undergone similar degrees of demethylation and sulfidation despite the differences in the residual lignin content of these two pulps.

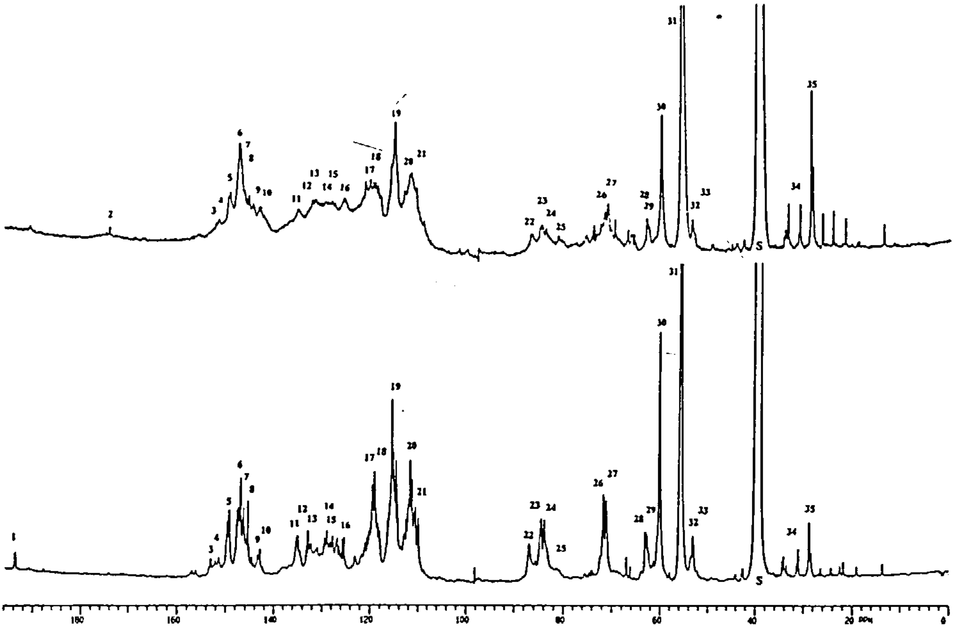

FIGURE 1. Qualitative ^{13}C-NMR spectra of wood lignin (bottom) and conventional kraft pulp residual lignin (top). For signal assignments see Table 3. (S=solvent, DMSO-d_6)

Qualitative ^{13}C-NMR Analysis of Residual Lignin

^{13}C-NMR spectroscopy is a useful technique to analyze lignin structure and is often done for structural characterization purposes.[6,9,27-30] Qualitative ^{13}C-NMR spectra were recorded on the wood lignin and the three residual lignins. Figure 1 contains the spectra for the wood and conventional kraft residual lignin. The spectrum for the residual lignin from the EMCC® pulp was quite similar to the conventional kraft residual lignin and was not included here. The chemical shifts for the labeled signals in these spectra are reported in Table 3.

A comparison between the spectra of wood lignin and residual lignin suggests that significant changes to the lignin have occurred during pulping.

TABLE 3.

Chemical Shifts (δ) and Signal Assignments for the ^{13}C-NMR Spectra of Wood Lignin and Conventional Kraft Residual Lignin as shown in FIGURE 1.[29]

Signal #	δ (ppm)	Assignment
1	194	γ-CHO in cinnamaldehyde
2	173-171	C=O in aliphatic acids
3	152.9	C3/C3' 5-5 e units
4	152.6	C4 in G e with a-C=O, C3/C5 in 4-O-5, Cα in cinnamaldehyde
5	149.1	C3 in G e units
6	147.4	C4 in G e units
7	146.9	C3 in G ne units
8	145.3	C4 in G β-O-4 ne units
9	144	C4 in β-5 units
10	143.4	C4/C4' in e 5-5 units
11	135.3	C1 in G β-O-4 e units
12	133	C1 in G β-O-4 ne units
13	132.4	C5/C5' in 5-5 e units
14	128-130	-
15	128-129	Cα and Cβ in Ar-CH=CH=CH$_2$OH
16	126.3	Cβ of cinnamaldehydes and C5/C5' in 5-5 ne units
17	120.3	C6 in G e and ne units
18	119.5	C6 in G e and ne units
19	115.2	C5 in G e and ne units
20	111.4	C2 in G units
21	110.9	C2 in G-G stilbene units
22	87.2	Cα in β-5 units
23	85.5	Cβ in G β-O-4 threoform
24	84.7	Cβ in G β-O-4 erythroform
25	82-80	Cβ and Cα in β-O-4/α-O-4 units
26	72.5	Cα in G β-O-4 erythroform
27	71.4	Cα in G β-O-4 threoform
28	63	Cγ in β-5/β-O-4 units with αC=O
29	61.7	Cγ in cinnamyl alcohol units
30	60.0	Cγ in G β-O-4
31	55.9-55.7	Aromatic methoxyl groups
32	53.7	Cβ in β-β units
33	53.1	Cβ in β-5 units
34	40-15	CH$_3$ and CH$_2$ in saturated aliphatic side chain
35	29.7	CH$_2$ in diarylmethane structure

G=guaiacyl; e=etherified; ne=nonetherified

The wood lignin spectrum contains relatively sharp signals in both the aromatic and aliphatic regions while the residual lignin has broader signals suggesting a larger chemical heterogeneity and an altered structure. The dominate signals in the wood lignin spectrum are due to the β-O-4 structure. In addition to various aromatic carbons and the γ carbon of the arylglycerol β-O-4 structure, the α and β carbons belonging to the both the erythro and threo forms of the β-O-4 structure are clearly observed (signals 23,24,27,28 in Figure 1). The intensity of the erythro and threo signals are about the same suggesting an equal concentration of each diasteromer in the wood lignin. The residual lignins also contain signals from the β-O-4 structure but at a significantly reduced relative intensity. The presence of β-O-4 aryl ether units at the end of the cook for conventional kraft pulps has been previously noted and the results from this study extends this observation to extensively delignified kraft pulps. The erythro and threo forms of the β-O-4 structure are also observed in the residual lignins. The signal from the threo form is more intense than the erythro form providing further evidence for the selective degradation of the erythro form during kraft pulping.[11,12]

The wood lignin has a clear signal at 194 ppm (1) indicating the presence of cinnamaldehyde. This signal is absent in the residual lignin spectrum suggesting such structures do not survive the kraft cook. The small broad signal centered at δ175 ppm (2) in the residual lignin spectrum has been attributed to the presence of carboxylic acid groups which are most likely due to an enrichment process during pulping. Examination of the signals attributed to etherified (5) and nonetherified (6) aromatic C3 guaiacyl carbons in the wood and residual lignins suggest the dramatic loss in etherified structures. Inspection of the spectral data for the interrupted extended kraft pulp residual lignin (not included in Figure 1) suggests that it's structure is between the starting wood lignin and the final residual lignins.

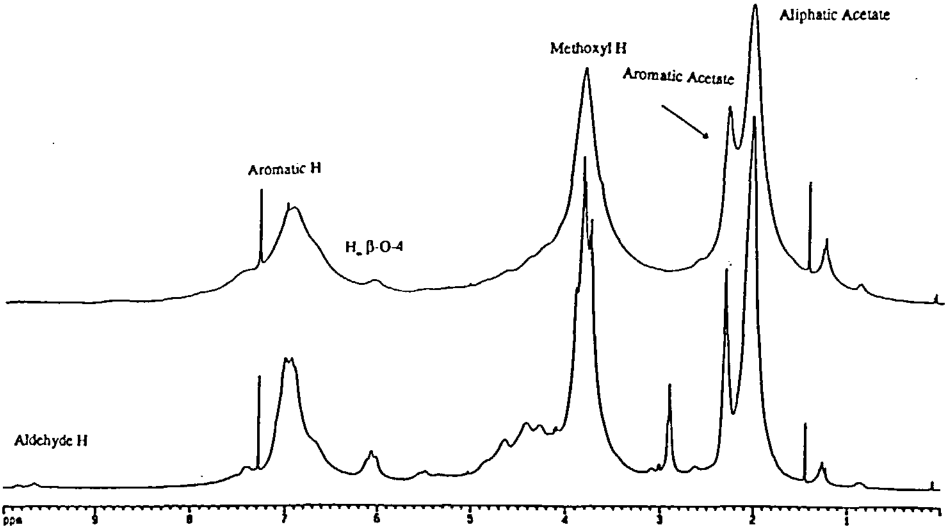

FIGURE 2. ^{1}H-NMR spectra of acetylated wood lignin (bottom) and acetylated conventional kraft pulp residual lignin (top). (solvent=$CDCl_3$)

^{1}H-NMR Analysis

Quantitative proton NMR analysis of the acetate derivatives from the wood and residual lignin samples was performed. Various regions in the ^{1}H-NMR spectra corresponding to different functional group protons were integrated. These regions included aromatic protons, Hα protons in arylglycerol β-O-4 structures, methoxyl protons, and methyl protons in the aromatic and aliphatic acetates.[23] Integration of these regions can be informative on the degree of aromatic ring substitution, the quantity of β-O-4 structures and the content of aromatic and aliphatic hydroxyl groups. Some representative spectra and the integration regions are shown in Figure 2. For each spectra quantitative estimates were made by assigning the methoxyl region an integration value corresponding to the methoxyl content

TABLE 4.
^{1}H-NMR Functional Group Analysis of Wood and Residual Lignins. The values are expressed as frequency per C100 unit.

Functional group	Wood	Int. EMCC®	Conv.	EMCC®
Aromatic protons	22.0	18.2	18.7	18.4
Hα of a β-O-4 aryl ether unit	3.2	2.2	1.7	1.7
OCH_3	9.3	8.5	8.1	8.1
Aromatic-O-C(O)Me	2.4	2.5	3.4	3.1
Aliphatic-O-C(O)Me	8.4	6.9	6.8	6.4

as determined by the elemental analysis. In this manner, the various functional group protons were quantified as frequency per C100 unit. Table 4 presents the results from this analysis.

The residual lignins contained the lowest amount of aromatic protons suggesting that these lignins contain more substituted aromatic groups or 'condensed' type lignin. Differences in the aromatic proton content between the interrupted EMCC® residual lignin and the other residual lignins were observed but suggested the interrupted EMCC® residual lignin to be more condensed, which is most likely not the case. This result suggests that the technique may not be sensitive enough to detect significant differences between lignins with small differences in aromatic proton contents. The aromatic proton content differences between the wood and residual lignins may be due to the combined effects of enrichment of unreactive condensed aromatic structures present in the wood lignin and/or the occurrence of condensation reactions during pulping. The wood lignin contained the greatest amount of β-O-4 structures. The content of these structures are nearly halved in the kraft residual lignins. The conventional and EMCC® residual lignins were found to have the similar amounts

Integration of the aromatic and aliphatic acetate signals allows for the quantification of aromatic and aliphatic hydroxyl groups. Although these two signals are not completely resolved and biphenyl (5,5') aromatic acetate signals have chemical shifts in the aliphatic acetate region, the analysis suggests that the phenolic hydroxyl content is higher and the aliphatic hydroxyl content is lower in the residual lignin compared to wood lignin. The generation of phenolic groups is due to the cleavage of aryl ether linkages in the lignin while the loss in aliphatic hydroxyl groups is largely due to the loss of primary hydroxyl groups in β-O-4 aryl glycerol structures.

^{31}P-NMR Analysis

The wood lignin and the three residual lignins were also subjected to selective phosphorylation with 1,3,2-dioxaphospholanyl chloride and quantitative ^{31}P-NMR analysis. This technique, developed by Argyropoulos,[24,25] has been found to be a versatile and efficacious means to quantify the content of various lignin hydroxyl groups including primary, secondary (both erythro and threo forms of β-O-4 structures), and aromatic (guaiacyl and condensed/biphenolic) hydroxyl groups. The results from this analysis are presented in Figure 3 and Table 5.

The ^{31}P-NMR analysis showed that the EMCC® and conventional residual lignin samples differed substantially from the wood lignin. Structural differences were also noted between the conventional and EMCC® pulp samples. Wood lignin undergoes many changes during pulping as evidenced by the lower content of aromatic hydroxyl groups and higher content of primary (on gamma carbons) and secondary (mainly on alpha carbons) hydroxyl groups compared to the kraft residual lignin.

The total content of aromatic hydroxyl groups for wood lignin was found to be smaller than residual lignin samples yet the content of guaiacyl aromatic hydroxyl groups is comparable in all four samples. The difference in aromatic hydroxyl content comes about due to the higher contents of biphenyl/condensed aromatic hydroxyl groups in the residual kraft lignins.

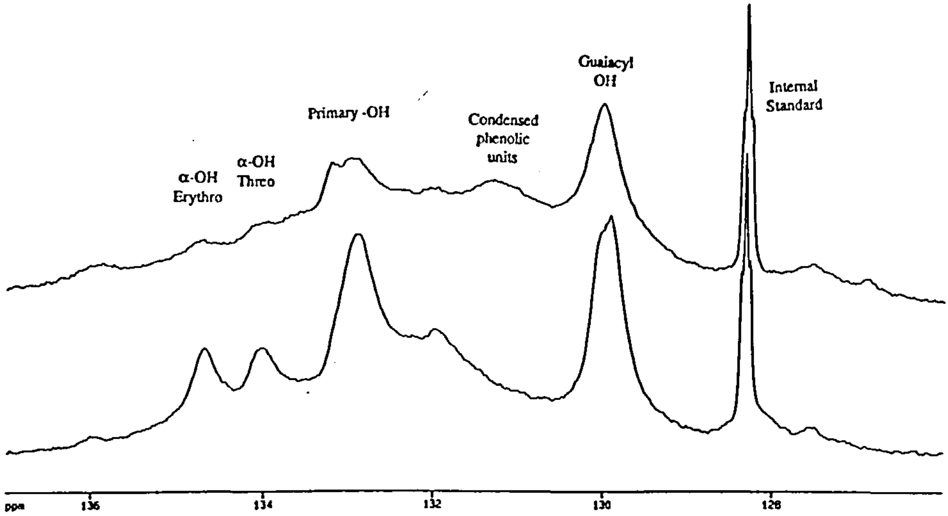

FIGURE 3. Quantitative ^{31}P-NMR spectra of wood lignin (top) and conventional kraft pulp residual lignin (bottom) derivatized with 1,3,2 dioxaphospholanyl chloride.

This suggests that either such structures originate in the wood lignin (in their etherified form) and are enriched in the residual lignins (in their non-etherified or phenolic form) or that such structures are formed during pulping.

The wood lignin has a high content of primary hydroxyl groups due mainly to hydroxyl groups on gamma carbons. The primary hydroxyl content can be expected to diminish during pulping because of known reactions in which the gamma carbon is eliminated as formaldehyde. The interrupted residual lignin was shown to have a similar content of such groups suggesting that it is not until well into the cook before significant elimination of this terminal carbon group occurs in the residual lignin.

As observed in the proton NMR studies, the content of β-O-4 structures in residual lignin diminishes with the extent of delignification. A

TABLE 5.
Quantification of various hydroxyl groups in wood and residual lignins by ^{31}P-NMR (mmol/g lignin).

Lignin	Aromatic OH			Primary OH	Secondary OH (β-O-4)			Total OH
	Guaiacyl	Biphenyl/ Cond.	Total Phenolic		E	T	Total	
Wood	0.86	0.37	1.23	1.51	0.35	0.35	0.70	3.44
Int. EMCC®	0.83	0.57	1.40	1.55	0.25	0.30	0.55	3.50
Conv.	0.87	0.63	1.50	1.23	0.24	0.37	0.51	3.24
EMCC®	0.85	0.66	1.51	1.23	0.18	0.23	0.41	3.15

E-erythro isomer; T-threo isomer

comparison of relative amounts of β-O-4 structures determined by ^{31}P and ^{1}H-NMR indicates a discrepancy (the ^{31}P-NMR analysis shows a difference while the ^{1}H-NMR analysis shows no difference). We believe this is due to an inaccuracy in the ^{1}H-NMR analysis since the Hα signal employed to measure concentration of β-O-4 overlaps the aromatic signal and data analysis of peak intensities becomes difficult. In comparison, the use of Argyropoulos' ^{31}P-NMR method is a more accurate quantification of this functional group.

Interestingly at the point where pulping must be terminated due to the poor selectivity of both conventional and EMCC® pulping, the residual lignin in the EMCC® pulp contains less β-O-4 structures (0.41 versus 0.51 mmol/g lignin). This suggests that either the EMCC® pulping conditions are more efficient at cleaving this linkage or that the more extensive degree of delignification resulted in the cleavage of more aryl ether linkages.

By adding together the values for the aromatic and aliphatic hydroxyl groups a total hydroxyl content can be calculated for each lignin. The total hydroxyl content was found to be the smallest in the EMCC® residual lignin suggesting that lignin with a low hydroxyl content is present in the pulp at the end of the cook.

CONCLUSIONS

In summary we have observed an enrichment of condensed lignin in extensively delignified kraft pulp. Lignin isolated from the interrupted EMCC® pulp appeared to have a structure which was intermediate between wood lignin and the fully cooked kraft pulp residual lignin. The presence of β–O–4 aryl ether linkages in the conventional pulp is consistent with published results and we have extended these studies to low kappa modified kraft pulps. Studies by Hortling have noted some of the trends reported in this paper employing pulps from mill trials with Super-Batch® and MCC® cooking methods. Our studies, using laboratory cooks from a common wood source, eliminate the potential variability associated with studying mill pulps.

Ongoing studies in our laboratory have begun to examine kraft pulps that are even further delignified than the pulps reported on in this paper and these results will be reported shortly.

ACKNOWLEDGMENTS

The authors wish to thank the member companies of the Institute of Paper Science and Technology and Ahlstrom Machinery Inc. for their support of these studies. This work was used by P.F. as partial fulfillment of the requirements for the M.S. degree at the Institute of Paper Science and Technology.

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