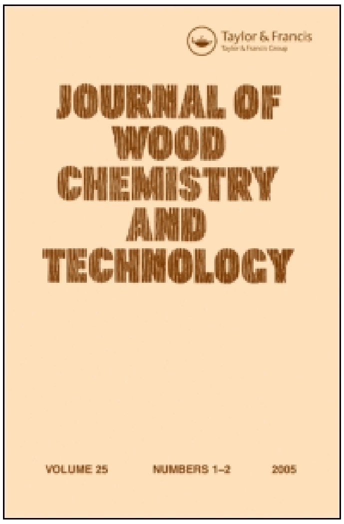

Journal of Wood Chemistry and Technology

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 Gellerstedt, G. , Pranda, J. and Lindfors, E. -L.(1994) 'Structural and Molecular Properties of Residual Birch Kraft Lignins', Journal of Wood Chemistry and Technology, 14: 4, 467 — 482
To link to this Article: DOI: 10.1080/02773819408003108
URL: http://dx.doi.org/10.1080/02773819408003108

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 14(4), 467-482 (1994)

STRUCTURAL AND MOLECULAR PROPERTIES OF RESIDUAL BIRCH KRAFT LIGNINS

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ABSTRACT

The residual lignins from unbleached and oxygen-bleached birch kraft pulps were isolated by acid hydrolysis and characterized by elemental analysis, methoxyl content, permanganate degradation, size exclusion chromatography and quantitative 13-C NMR. Calculations based on the reduction in kappa number after the acid hydrolysis revealed that only about one third or less of the material assumed to be lignin could be isolated as polymeric lignin. This was shown to be a syringyl-guajacyl type of lignin with a syringyl-to-guaiacyl ratio of approximately 1:1. The rest of the material found in the acid solution after hydrolysis and identified by GC-MS and by pyrolysis-GC-MS was to a large extent low molecular weight furanoid structures probably originating from polysaccharide degradation products, with only traces of lignin-derived compounds present.

INTRODUCTION

In the bleaching of chemical pulps, a lignin which has been structurally altered during the cook has to be removed from the fibers. Traditionally, this has been done with chlorine-containing bleaching chemicals like elemental chlorine, hypochlorite and chlorine dioxide. In recent years, the use of these chemicals, notably chlorine and hypochlorite, have been questioned for environmental reasons. Apart from

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chlorine dioxide new bleaching agents like oxygen, hydrogen peroxide and ozone have, therefore, been suggested and today these have been/are being introduced in pulp mills. The lack of knowledge about the structure of the residual lignin present in unbleached (kraft) pulps makes it difficult, however, to thoroughly understand which chemical and physical factors are of particular importance in the further delignification and brightening of the pulp.

It is well-known that kraft cooking proceeds in three distinct phases with respect to rate of lignin and carbohydrate dissolution , the final phase being extremely slow and thus having a poor delignification selectivity. In normal kraft cooking, the cook is therefore interrupted around the transition point between bulk and final delignification in order not to detrimentally affect the pulp yield and quality.

For hardwoods, like birch, it is particularly important that the cook is not allowed to proceed far into the final delignification phase since this will cause a rapid yield loss without any concomitant dissolution of lignin. It has also been shown that the kappa number region between the fiber separation point and a deterioration in the pulp quality parameters is very narrow in the case of birch[1,2].

The reason for the dramatic change in delignification selectivity is not known with certainty although (in work with softwood pulps and softwood lignin model compounds) several factors have been suggested. Among these, condensation reactions in the lignin giving rise to the formation of unreactive carbon-carbon linkages have frequently been suggested as the most probable cause of the difficulty in removing the last part of the lignin[3]. The possibility that alkali-stable chemical linkages between lignin and polysaccharides are formed during the cook and/or are present in the original wood itself has also been suggested by several researchers[4-9]. The fact that the majority of the phenylpropane-ß-aryl ether linkages originally present in lignin are cleaved during a kraft cook as well as a greater relative amount of "condensed" lignin units towards the end of the cook can also contribute to a lower reactivity[10,11]. The reactivity of the lignin towards the end of the cook can also be expected to be lower due to the formation of a certain amount of enol ether structures from originally present ß-aryl ethers[12] and to the fact that a substantial amount of lignin side-chain structures carrying CH_x-groups ($x = 1$-3) are present at the end of the cook[13].

In order to obtain further knowledge about the structural features of residual lignin present in kraft pulp fibers such lignin has been isolated from unbleached and oxygen-bleached birch kraft pulps. Subsequently the lignin samples have been subjected to various analyses like permanganate oxidation, elemental and methoxyl analysis, SEC and C-13 NMR. All the lignin samples were isolated by acid hydrolysis of the corresponding pulp.

EXPERIMENTAL

Pulp Samples

Laboratory-made birch (*Betula verrucosa*) kraft pulp (kappa number = 16.1) was prepared using a white liquor with 18% effective alkali and 33% sulfidity and with a cooking time of 90 min at 170 °C. Industrial birch kraft pulps, unbleached and oxygen-bleached, were obtained from a Swedish mill. The kappa numbers were 18.2 and 13.2 respectively. All pulps were thoroughly washed with distilled water and air dried. In order to remove extractives, they were subsequently extracted first with acetone for 12 h and then with dichloromethane for a further 12 h in a Soxhlet extractor.

Acid Hydrolysis

Each pulp sample (100 g dry weight) was refluxed under nitrogen for 2 h with 3000 ml of 0.1 M HCl in dioxane-water 82:18 (v/v, azeotrope, bp. 88 °C). Subsequently, the pulp was filtered and washed with 3x300 ml of dioxane-water 82:18 and then with water to a neutral pH. Approximately 2.5 l of distilled water was added to the filtrate which was then film evaporated at 40 °C until all dioxane had been removed. The total volume of water (containing hydrochloric acid) was never allowed to be reduced below 1500 ml in order not to increase the acidity of the solution too much. After leaving the solution overnight in a refrigerator to support a coagulation of the lignin, this was collected by filtration through a fine porous glass filter, washed with water to a neutral reaction and again suspended in water. After freeze-drying the isolated lignin was extracted with pentane in a Soxhlet extractor for 8 h in order to remove any remaining traces of low molecular weight material.

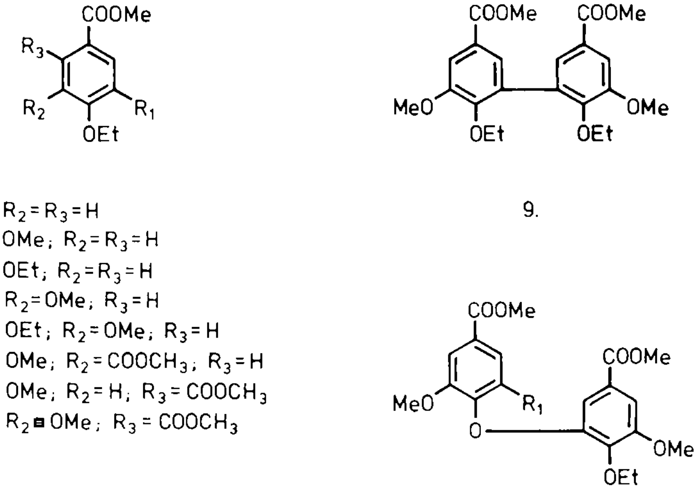
Lipophilic Fraction

The acidic aqueous solution (from the unbleached industrial pulp) was, after filtering off the lignin, extracted with ethyl acetate in a continuous extractor for 24 h and the organic phase was dried over Na_2SO_4 and film evaporated. (Extraction after partial or complete neutralisation of the solution considerably decreased the yield of extractable material, indicating a partially acidic material.) Further separation was accomplished by straight phase HPLC (NUCLEOSIL 50-5, 5um, 4.6x250 mm) using a gradient of ethyl acetate - petroleum ether from 10 to 100% ethyl acetate. A total of 9 fractions were collected and further analysed by GC/MS (GC-conditions as below but with the temperature program ending at 300 ^{o}C). Two very predominant products were obtained (calculated to comprise more than 80% of the total extract) together with several components in low yields. The former were identified as 2-furancarboxylic acid and 5-carboxy-2-furaldehyde, i.e. degradation products from polysaccharides. Among the other products, trace amounts of 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone and the corresponding syringyl analogue were found, which presumably originated from small amounts of remaining ß-aryl ether structures in the lignin and were formed in the acid hydrolysis reaction[14]. The mass spectral analysis also revealed the presence of trace amounts of vanillin, syringol and diguaiacylstilbene. No other simple monomeric or dimeric product derived from lignin could be detected.

Oxidative Degradation with Permanganate

The permanganate oxidation was performed as described elsewhere with 10 mg of lignin or with a corresponding amount of pulp (calculated as lignin)[15]. Gas chromatography was run on a HP 5890A using a fused silica capillary column, 30 m DB-1 (J&W Scientific), under the following conditions; Initial temperature 150 ^{o}C with a temperature increase of 5.0 ^{o}C/min to a final temperature of 270 ^{o}C, injector temperature 200 ^{o}C, detector temperature 300 ^{o}C, split ratio 1:30 at a pressure of 40 kPa at the head of the column.

A synthetic mixture of the esters **1**, **2**, **4**, **6** and **9** (Figure 1) was used for analytical purposes together with pyromellitic acid tetramethyl ester as internal standard. The response factor of ester **3** was assumed to be the same as that of **2**, that of **5** the same as that of **4**, those of **7** and **8** the same as that of **6** and those of



1. $R_1 = R_2 = R_3 = H$
2. $R_1 = OMe$; $R_2 = R_3 = H$
3. $R_1 = OEt$; $R_2 = R_3 = H$
4. $R_1 = R_2 = OMe$; $R_3 = H$
5. $R_1 = OEt$; $R_2 = OMe$; $R_3 = H$
6. $R_1 = OMe$; $R_2 = COOCH_3$; $R_3 = H$
7. $R_1 = OMe$; $R_2 = H$; $R_3 = COOCH_3$
8. $R_1 = R_2 = OMe$; $R_3 = COOCH_3$

9.

10. $R_1 = H$
11. $R_1 = OMe$

FIGURE 1. Major Products from Oxidative Degradation of Hardwood Lignins.

10 and **11** the same as that of **9**. The individual esters were identified by comparison of GC retention times and further by their mass spectra (Finnigan INCOS 50).

Analytical Techniques

Quantitative 13-C NMR spectra were run on acetylated lignin samples in acetone-d_6 using a Bruker AMX 300 spectrometer operating at 75.5 MHz for carbon. An inverse gated decoupling pulse sequence with a flip angle of $\pi/2$ was used. A pulse delay time of 11 s was employed and between 8 000 and 10 000 scans were collected.

Pyrolysis-GC-MS was done on a foil pulse pyrolyser (PYROLA, Pyrol AB, Lund, Sweden) interfaced with GC (HP 5890A, DB-1 column) and MS (Fisons TRIO-1). The pyrolysis was carried out at 550 °C as described elsewhere[16] and the gas chromatographic separation was done with a temperature program from 180 to 300 °C with a temperature increase of 10 °C/min.

High-performance size exclusion chromatography (HPSEC) of acetylated lignins was done on a Waters M45 System equipped with three Ultrastyragel columns coupled in series (having pore sizes of 10 000, 500 and 100 Å). Purified tetrahydrofuran was used as solvent and the flow-rate was 1.0 ml/min. The time/eluent volume scale was calibrated with polystyrene standards of known molecular weights. Elemental and methoxyl analyses were carried out by Analytische Laboratorien, Gummersbach, Germany.

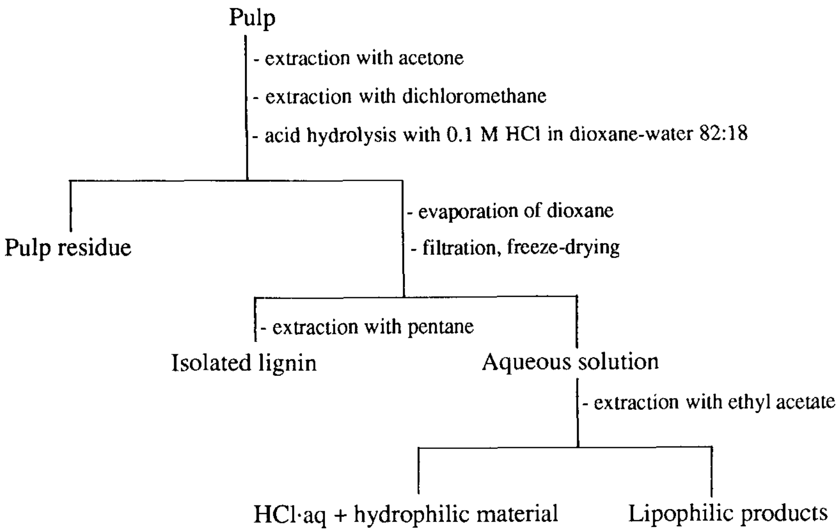
RESULTS AND DISCUSSION

Work-up Procedure

In preliminary experiments, residual lignin from acetone-extracted birch kraft pulp was isolated by acid hydrolysis in dioxane-water as described in Experimental. Such lignin samples were found to contain high amounts of extractives and analysis by pyrolysis in combination with gas chromatography and mass spectrometry demonstrated the presence of squalene as a predominant product together with lignin-derived decomposition products. In order to prepare pure lignin samples from birch pulps using acid hydrolysis it was, therefore, found necessary to remove all the remaining pulp extractives by a comprehensive extraction procedure employing both acetone and, in a second step, dichloromethane. In addition, the isolated lignin samples were subjected to a further extraction with pentane. None of these extracts was analysed further. The complete procedure is outlined in Scheme 1.

Acid hydrolysis of purified pulp samples using the azeotrope between dioxane and water together with hydrochloric acid is a convenient and comparatively rapid way of obtaining pure and carbohydrate-free lignins for further analysis. The drawback encountered in this method is the rather strong acidic conditions which are necessary to liberate the lignin from the pulp fibers. Under such conditions it can be assumed that any remaining α-aryl and α-alkyl ether linkages in the lignin together with ß-aryl ethers in benzyl alcohol structures are cleaved[14].

SCHEME 1. Isolation of Residual Lignin from Birch Kraft Pulp.



Under strong acidic conditions, condensation reactions between aromatic C-6 units and adjacent benzyl alcohol groups may also be expected to occur. This reaction type would lead to a greater yield of metahemipinic acid, **7**, (and the corresponding syringyl analogue, **8**) after oxidative degradation of the lignin with permanganate. Such analysis when carried out on both unbleached pine kraft pulp and on the corresponding isolated residual lignin obtained after acid hydrolysis of the pulp revealed no differences in the yield of this particular acid, however[17]. Similar results were obtained in the present work (see Table 3 below) although a tendency towards greater values for acid **8** was noticed (Figure 1).

One important reason for the apparently low tendency to form a condensed lignin under acidic conditions could be the low amount of residual benzyl alcohol and benzyl ether structures in the lignin after a completed kraft cook. Thus, based on 13-C NMR analysis of dissolved kraft lignin as well as of isolated residual lignin from both softwood and hardwood kraft pulps, it has been found that several of

TABLE 1
Kappa Numbers of Pulps and Yields of Individual Fractions Obtained from 100 g of a.d. Pulp and Isolated Acording to Scheme 1.

	Lab. unbleached	Ind. unbleached	Ind. O-bleached
pulp	pulp	pulp	
Kappa number of starting pulp	16.1	18.2	13.2
Kappa number of pulp after extraction	15.7	16.8	12.5
Acetone extract, g	0.35	0.47	0.38
Dichloromethane extract, g	0.01	0.01	0.01
Kappa number of pulp after acid hydrolysis	1.6	3.6	2.9
Theoretical yield of dissolved lignin[a], g	2.1	2.0	1.4
Isolated lignin, g	0.7	0.7	0.2
Ethylacetate extract, g	2.15	1.73	1.66

a) Based on a conversion factor of 0.15 between kappa number and lignin content.

these groups seem to have been reduced to methylene and methine groups during the course of the cook[13,18].

In preliminary work ,it was demonstrated that the release of lignin from kraft pulps requires a high temperature in the acid hydrolysis step. It was also found that an acid concentration of 0.1 M is needed to give an optimal yield of lignin. These conditions, when applied to unbleached and oxygen-bleached birch kraft pulps, were found to reduce the kappa numbers of the pulps to very low values as depicted in Table 1. However, the amount of isolated lignin was, in each case, much lower than the theoretical amount of dissolved lignin using a conversion factor of 0.15 to calculate the lignin content from the corresponding kappa number difference. This large discrepancy has not been found earlier in work with pine kraft pulps[19].

The reason for this difference could be the formation of low molecular weight fragments formed e.g. from remaining ß-aryl ether structures in the residual birch kraft lignin during the acid hydrolysis procedure. Therefore, after acid hydrolysis of the pulp and collection of the polymeric lignin, the remaining acidic aqueous solution was thoroughly extracted with ethyl acetate.

Ethyl Acetate Extract

Direct analysis of the extracted residue by pyrolysis in combination with GC/MS revealed the presence of two predominant products, viz. 2-furancarboxylic acid and 5-carboxy-2-furaldehyde, together with small amounts of different lignin-derived products. Altogether, 14 different lignin fragments were identified, with guaiacol and syringol constituting the major components.

After quantitative separation of the ethyl acetate extract by HPLC and subsequent analysis by GC/MS, the predominant products present were again identified (by comparison with MS library data) as 2-furancarboxylic acid and 5-carboxy-2-furaldehyde, i.e. compounds originating from polysaccharides in the pulp. In addition, small amounts of vanillin, syringol and diguaiacyl stilbene were found. Hibbert ketones, originating from ß-aryl ether structures in lignin, were present in trace amounts only. Therefore, the discrepancy in the lignin mass balance obtained in this work indicates that kappa number measurements on birch kraft pulps may give too high values and are not representative of the true content of the remaining lignin in the pulp.

Elemental and Methoxyl Analysis

The elemental compositions and methoxyl contents of the three polymeric lignin samples are listed in Table 2 together with values for birch milled wood lignin (MWL) and birch kraft lignin.

The low methoxyl values encountered in the isolated lignins are difficult to explain. Both NMR-data and oxidative degradation (see below) of the samples reveal the presence of substantial amounts of syringyl units in all three lignins, although the methoxyl values given in table 2 are more in accordance with a guaiacyl lignin. A "contamination" of the lignins by material such as aromatized carbohydrates originating from non-lignin constituents in the pulps cannot, therefore, be ruled out (22). All isolated lignins contain sulfur, as expected for lignins isolated after a kraft cook. In addition, the oxidative treatment encountered in oxygen bleaching is reflected in a higher value for oxygen in that lignin (cf. Ref. 23).

TABLE 2
Elemental and Methoxyl Analysis of Birch Lignins Together With Calculated Molecular Formulae Based on an Abitrary Value of 100 Carbon Atoms in the Lignin Polymer.

Lignin sample	C (%)	H (%)	O (%)	S (%)	OMe (%)	Molecular formula
Lab. unbleached pulp	62.85	5.85	29.10	2.20	14.54	$C_{100}H_{92.4}O_{28,3}S_{1.4}(OCH_3)_{9.8}$
Ind. unbleached pulp	63.40	5.85	28.22	2.51	14.17	$C_{100}H_{92.5}O_{27.1}S_{1.6}(OCH_3)_{9.5}$
Ind. O-bleached pulp	62.89	6.16	29.00	1.95	8.51	$C_{100}H_{106.7}O_{31.0}S_{1.2}(OCH_3)_{5.5}$
MWL[a]	59.7	6.1	34.2		21.4	$C_{100}H_{93.3}O_{33.8}(OCH_3)_{16.1}$
Kraft lignin[b]	62.46	6.00	27.77	2.39	18.83	$C_{100}H_{88.5}O_{23.9}S_{1.6}(OCH_3)_{13.8}$

a) Data from Ref. 20
b) Data from Ref. 21

Analysis by 13-C NMR

From quantitative 13-C NMR data, the contents of different types of hydroxyl groups were calculated using the integrals obtained from the acetyl carbonyl carbons. In all cases, the calculation was done with the methoxyl signal as the base unit. It was found that the lignin from the unbleached pulp samples gave very similar values with 0.3 primary, 0.3 secondary and 0.6 phenolic hydroxyl groups per methoxyl. In the case of the lignin from the oxygen-bleached pulp, the corresponding values were 0.5, 0.7 and 0.5, indicating a substantial oxygenation and/or liberation of aliphatic hydroxyl groups in the lignin side-chains during the oxygen bleaching stage. Furthermore, the oxidative degradation of phenolic structures known to take place in oxygen bleaching can be assumed to be compensated for by a considerable liberation of new phenolic units as a result of the acidic treatment in the lignin isolation procedure (cf. the absolute yields of permanganate oxidation products, table 3).

The evidence for a syringyl-guaiacyl type of lignin was for all three lignins supported mainly by the presence of NMR-signals centred around 153 ppm and 106 ppm (aromatic C3/C5 and C2/C6 carbon atoms in syringyl units) and around 113

TABLE 3

Relative Frequency of Occurrence of Phenolic Phenylpropane Units (mol-%) Corresponding to Degradation Acids Obtained from Permanganate Oxidation of Lignin and Identified as Methyl Esters (Depicted in Figure 1).

	Lab. unbleached pulp		Ind. unbleached pulp		Ind. O- bleached pulp	
Ester	lignin	pulp	lignin	pulp	lignin	pulp
1	0.5	1.7	0.9	1.8	0.8	1.3
2	19.9	23.3	21.8	25.0	19.8	21.0
3	0.2	1.3	0.2	0.7	0	0
4	49.0	49.2	32.4	36.0	23.7	30.3
5	0.8	1.5	0.9	0.6	1.1	0
6	6.8	7.0	14.0	13.5	21.8	22.9
7	3.3	4.9	5.1	4.7	8.7	11.9
8	3.5	2.1	3.2	3.1	3.8	2.7
9	5.0	2.7	8.5	4.9	8.2	4.2
10	3.2	2.0	5.2	3.6	3.9	2.2
11	7.7	4.3	7.7	6.2	8.1	3.4
Absolute yield, mg/g lignin	138	105	85	62	21	34

ppm and 119 ppm (aromatic C2 and C6 carbon atoms in guaiacyl units) respectively[24]. A value of approximately 1:1 for the syringyl-to-guaiacyl ratio was calculated, i.e. a value similar to that previously found in a birch lignin isolated after a kraft cook to 76% delignification[21]. Further NMR-data on lignins from kraft cooking of birch will be published elsewhere.

Permanganate Oxidation

The types and frequencies of various end-groups in the lignin were studied by oxidative degradation with permanganate[15]. In this procedure, the lignin is reacted with diethyl sulfate in order to protect all free phenolic hydroxyl groups by ethylation and subsequently oxidized in two steps first with alkaline permanganate and then with hydrogen peroxide. The aromatic carboxylic acids formed are esterified and the resulting mixture is separated and quantified by gas chromatography. The acids identified and used for quantification are depicted in Figure 1.

In Table 3, the calculated frequencies of occurrence of the various acids (i.e. lignin end-groups) are given together with the absolute yields of the esters. As before, the frequency values have been calculated using an assumed overall yield of reaction of 60% per carbon substituent attached to the same aromatic ring. From the same calculation, the absolute yield values can be used to obtain a rough estimate of the number of free phenolic hydroxyl groups present in the various samples.

From the data in table 3 it can be seen that acid hydrolysis of the pulps in all cases leads to somewhat different ratios between different types of lignin end groups. The abundances of the "condensed" dimeric acids (**9**, **10** and **11**) increase at the expense of all other acids in the mixture except acid **8**. The latter (together with acid **7**) originates from lignin units which have undergone an acid-catalysed condensation reaction between a benzylic carbon atom and an adjacent C-6 aromatic carbon[25]. These acids are always present to some extent in native lignins. The fact that this particular acid has increased in relative abundance when going from the pulp sample to the corresponding isolated lignin demonstrates, however, that condensation reactions may to a certain extent have taken place during the lignin isolation procedure.

The acids **9**, **10** and **11** are more abundant in the isolated lignins (table 3) indicating that the acid hydrolysis has led to a cleavage of ether linkages, presumably α- and ß-aryl ethers in lignin, in which the aromatic moiety is of the "condensed" type, i.e. of the biphenyl or biphenyl ether type. Furthermore, the analytical data confirm that oxygen bleaching leads to relatively minor changes in the lignin. The two major end groups present in lignins, viz. simple guaiacyl and syringyl units decrease, however, in relative abundance due to oxidation by oxygen (cf. Ref. 26). (This is particularly noticeable in the case of the syringyl structure, acid **4**.) In addition, a strong increase in the amount of acid **6** can be seen as a result of oxygen bleaching. This acid may originate from phenyl coumaran structures in lignin but it has also been demonstrated that biphenyl structures of the mono- as well as of the diphenolic type can give rise to the same structure[15,27]. The high value obtained may, therefore, reflect the "selectivity" in oxygen bleaching encountered earlier[28], i.e. the low reactivity of "condensed" lignin structures. As a further result of the action of oxygen, the amount of catechol structures formed during the kraft cook, has, as expected, decreased below the detection level.

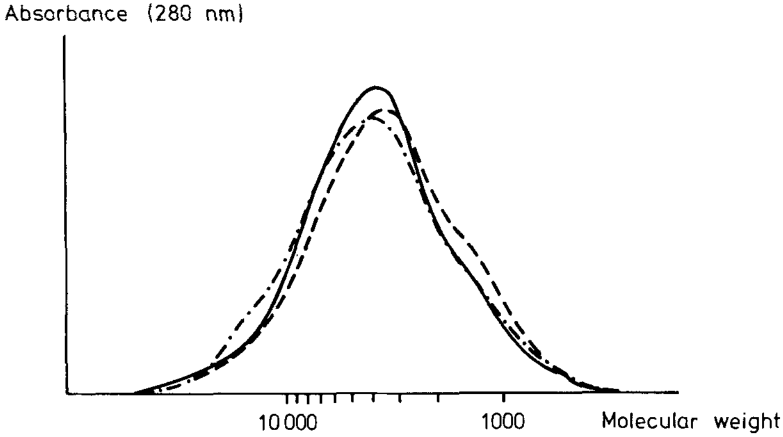


FIGURE 2. Size Exclusion Chromatography of Residual Lignins Isolated from Industrial Kraft Pulp (-·-·), Laboratory Kraft Pulp (——) and Industrial Oxygen Bleached Pulp (----).

Size Exclusion Chromatography

The isolated lignin samples were also subjected to high performance size exclusion chromatography on polystyrene gels using polystyrene fractions for molecular weight calibration purposes. The results demonstrate that all three lignins are very similar ,as shown in Figure 2 and Table 4. Also, in comparison with both an isolated lignin from unbleached pine kraft pulp and a corresponding lignin isolated from black liquor, the birch lignins were found to be similar[19].

Altogether, these results demonstrate that the residual lignin present in kraft pulps does not remain insoluble because of any restrictions in the molecular structure. Alkali-stable but acid-sensitive ether linkages between the residual fiber lignin and polysaccharides resulting in individual molecules of very high molecular weight and with restricted solubility may, however, explain the observed behaviour. It should be noted here that dioxane - water alone is not sufficient to liberate lignin from kraft pulp fibers. Another possibility may be the presence of lignin molecules of very high molecular weight (large size) unable to diffuse out through the fiber wall because of pore size restrictions unless they are degraded to smaller fragments (cf. Ref. 29).

TABLE 4
Apparent Molecular Weight Data of Birch Lignins Calculated from Size Exclusion Chromatography after Calibration with Polystyrene Fractions.

Pulp sample	Mw	Mn	Mw/Mn
Lab. unbleached pulp	4790	2490	1.92
Ind. unbleached pulp	4330	2190	1.98
Ind. O-bleached pulp	4900	2410	2.00

CONCLUSIONS

Both unbleached and oxygen-bleached kraft pulps from birch contain a residual lignin which is rich in syringyl units. However, the amount of residual lignin in the various pulps is not reflected in the corresponding kappa numbers, nor is the elemental analysis data of the isolated lignins in accordance with a syringyl-guaiacyl lignin. Therefore, the results obtained indicate that a major portion of the kappa number is in fact a measure of a non-lignin but permanganate-consuming material. Such material can also constitute part of the lignin isolated by acid hydrolysis. From the results obtained so far, this non-lignin material seems to be of polysaccharide origin, a predominant portion having furanoid structures. In the bleaching of birch kraft fibers, a substantial consumption of bleaching chemicals may thus be attributable to the oxidation of this non-lignin material.

ACKNOWLEDGEMENTS

Grants to one of us (J.P.) from ”59 års Fond” and from ”Stiftelsen Cellulosa- och Pappersforskning” are gratefully acknowledged. Thanks are due to H-L. Hardell, STFI, for carrying out the pyrolysis experiments.

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