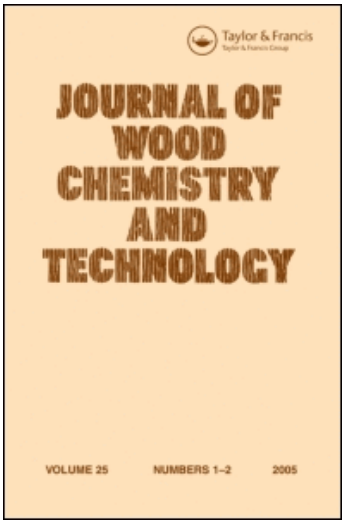

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Structural Changes in Lignin During Kraft Cooking Part 3. On the Structure of Dissolved Lignins

Danielle R. Robert[ab]; Michel Bardet[a]; Göran Gellerstedt[c]; Eva Lisa Lindfors[c]
[a] Laboratoires de Chimie Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, Grenoble Cedex, France [b] Scientific and Medical University of Grenoble, France [c] Swedish Forest Products Research Laboratory, Stockholm, Sweden

To cite this Article Robert, Danielle R. , Bardet, Michel , Gellerstedt, Göran and Lindfors, Eva Lisa(1984) 'Structural Changes in Lignin During Kraft Cooking Part 3. On the Structure of Dissolved Lignins', Journal of Wood Chemistry and Technology, 4: 3, 239 — 263
To link to this Article: DOI: 10.1080/02773818408070647
URL: http://dx.doi.org/10.1080/02773818408070647

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 4(3), 239-263 (1984)

STRUCTURAL CHANGES IN LIGNIN DURING KRAFT COOKING PART 3.* ON THE STRUCTURE OF DISSOLVED LIGNINS.

Danielle R. Robert** and Michel Bardet
Laboratoires de Chimie
Département de Recherche Fondamentale
Centre d'Etudes Nucléaires de Grenoble
85 X, F-38041 Grenoble Cedex, France

Göran Gellerstedt and Eva Lisa Lindfors
Swedish Forest Products Research Laboratory
Box 5604, S-114 86 Stockholm, Sweden

Paper dedicated to Dr. Joseph L. McCarthy on the occasion of his 70th birthday.

ABSTRACT

Two series of pine kraft lignins were prepared by a) normal kraft cooks to different pulp yield levels and precipitation of the lignins from the black liquors by acidification and b) by successive acidification of the black liquor obtained from a flow-through cook. All the lignins were extensively purified, subjected to elemental and methoxyl analysis and subsequently acetylated.

Quantitative ^{13}C-NMR analysis was carried out on acetylated samples and the results were combined with the results of phenolic group determination by means of aminolysis and with elemental analysis data. The various acetylated lignins were also subjected to analysis by size exclusion chromatography.

All results are discussed with reference to known features of kraft cooking and of kraft lignins.

*Part 2. See Ref. 1.
**Member of the Scientific and Medical University of Grenoble, France.

 0277-3813/84/0403-0239$3.50/0

INTRODUCTION

During the kraft cooking process the lignin is fragmented predominantly by ether cleavage reactions in phenylpropane-α- and β-aryl ether structures.[2] These reactions lead simultaneously to the formation of new phenolic hydroxyl groups in the lignin macromolecules, thus increasing their solubility in aqueous alkaline media. These reactions promoting delignification are assumed to be counter-balanced to some extent by a number of different condensation reactions.[3] Particularly towards the end of the kraft cook the latter may increase in relative importance.[2] This view is further supported by the fact that the last portion of the residual lignin in a kraft pulp is removed in the cooking process only with considerable difficulty and at the expense of both pulp yield and pulp quality.[4,5]

In order to gain further knowledge about the structural changes which take place in the lignin during kraft cooking and their importance for delignification, kraft lignin samples withdrawn after various cooking times have been analysed for phenolic hydroxyl groups. The analyses were carried out on acetylated lignin samples using two different techniques viz. quantitative ^{13}C-NMR spectroscopy and selective deacetylation of phenolic acetyl groups. In addition the data from the ^{13}C-NMR analyses were used to calculate the number of primary and secondary aliphatic hydroxyl groups as well as to provide a rough estimation of the proportions of side-chain carbon atoms present in the lignins. Furthermore, the average elemental compositions of the various lignin samples were calculated, thus permitting a comparison of the degree of condensation as given by the number of double-bond equivalents (DBE). Corresponding analytical data were collected on a series of kraft lignins obtained from a flow-through cook, since in this case the lignins should be expected to be less modified due to a shorter residence time in the cooking liquor. These lignins were analysed by size exclusion

chromatography (SEC) on μ-Spherogel and the results compared with previously published SEC curves run on normal kraft lignins.[6]

RESULTS AND DISCUSSION

Preparation of and Analytical Data for Flow-through Lignins

The two series of kraft lignins used in the present work were both obtained by acidification of the black liquors obtained from kraft cooks of pine. Within each series the cooking time was varied in order to obtain lignin samples characteristic of different parts of the cook. The first series of lignins came from normal kraft cooks (designated SK 1 -SK 7) and was the same as previously described (analytical data in Ref. 6) whereas the second (designated GSK 1 - GSK 6) was obtained by cooking the chips in a flow-through reactor. In this reactor (see Ref. 5 for a closer description), the original cooking liquor can be continuously replaced by fresh white liquor in which the concentration of hydroxyl ions simulates the actual alkali profile employed in a normal kraft cook. This makes it possible to obtain highly representative lignin samples from different parts of the cook by sampling the outlet of black liquor. In this way, six black liquor fractions were collected as shown in Fig. 1. Of these, the last fraction (GSK 6) is assumed to be representative of the lignin which is removed in the final delignification phase of a kraft cook.

After acidification, the resulting precipitated lignins were purified following the scheme described in Ref. 6. Subsequently these lignins were subjected to elemental and methoxyl analyses. In addition the amounts and distribution of sugars were determined. From the data in Table 1 and Table 2 it can be seen that all the samples contained small amounts of sugars. However, as in previously analysed kraft lignins, the sugar content was found to be somewhat higher in the beginning and towards the end of the

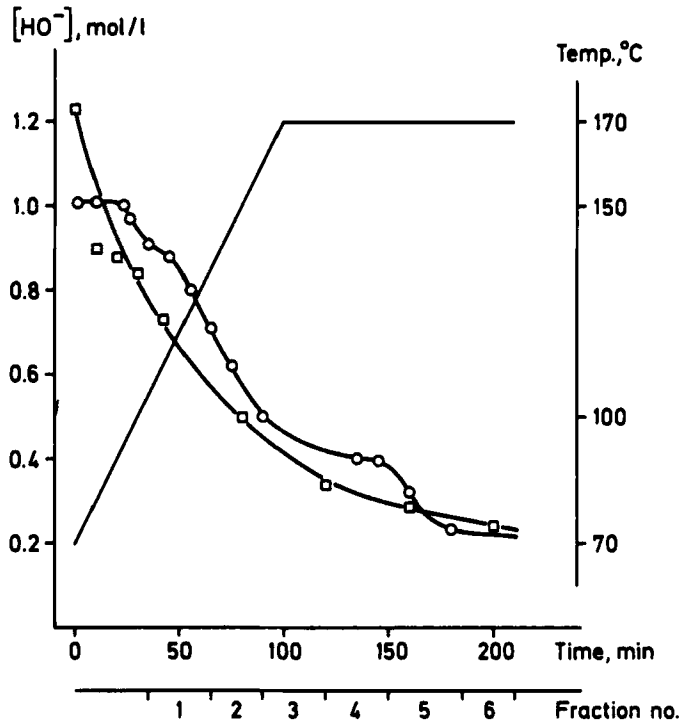

FIGURE 1. Alkali profile for the flow-through kraft cook (o) and for a batch kraft cook (□) with 20 % effective alkali and a liquor-wood ratio of 4:1. Lignin samples GSK 1 - GSK 6 obtained by precipitation of the black liquor fractions 1-6.

cook.[6] The lignin dissolved early in the cook contained glucose as the predominating sugar component whereas arabinose and xylose constituted the major sugars in the lignin which was dissolved in the later stages. The data in Table 1 also confirm that the first lignin to be dissolved in a kraft cook contains a small amount of protein.

After acetylation, the lignin samples from the flow-through cook were subjected to analysis by size exclusion chromatography on a series of μ-Spherogel columns ranging in pore size from $10-10^4$ nm.[7] In agreement with the results obtained previously

TABLE 1

Analytical Data for Dissolved Lignins Obtained from a Flow-through Kraft Cook. Lignin Samples Withdrawn after the Cooking Times Indicated in Figure 1.

Sample No.	Carbohydrates, % on lignin	Protein, % on lignin[a]	Elemental analysis					
			C, %[b]	H, %[b]	O, %[b]	S, %[b]	OCH_3, %[b]	N, %
GSK 1	0.8	1.5	55.64	5.37	24.84	14.15	12.12	0.24
GSK 2	0.2	0.4	60.87	5.83	26.70	6.60	13.52	0.07
GSK 3	0.3	0	62.93	5.93	26.46	4.29	14.86	0
GSK 4	0.6	0	63.18	5.87	26.47	4.48	15.49	0
GSK 5	1.1	0	62.60	5.76	26.55	5.09	14.60	0
GSK 6	0.4	0	60.74	5.55	26.80	6.91	13.94	0

a) Content of protein calculated as 6.25 times the recorded percentage of nitrogen.

b) Corrected for carbohydrates and protein.

TABLE 2

Relative Abundance of Individual Sugars in Flow-through Kraft Lignins.

Sugar component	Lignin fraction number					
	GSK 1	GSK 2	GSK 3	GSK 4	GSK 5	GSK 6
Arabinose	14	28	45	32	46	52
Xylose	30	39	12	26	23	30
Mannose	0	7	5	2	3	0
Galactose	6	17	26	11	12	18
Glucose	50	9	12	29	16	0

with the series of normal kraft lignins, it was found that the average molecular size of the flow-through lignins increased as the cook proceeded (Fig. 2).[6] However, no major differences in molecular size distribution could be observed when the SEC curve obtained for a flow-through cook lignin withdrawn towards the end of the cook was compared with the curve from a normal kraft lignin sample subjected to the whole cooking cycle (Fig. 3). This result suggests that the number of secondary reactions, i.e., reactions taking place in the lignin after dissolution, is rather low. Alternatively the similarity of the SEC curves may reflect a distribution of pore sizes in the cell walls of the fibres (cf. Ref. 8).

Selective Deacetylation of Phenolic Acetyl Groups

The free phenolic hydroxyl groups present in lignin are known to exert a dominating influence during pulping procedures in alkaline and neutral media.[2,9] Not only is this functional group able to ionize and thus improve the solubility of lignin in aqueous solution but the free phenolic lignin units also constitute by far the most reactive structures in both fragmenta-

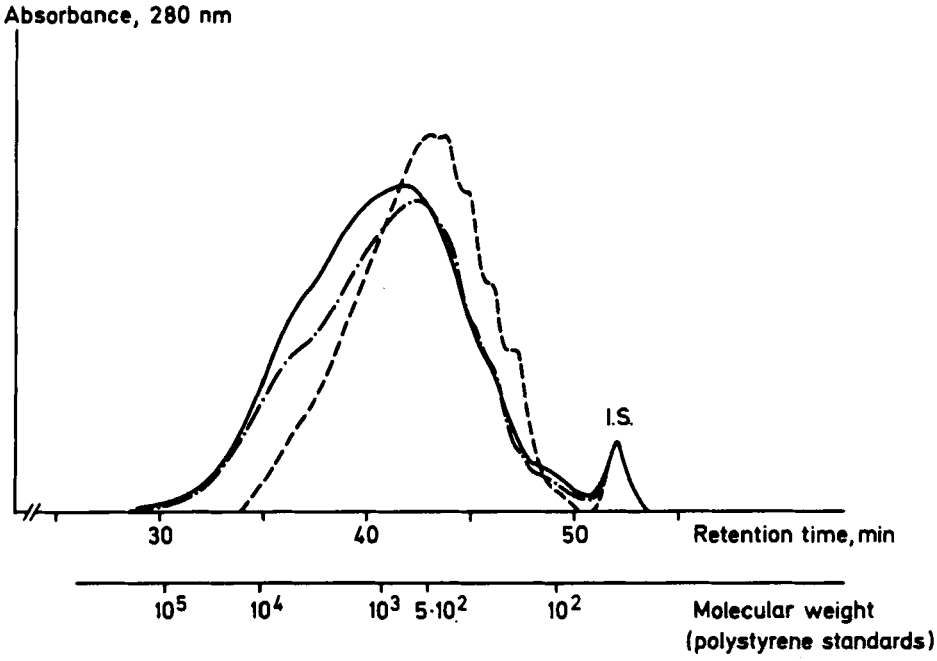

FIGURE 2. Size exclusion chromatograms of acetylated kraft lignins obtained from a flow-through cook. I.S. = acetone. Lignin sample GSK 2 (---), GSK 4 (-·-·), GSK 6 (———).

tion and condensation reactions known to take place under pulping conditions.[2]

In the present work the number of free phenolic hydroxyl groups has been determined for the two series of kraft lignins by two different methods. In the first of these the difference in rate of deacetylation between phenolic and aliphatic acetyl groups was utilized. Thus, the acetylated lignin samples were treated with pyrrolidine according to the method described in Ref. 10 and the amount of 1-acetylpyrrolidine being formed was followed by gas chromatography. The number of phenolic hydroxyl groups can be calculated by quantitative determination of the amount of 1-acetylpyrrolidine rapidly formed by aminolysis of the phenolic acetyl groups.

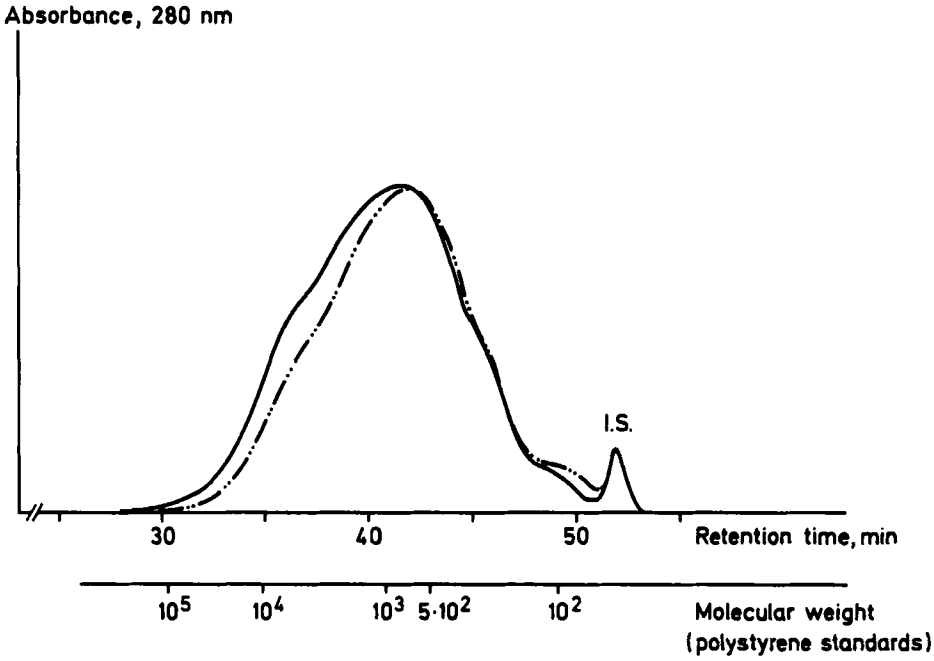

FIGURE 3. Size exclusion chromatograms of the acetylated kraft lignin samples GSK 6 (——) and SK 7 (-···-). I.S. = acetone.

The results of these analyses are given in Table 3 for the two series of lignins. It can be seen that the frequency of free phenolic hydroxyl groups is high in all of the lignin samples and that it increases only slightly as the cook proceeds. Again the results indicate that the major part of the chemical reactions in kraft cooking take place in the solid (or gel) phase. These must involve a certain number of reactions leading to the cleavage of inter-unit lignin bonds in order to separate the individual lignin molecules from the solid matrix. In addition, the content of phenolic hydroxyl groups seems to increase up to a minimum level in order to attain solubility (cf. Ref. 6). It should also be noted that the soda lignin, which was analysed for the sake of comparison, contained approximately the same amount of phenolic

TABLE 3

Content of Phenolic Hydroxyl Groups, determined by Aminolysis, in Dissolved Kraft Lignin Samples Obtained from a) Normal Kraft Cooks to Different Pulp Yield Levels and b) from a Flow-through Kraft Cook.

Sample No.	Pulp Yield %	Cooking time min	Cooking temp. °C	Phenolic hydroxyl groups, mmoles/g of lignin[a]	Calculated molecular weight/phenyl-propane unit[b]	Frequency of phenolic hydroxyl groups
SK 1	90.0	45	115	2.9	191	55
SK 2	81.6	75	145	3.2	175	56
SK 3	75.7	90	160	3.5	175	61
SK 4	71.5	100	170	3.6	174	63
SK 5	59.1	125	170	3.6	172	62
SK 6	51.1	165	170	3.7	170	63
SK 7	48.5	210	170	4.1	170	70
GSK 1		35-65	135	3.0	197	59
GSK 2		90	160	3.4	180	61
GSK 3		120	170	3.6	173	62
GSK 4		150	170	3.7	173	64
GSK 5		185	170	3.8	175	66
GSK 6		210	170	3.8	180	68
SK 9[c]	45.3		170	3.6	169	61

a) Mean value of two analyses.

b) Molecular weight for one phenylpropane unit (based on 9.1 carbon atoms[11,12]) calculated from elemental analysis data in Ref. 6 and Table 1.

c) Soda lignin.

hydroxyl groups as the kraft lignins. Furthermore, it has been demonstrated previously by SEC analysis that there is no significant difference in molecular size distribution between a soda and a kraft lignin.[6]

Quantitative Analysis of Acetylated Kraft Lignins by ^{13}C-NMR

Recent work on the ^{13}C-NMR analysis of various acetylated lignin preparations has shown that by employing a high field operating magnet it is possible to observe well separated signals for the different types of acetyl groups present.[13] Using special experimental conditions including a selected antigate pulse sequence the Nuclear Overhauser Effect can be minimized and then the pertubing effects on the signal intensities due to different spin-lattice relaxation times (T_1) for the different carbon atoms can be virtually avoided[14-16] (cf. also Ref. 17). It is thus possible to obtain information about the quantity of primary, secondary and phenolic hydroxyl groups in lignin by integrating the carboxyl signals from the different acetyl groups (found at δ = 170.8, 170.0 and 168.9 ppm respectively). This is exemplified in Fig. 4 which shows the same kraft lignin sample analysed in a "routine" and in a "quantitative" mode. It is also possible to integrate the other regions of the NMR spectrum and thus obtain information about the methoxyl content (δ = 56.3 ppm) as well as the number of aromatic and aliphatic carbon atoms. Such analyses have now been carried out on some of the samples from the two series of kraft lignins employed in this work. The analyses were carried out at room temperature and with acetone-d_6 as solvent.

The contents of methoxyl and different types of hydroxyl groups were calculated in relation to the aromatic ring. In addition, attempts were made by integration of the region between 60 and 90 ppm to estimate the number of aliphatic side chain carbon atoms still carrying an oxygen. On one sample, the NMR

analysis was run in $CDCl_3$ in order to obtain quantitative information about the number of saturated carbon atoms in the region between 10 and 50 ppm. This attempt was, however, unsuccessful due to the difficulty of getting a meaningful integral from these signals which have very low signal to noise ratios.

Vinylic carbon atoms e.g. from stilbenes and styryl aryl ethers have shift values within the aromatic region (105-155 ppm)[18] and the presence of such structures thus introduces a certain error into the integral for the aromatic carbon atoms. All integral values were therefore related to the integral for the phenolic acetyl carboxyl group. Using the value for the amount of phenolic hydroxyl groups given by aminolysis (see above), the integral value for one aromatic carbon atom could be calculated. The difference between the measured total integral for the aromatic carbon region and the calculated value for six aromatic carbon atoms was then used to estimate the number of vinylic carbon atoms. The results of these calculations are given in Table 4 together with the corresponding value for a spruce milled wood lignin sample.

It can clearly be seen that the number of primary hydroxyl groups, assumed to correspond to the number of γ-hydroxymethyl groups in lignin, is much lower in all the samples than in the milled wood lignin. Thus, not only the lignin which is dissolved early in the kraft cook but also the flow-through lignins have suffered a comprehensive elimination of the terminal hydroxymethyl group. This elimination reaction seems to take place before and/or when the lignin is dissolved and the results again tend to indicate that the proportion of reactions taking place after dissolution is comparatively small in number.

The number of secondary hydroxyl groups in the kraft lignin samples was found to be comparable to the value for milled wood lignin. However, samples withdrawn in the later stages of the

cook showed a certain decrease, thus indicating a slight formation of unsaturated and/or condensed structures.

The shift area between 60 and 90 ppm contains virtually all aliphatic carbon atoms in lignin still carrying a hydroxyl, acetoxyl or ether group.[13,18,19] Assuming that the number of primary hydroxyl groups found in the lignin samples (Table 4) is identical with the residual number of γ-carbon atoms in the lignin side chains, the figures for oxygen-bonded carbon atoms were obtained. In agreement with the low number of aliphatic hydroxyl groups rather low values for the numbers of these carbon atoms were found for all the lignin samples. Again a certain decrease was noticed for the samples withdrawn late in the cook.

The relatively low amounts of carbon atoms found in the NMR spectra between 60 and 90 ppm indicate that a substantial part of the side chain carbons in kraft lignins are included in alkyl and carboxyl groups. The former are found in the range between 10-50 ppm and, as can be seen in Figure 4B, a kraft lignin contains several signals in this region (cf. also Ref. 18). As mentioned above, it was not, however, possible to obtain any quantitative NMR-data on these. The origin of the alkyl groups in kraft lignins is still largely unknown. In model experiments it has, however, been demonstrated that condensation reactions between lignin structures with and without the participation of formaldehyde as well as reactions between lignin and carbohydrate--derived structures may lead to the formation of alkyl groups.[3,20] Alternatively such groups can be formed by the addition of water or hydrogen sulfide to double bonds.

Kraft lignins also contain a certain amount of carboxylic acid groups.[21] No signals attributable to such groups could, however, be found in the spectra in the region between 165-180 ppm. This may be due to overlap by the acetyl signals or to the presence of very broad low intensity signals buried in the base line. According to recent analytical data, 0.8 mmoles of

TABLE 4

Number of Methoxyl Groups, Hydroxyl Groups, Aliphatic Carbon Atoms and Vinylic Carbon Atoms Calculated per Aromatic Ring for Kraft Lignins, a Soda Lignin and for a Milled Wood Lignin as given by Quantitative ^{13}C-NMR Analysis.

Sample	Functional group per aromatic unit						
No.	OCH_3	Total OH	Prim. OH	Sec. OH	Phen. OH[a]	Carbon atoms in C-O-	Vinylic C
SK 1	0.67	1.32	0.43	0.34	0.55	0.36	0.1
SK 3	0.79	1.26	0.41	0.24	0.61	0.38	0
SK 5	0.79	1.25	0.35	0.25	0.62	0.35	0
SK 7	0.74	1.24	0.35	0.17	0.70	0.22	0
GSK 2	0.85	1.37	0.45	0.31	0.61	0.43	0.2
GSK 3	0.81	1.32	0.44	0.25	0.62	0.35	0.2
GSK 5	0.81	1.25	0.37	0.21	0.66	0.30	0.1
GSK 6	0.80	1.24	0.34	0.21	0.68	0.33	0
SK 9[b]	0.79	1.29	0.41	0.25	0.61	0.34	0
MWL[c]	0.96	1.39	0.81	0.33	0.21		0

a) Values from Table 3.

b) Soda lignin

c) Milled wood lignin from spruce. Data from Ref. 16.

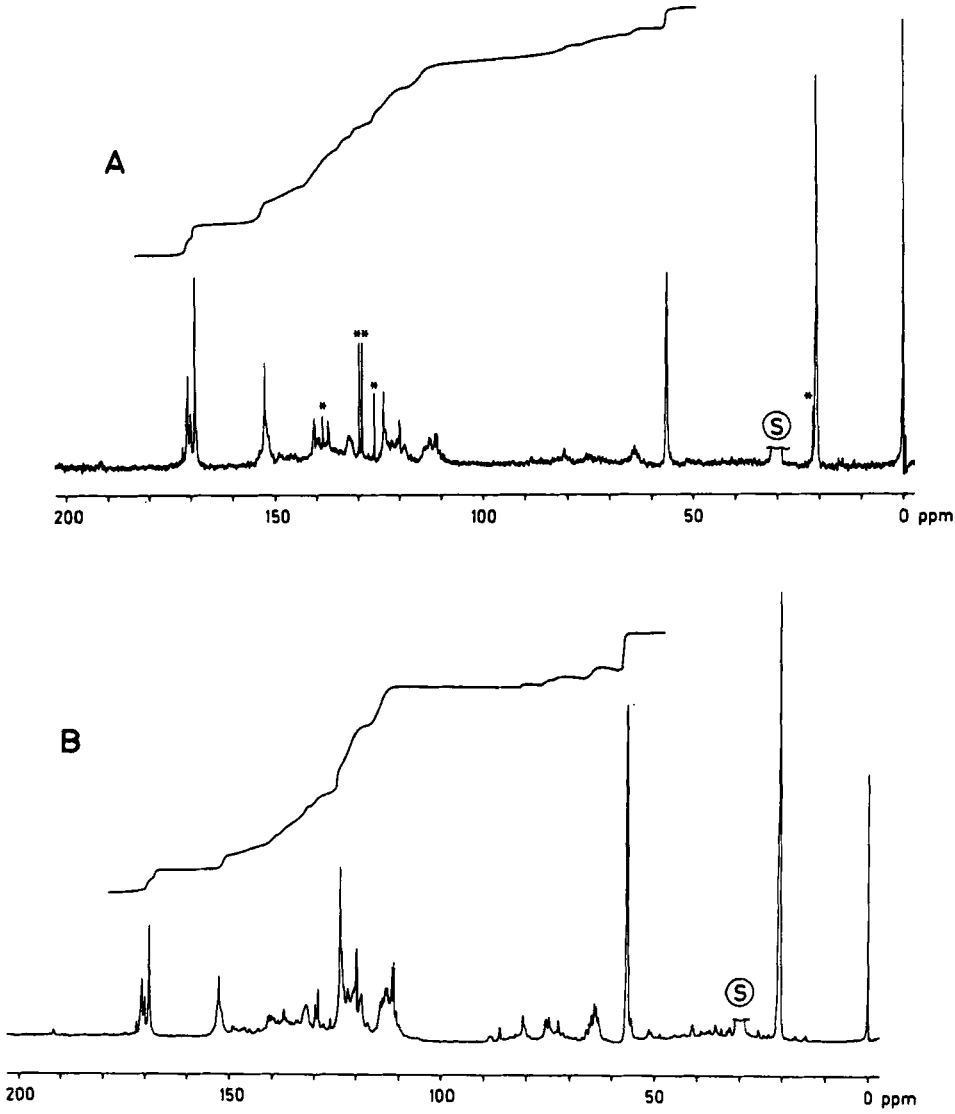

FIGURE 4. ^{13}C-NMR spectra of the kraft lignin sample GSK 3 recorded at 62.9 MHz. Spectrum A recorded in a quantitative mode using an antigate NMR sequence with a pulse delay of 12 s. Spectrum B recorded in a routine mode with a pulse delay of 0.2 s. S = solvent signal. (Signals denoted by * are from toluene. See Experimental.)

carboxylic acid groups can be found per gram of a softwood kraft lignin.[22] This corresponds to 0.13–0.14 carboxylic acid groups per phenylpropane unit.

The indirect method of calculating the number of vinylic structures present in the lignin gave, as shown in Table 4, values close to zero for most of the samples. Since the integral values for such carbon atoms will be low in comparison with the values for the aromatic carbon atoms, it must, however, be pointed out that the values obtained for the vinylic carbon atoms can only be regarded as indicative. Previously published data on kraft lignins have also demonstrated the presence of both stilbenes and styryl aryl ether structures.[1,23,24] For the former structures a value of 0.06–0.07 groups per phenylpropane unit has been calculated.

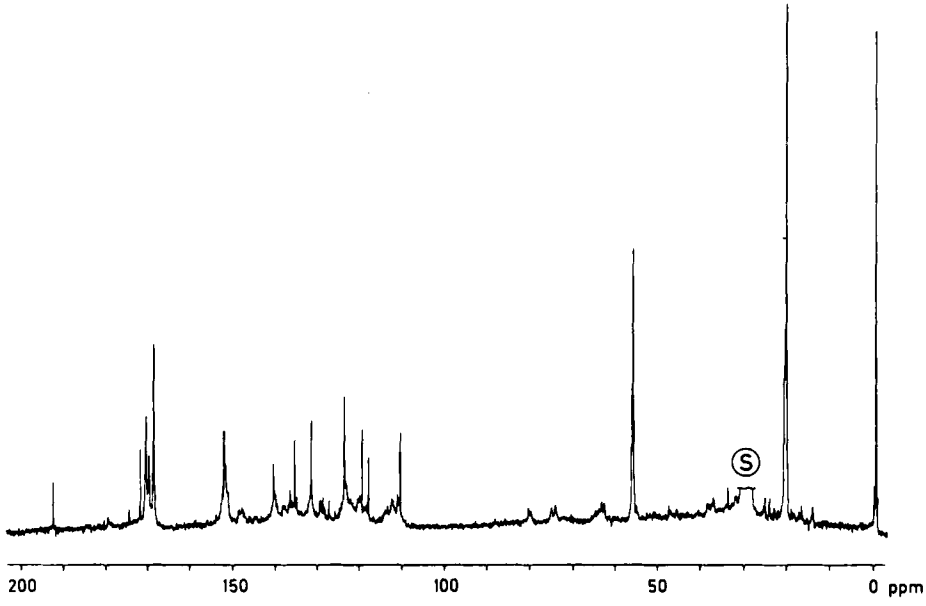

FIGURE 5. ^{13}C-NMR spectrum of the kraft lignin sample SK 1 recorded in a quantitative mode. See Experimental for shift values. S = solvent signal.

The sample SK 1 was found to contain a number of very sharp signals indicating the presence of low molecular weight compound(s) (Fig. 5). The shift values for these signals were found to be in fairly good agreement (but not identical) with the shifts for trans-3-(4-acetoxy-3-methoxyphenyl)-2-propenyl thioacetate (see Experimental). The formation of this and some similar sulfur-containing compounds has previously been shown to take place by addition of hydrogen sulfide (polysulfide) ions to the extended quinone methide corresponding to coniferyl alcohol.[25] It has also been shown that a number of other compounds containing vinylic carbon atoms can be formed from coniferyl alcohol during the initial part of a kraft cook.[25,26] It therefore seems reasonable to assume that the lignin which is dissolved early in the kraft cook contains these types of structures. It is also well-known that fairly large amounts of the precursor, coniferyl alcohol, are present in the black liquor during the initial phase of a kraft cook[27] (cf. also Ref. 28).

Elemental Composition of Kraft Lignins

From the elemental and methoxyl analysis data (Table 1 and Ref. 6), the average elemental composition for the various lignin samples was calculated. In the calculations, the assumption was made that the number of primary hydroxyl groups present in the lignin samples (Table 4) is identical to the residual number of γ-carbon atoms in the phenylpropane units. It was found that, with the exception of sample SK 1, the elemental composition of the dissolved lignin undergoes relatively minor changes as the kraft cook proceeds (Table 5). The coefficients obtained for the individual elements were also found to be very similar to previously published figures.[11] However, at the beginning of the cook the dissolved lignin contains a high proportion of sulfur due to the rapid reactions between quinone methides,

TABLE 5

Elemental Composition of Kraft Lignin Samples and Corresponding Calculated Numbers of Double Bond Equivalents (DBE).

Sample No.	Elemental composition	DBE	OCH_3[a]
SK 1	$C_{8.43}H_{8.77}O_{2.25}S_{0.76}(OCH_3)_{0.65}$	4.72	0.67
SK 3	$C_{8.41}H_{8.20}O_{2.35}S_{0.19}(OCH_3)_{0.74}$	4.94	0.79
SK 5	$C_{8.35}H_{8.19}O_{2.21}S_{0.14}(OCH_3)_{0.77}$	4.87	0.79
SK 7	$C_{8.35}H_{7.86}O_{2.19}S_{0.09}(OCH_3)_{0.75}$	5.05	0.74
GSK 2	$C_{8.45}H_{8.18}O_{2.25}S_{0.38}(OCH_3)_{0.80}$	4.96	0.85
GSK 3	$C_{8.44}H_{7.90}O_{2.08}S_{0.24}(OCH_3)_{0.85}$	5.07	0.81
GSK 5	$C_{8.37}H_{7.62}O_{2.10}S_{0.28}(OCH_3)_{0.83}$	5.15	0.81
GSK 6	$C_{8.34}H_{7.54}O_{2.22}S_{0.39}(OCH_3)_{0.81}$	5.17	0.80
SK 9[b]	$C_{8.41}H_{8.05}O_{2.36}(OCH_3)_{0.74}$	5.02	0.79
MWL[c]	$C_{8.90}H_{8.20}O_{2.69}(OCH_3)_{0.96}$	5.32	0.96
MWL[d]	$C_{8.90}H_{7.89}O_{2.37}(OCH_3)_{0.91}$	5.50	

a) Values from Table 4.

b) Soda lignin.

c) Milled wood lignin from spruce. Analytical data from Ref. 16.

d) Milled wood lignin from spruce. Analytical data from Ref. 30.

formed from phenolic phenylpropane units, and hydrogen sulfide ions.[29]

This particular lignin also contains a surprisingly small amount of methoxyl groups. In Table 5 it can further be seen that the number of methoxyl groups per phenylpropane unit, except for sample SK 1, is maintained at a rather constant level throughout the cook. All methoxyl values were found to be in good agreement with those obtained from the NMR analyses.

With a knowledge of the elemental composition of the various lignin samples it is possible to calculate the average number of double bond equivalents (DBE), i.e. the degree of unsaturation according to the general equation

$$C_aH_bO_cS_d : \qquad DBE = \frac{(2a + 2) - b}{2}$$

The numbers obtained can be used to estimate the number of double bonds, the presence of ring structures and the frequency of interunit linkages in the individual phenylpropane moieties. The calculated DBE-values included in Table 5 reveal that in comparison with milled wood lignin all the kraft (and the soda) lignin samples possess a lower degree of unsaturation. It must also be assumed that the numbers obtained mainly reflect the presence of the aromatic ring together with the degree of interunit linkages in the individual lignin units, since the ^{13}C-NMR data did not reveal the presence of any, or only a small amount of, vinylic structures.

As shown in Table 5, only minor increases in the DBE-values were found for both the series of kraft lignins as the cook proceeded. The flow-through lignins (GSK 1 - GSK 6) showed, however, somewhat higher values throughout. This difference may be attributed to a slightly higher amount of residual phenylpropane-β-aryl ether structures in the flow-through lignins[31] due to a shorter residence time in the cooking liquor. For both series of

lignins, however, the decrease in the DBE-number compared with the milled wood lignin can to a large extent be attributed to the cleavage of β-aryl ether bonds and to the extensive formation of free phenolic hydroxyl groups.

In Table 5 the elemental analysis data for the various lignin samples give values between 2.45 and 2.34 for the total number of side chain carbon atoms in the phenylpropane units. From the NMR-data, on the other hand, the total number of side chain carbons only amount to between 1.39 and 0.74 per aromatic ring. The discrepancy between these figures indicate that the side chains in kraft lignins contain a substantial portion of saturated carbon atoms since the total number of carboxylic acid and vinylic groups can be assumed to be rather small.

The analytical data for the soda lignin, included in Tables 4 and 5 for the sake of comparison, clearly demonstrate that the well-known differences between the kraft and soda pulping processes do not show up as any noticable differences in the analytical characteristics of the corresponding dissolved lignins. Thus, the degree of condensation revealed by the DBE-number does not differ from the data for the kraft lignins, nor does the content of phenolic hydroxyl groups show any differences. A slightly higher amount of residual primary hydroxyl groups was indicated from the ^{13}C-NMR data (Table 4) but the difference is within the limits of error for this analysis.

CONCLUSIONS

From the analytical data obtained in this work it has not been possible to identify any major changes in the chemical structure of the dissolved lignins which can be attributed to the differences in delignification rates in different parts of a kraft cook. Nor has it been possible to find any clear indication of condensation reactions assumed to contribute to the slow rate of delignification in the final phase of a kraft cook. The lignin

sample designated GSK 6 and assumed to be representative of the last fraction of lignin to be dissolved gave no analytical data indicative of a "different" type of lignin.

The results tend rather to indicate that the major part of the chemical reactions of lignin in kraft cooking take place in the solid (gel) phase thus leading to comprehensive changes in the lignin structure. These changes include cleavage reactions of α- and β-aryl ether structures which increase the content of phenolic hydroxyl groups, and also reactions resulting in the elimination of terminal hydroxymethyl groups. In order to attain solubility for a certain lignin fragment it seems to be necessary that the frequency of phenolic hydroxyl groups exceeds a certain minimum value. In addition the kraft lignins seem to contain a fairly large proportion of saturated side-chain carbon atoms with bonds only to carbon and hydrogen.

EXPERIMENTAL

Preparation of Samples

The lignin samples designated SK 1 - SK 7 were obtained from a series of laboratory kraft cooks of pine (Pinus silvestris). All cooks were carried out with a white liquor having a sulfidity of 30 % and an effective alkali charge of 18 %. In the soda cook (SK 9), carried out to a kappa number of 41.1, an effective alkali charge of 25 % was employed. The precipitation and purification of these lignin samples have been described in Ref. 6.

The flow-through kraft cook was carried out on pine chips in the apparatus described in Ref. 5. The starting white liquor had a concentration of 0.29 mol/l of Na_2S and 1.0 mol/l of NaOH. This liquor was continuously replaced with liquor of lower alkalinity as shown in Fig. 1. The concentraton of Na_2S was stepwise reduced during the cook to a final concentration of

0.22 mol/l. After a total cooking time of 210 min the yield of pulp was 43.8 % and the kappa number 16.3. From the cook, six fractions of black liquor were collected and acidified to recover the kraft lignins (designated GSK 1 - GSK 6). These were purified as above and subjected to carbohydrate analysis (gas chromatography of alditol acetates) and to elemental and methoxyl analysis (A. Bernhardt, Elback, West Germany).

Size Exclusion Chromatography

Size exclusion chromatography was performed on acetylated lignin samples employing a series of five columns (ALTEX, μ-Spherogel, 8 mm I.D. x 30 cm) having different pore sizes in the range of $10-10^4$ nm. Tetrahydrofuran served as the solvent and acetone was used as an internal standard. The columns were calibrated by a series of polystyrene standards of different molecular weights.

Aminolysis

The procedure described in Ref. 10 was used with some minor modifications.

A weighed amount of lignin (of the order of 20 mg) was acetylated at room temperature overnight with 1 ml of pyridine--acetic anhydride (1:1). After addition of methanol and evaporation to dryness, the residue was suspended in toluene, evaporated (repeated three times) and subsequently suspended in methanol and evaporated again. (It was later found that this work-up procedure probably leads to the introduction of methyl ester groups in the lignin via the formation of mixed anhydrides between carboxylic acid groups in lignin and acetic anhydride. The first addition of methanol was therefore replaced with a methanol-water mixture.) The lignin samples were subsequently placed under vacuum at 50°C overnight. The acetylated lignin

sample was dissolved in 1.0 ml of dioxane containing a weighed amount of the internal standard 1-propionylpyrrolidine. To this solution was added 0.5 ml of dioxane containing 20 % water and 1.0 ml of dioxane-pyrrolidine (2:3).

After the addition of pyrrolidine, samples were taken from the reaction mixture at different times (total reaction time, approximately 120 min) and analysed by gas chromatography. The amount of 1-acetylpyrrolidine being formed (and equivalent to the amount of hydroxyl groups being liberated) was recorded as a function of time. The content of phenolic hydroxyl groups (in mmoles/g of lignin) was calculated by extrapolation of the curve to zero time.

^{13}C-NMR Analysis

Due to the long time of analysis only those lignin samples tabulated in Table 4 were recorded. These were acetylated as described above. In each case 350-400 mg of sample, dissolved in 2.0 ml of acetone-d_6, was analysed. TMS was used as an internal reference. The Fourier transform ^{13}C-NMR spectra were recorded at 62.9 MHz and 25°C on a Bruker WM 250 spectrometer under the same experimental conditions as given in Ref. 16 but with the number of scans ranging from 7000 to 9000. The integral trace was recorded as exemplified in Fig. 4. The acetyl carboxyl region (165-175 ppm) was, however, expanded ten times before integration (cf. Ref. 16). The error in the analysis of the acetyl carboxyl, the aromatic and the methoxyl carbon atoms was estimated to $\pm$5 %. All of the spectra except SK 1 contained traces of toluene as shown in Fig. 4A. The small contribution from toluene in the integral trace was in all cases subtracted before calculation.

In a separate experiment, trans-3-(4-acetoxy-3-methoxy-phenyl)-2-propenylthioacetate was analysed by ^{13}C-NMR to obtain the shifts for this compound in acetone (cf. Ref. 32): δ = 20.4 (CH_3 in phenolic acetate), 30.4 (CH_3 in thioacetate), 56.2

(OCH_3), 111.0 (C-2), 119.6 (C-6), 123.7 (C-5), 125.8 (C-β), 133.1 (C-α), 136.5 (C-1), 140.5 (C-4), 152.3 (C-3), 168.8 (CO in phenolic acetate), 194.8 (CO in thioacetate). (The shift for C-γ was overlapped by the solvent signals.)

From the lignin sample SK 1 (Fig. 5) sharp signals were obtained at δ-values: 110.9, 118,2, 119.7, 123.9, 131.8, 135.8, 140.8, 152.4, 192.7.

ACKNOWLEDGEMENTS

Thanks are due to the Magnetic Resonance Center in Grenoble for providing the NMR facilities. A gift of trans-3-(4-acetoxy-3-methoxyphenyl)-2-propenylthioacetate from O. Lindeberg is gratefully acknowledged. The flow-through cook was performed by K. Sjöblom, Royal Institute of Technology, Stockholm. Thanks are also due to K. Kringstad, P. Månsson and R. Mörck for many valuable discussions during the course of this work.

REFERENCES

1. G. Gellerstedt, E.L. Lindfors, C. Lapierre and B. Monties, Sven. Papperstidn., in press.

2. J. Gierer, Wood Sci. Technol., 14, 241 (1980).

3. J. Gierer, F. Imsgard and I. Pettersson, Appl. Polym. Symp., 28, 1195 (1976).

4. P. Axegård and J.-E. Wikén, Sven. Papperstidn., 86(15), R 178 (1983).

5. K. Sjöblom, J. Mjöberg and N. Hartler, Pap. Puu, 65, 227 (1983).

6. G. Gellerstedt and E.L. Lindfors, Holzforschung, in press.

7. P. Månsson, "The Ekman Days 1981". International Symposium on Wood and Pulping Chemistry. Stockholm, June 9-12, 1981. Proceedings, Vol. 5, p. 94.

8. B.D. Favis, J.M. Willis and D.A.I. Goring, J. Wood Chem. Technol., 3, 1 (1983).

9. J. Gierer and I. Norén, Holzforschung, 34, 197 (1980).

10. P. Månsson, Holzforschung, 37, 143 (1983).

11. N. Terashima, H. Araki and N. Suganuma, Mokuzai Gakkaishi, 23, 343 (1977).

12. J. Marton, Tappi, 47, 713 (1964).

13. H.H. Nimz, D. Robert, O. Faix and M. Nemr, Holzforschung, 35, 16 (1981).

14. D. Robert and D. Gagnaire, Ref. 7. Proceedings, Vol. 1, p. 86.

15. D. Robert, 1982 Canadian Wood Chemistry Symposium, Extended Abstracts, p. 63.

16. D.R. Robert and G. Brunow, Holzforschung, in press.

17. H.H. Nimz, M. Nemr, P. Schmidt, C. Margot, B. Schaub and M. Schlosser, J. Wood Chem. Technol., 2, 371 (1982).

18. K.P. Kringstad and R. Mörck, Holzforschung, 37, 237 (1983).

19. H.H. Nimz and H.-D. Lüdemann, Holzforschung, 30, 33 (1976).

20. J. Gierer and S. Wännström, 1983 International Symposium on Wood and Pulping Chemistry. Tsukuba Science City, May 23-27 1983. Proceedings, Vol. 4, p. 76.

21. J. Marton and E. Adler, Tappi, 46, 92 (1963).

22. P. Månsson and R. Öster, Manuscript in preparation.

23. S.I. Falkehag, J. Marton and E. Adler, Adv. Chem. Ser., 59, 75 (1966).

24. T. Yamasaki, S. Hosoya, C.-L. Chen, J.S. Gratzl and H.-m. Chang, Ref. 7. Proceedings, Vol. 2, p. 34.

25. J. Gierer and O. Lindeberg, Acta Chem. Scand., B 32, 577 (1978).

26. H. Aminoff, G. Brunow, K. Falck and G.E. Miksche, Acta Chem. Scand., B 28, 373 (1974).

27. R.D. Mortimer, J. Wood Chem. Technol., 2, 383 (1982).

28. R.G. Hise, C.-L. Chen and J.S. Gratzl, Ref. 20. Proceedings, Vol. 2, p. 166.

29. J. Gierer and L.-Å. Smedman, Acta Chem. Scand., 19, 1103 (1965).

30. K. Freudenberg and A.C. Neish, Constitution and Biosynthesis of Lignin, p. 69. Springer-Verlag, Berlin, Heidelberg, New York, 1968.

31. G. Gellerstedt, E.L. Lindfors, C. Lapierre and B. Monties, results to be published.

32. O. Lindeberg, Acta Chem. Scand., B 34, 15 (1980).