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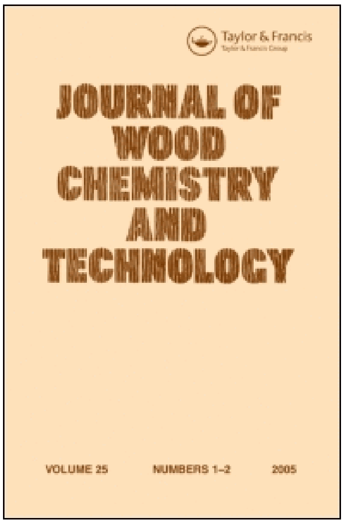

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Gellerstedt, Göran and Gustafsson, Kristina(1987) 'Structural Changes in Lignin During Kraft Cooking. Part 5. Analysis of Dissolved Lignin by Oxidative Degradation', Journal of Wood Chemistry and Technology, 7: 1, 65 — 80

To link to this Article: DOI: 10.1080/02773818708085253

URL: http://dx.doi.org/10.1080/02773818708085253

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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 7(1), 65-80 (1987)

STRUCTURAL CHANGES IN LIGNIN DURING KRAFT COOKING
PART 5. ANALYSIS OF DISSOLVED LIGNIN BY OXIDATIVE DEGRADATION

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Paper dedicated to Dr. David A.I. Goring with gratitude.

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ABSTRACT

Kraft lignins have been isolated from the black liquors obtained a) after normal kraft cooking of pine wood to different yield levels and b) after a flow-through cook. After purification, the two series of lignins have been subjected to oxidative degradation in a four step reaction sequence leading to the formation of substituted aromatic carboxylic acid methyl esters. The yields and distribution of the different esters obtained from the flow-through cook indicate that in kraft cooking the lignin which goes into solution undergoes structural changes which coincide with the transition points between the initial, the bulk and the final delignification phases. From the other series of cooks, changes in the frequency of occurrence of the individual esters were also observed as the cook proceeded. These changes could not, however, be attributed to the different phases of delignification but took place rather continuously during the cook. The observed results are discussed with reference to known features of delignification chemistry in kraft cooking.

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INTRODUCTION

In the work reported in a previous paper in this series, kraft lignin samples, obtained after acidification of black liquors, were subjected to quantitative analysis by carbon-13 nuclear magnetic resonance spectroscopy.[1] The data obtained were combined with the results of elemental analysis and with data for the content of phenolic hydroxyl groups in the various lignins. The results led to the conclusion that the dissolved lignin exhibits only minor chemical changes as the kraft cook proceeds. No clear indication of condensation reactions taking place within the lignin during cooking could be obtained.

Nevertheless, it is well known that the rate of delignification in kraft cooking changes as the cook proceeds and that these changes can be strongly influenced by the conditions prevailing during the cook.[2-4] In particular, the final delignification phase which is entered at a degree of delignification of about 90 % (on wood), involves a fairly slow and non-selective lignin dissolution. From both a technical and an economical point of view the cook can therefore not be extended too far into this phase of delignification.

Previous analyses of the structure of the lignin remaining in the fibres of pine wood after kraft cooks to different yield levels have revealed that several structural changes can be observed as the cook proceeds. In addition to changes in the amount of free phenolic hydroxyl groups and to an almost linear decrease in the amount of uncondensed phenylpropane-β-aryl ether structures, noticeable changes in the frequency of occurrence of the different aromatic acids obtained after oxidative degradation have also been observed.[5-7] These changes were found to coincide with the transition points from the initial to the bulk and from the bulk to the final delignification phases.

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In the present work, further attempts have been made to identify chemical changes taking place in the polymeric lignin structure during the process of kraft cooking. Two series of lignins precipitated from black liquors have therefore been subjected to analysis by oxidative degradation in order to permit a comparison of the frequencies of occurrence of different structural units in the various samples. For the purposes of comparison, a lignin sample obtained from the black liquor of a soda cook was also included in the analysis. In addition, attempts have been made to quantify one of the minor structures known to be present in kraft lignin viz. the catechol structure.

RESULTS AND DISCUSSION

The first series of lignins was prepared by kraft cooking of chips from pine to different yield levels under otherwise identical conditions. The pulp yield range covered was from 90 to 48 % with the latter pulp having a kappa number of 32. Acidification of the resulting black liquors precipitated the lignins. These were collected and purified as described in Ref. 5. The dissolved lignin fractions from a flow-through cook were collected by continuous addition of fresh white liquor to a layer of pine wood chips with simultaneous removal of black liquor. A gradient for the concentration of hydroxyl ions was employed thus simulating the actual alkali profile prevailing during a kraft cook. A step-wise reduction of the concentration of hydrogen sulfide ions during the cook was also adopted. A total of six fractions of black liquor were collected from this cook, each fraction containing the lignin passing into solution during a cooking period of approximately 30 min. The kappa number of the pulp resulting from the completed cook was 16. It was assumed that the last fraction of lignin obtained in this series was representative of the lignin passing into solution during the (slow) final delignification phase.

Due to its inferior pulping characteristics and pulp quality, the soda process is not used commercially. One lignin sample from a soda cook was, however, included in the present work, in order to show possible differences between the structures of lignin dissolved in this process and in the kraft process.

In the analytical method employed, the polymeric lignin structure is degraded into low molecular weight aromatic carboxylic acids.[8] After esterification, these can be analysed and quantified by gas chromatography. The structures and relative amounts of the individual acids reflect the amounts of different structural units present in the lignin sample under investigation, since each carboxylic acid group represents a lignin residue. The analytical method gives, however, well-defined low molecular weight acids only from lignin units containing free phenolic hydroxyl groups. The majority of these units constitute building blocks in linear parts of the polymer since there is only a very limited number of phenylpropane structures having side-chain linkages to two other lignin units.[9] Nevertheless, it is assumed that the non-phenolic parts of the lignin polymer also contain the same types of structures in approximately the same amounts as those analysed.

The number of branching points in the lignin should thus be represented by the frequency of occurrence of the various difunctional acids obtained since, in such structures, aryl ether linkages may constitute a third type of linkage to a new lignin unit. Consequently, lignins containing a high fraction of structures with free phenolic hydroxyl groups, such as kraft lignins, must have comparatively few branching points, unless secondary condensation reactions involving side-chain carbon atoms are abundant.

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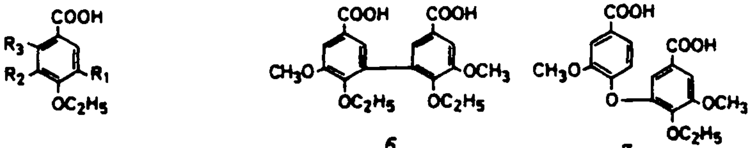

1 $R_1 = R_2 = R_3 = H$
2 $R_1 = OCH_3$ $R_2 = R_3 = H$
3 $R_1 = OC_2H_5$ $R_2 = R_3 = H$
4 $R_1 = OCH_3$ $R_2 = COOH$ $R_3 = H$
5 $R_1 = OCH_3$ $R_2 = H$ $R_3 = COOH$

6

7

FIGURE 1. Quantified acids from the oxidative degradation of various kraft lignin samples.

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Of the various types of condensation reactions which have been shown to occur when lignin model compounds are subjected to alkaline cooking conditions[10], not all can be traced by the analytical method employed in the present work. Reactions of coniferyl alcohol derived structures which lead to the formation of new carbon-carbon linkages between side chains cannot, for example, be identified. On the other hand, reactions involving the addition of (ionized) phenolic structures to carbonyl and conjugated carbonyl groups in lignin or carbohydrates should give rise to lignin structures which upon oxidative degradation might result in the formation of isohemipinic acid (4)(Fig. 1). If condensation reactions start to play a dominant role in *e.g.* the residual delignification phase, an increase in the amount of isohemipinic acid towards the end of the cook should thus be expected, although it must be emphasized that isohemipinic acid can also be formed from monophenolic biphenyl structures upon oxidative degradation.[8]

The two series of lignins employed in the present work were analysed in duplicate runs and the compounds depicted in Fig. 1 were quantified using a synthetic reference mixture consisting of known amounts of the (esterified) compounds 1-4,

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TABLE 1

Frequency of Occurrence of Phenolic Phenylpropane Units (mol-%) Corresponding to the most Abundant Carboxylic Acids in Lignin Samples after Kraft Cooking to Different Degrees of Delignification.

Lignin samples obtained at degree of delignification (% on wood)	Frequency of carboxylic acid No. (analysed as methyl ester)						
	1	2	3	4	5	6	7
9	2.8	62.1	0.4	17.4	2.0	12.4	2.9
13	2.4	60.7	0.3	17.2	2.2	12.6	4.6
28	2.1	56.6	0.2	16.8	3.8	14.2	6.3
37	1.4	54.8	0.3	18.7	3.4	14.1	7.3
69	0.8	50.0	0.3	19.7	3.6	16.3	9.3
87	0.7	49.0	0.4	18.4	4.2	17.7	9.6
91	0.7	47.5	0.5	19.5	4.1	18.4	9.3
7-12	3.1	62.3	0.1	17.3	2.3	11.4	3.5
12-29	1.9	53.8	0.2	18.1	4.0	16.3	5.7
29-66	1.3	50.3	0.2	18.4	3.8	17.8	8.2
66-85	0.9	47.9	0.3	18.6	4.2	18.5	9.6
85-93	0.7	44.8	0.5	19.5	4.2	19.9	10.4
93-95	0.6	40.0	0.5	20.5	4.5	22.0	11.9
89[1]	1.6	51.0	0.5	18.4	3.5	15.2	9.8

[1] Soda cook

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and 6. The results of these analyses are given in Table 1. In addition to the acids depicted in Fig. 1, several minor components were formed in the oxidative degradation procedure. degradation procedure. These were not included in the quantitative analysis, but their total contribution to the product mixture was calculated to be less than 5 % on a molar basis.

The frequency of occurrence of the individual acids 1-7 (analysed as esters) was calculated using the method described in detail in Ref. 11. In the calculations it was assumed that the average overall yield of ester per carbon substituent attached to one aromatic ring is 60 %. This figure is based upon results obtained from the oxidation of a variety of different lignin model compounds. Even though this mode of calculation probably leads to a slight underestimation of the frequencies of the dicarboxylic acids and a corresponding over-estimation of the monocarboxylic acids due to the heterogeneity of the lignin structure, the values given in Table 1 are considered reliable in comparison with each other.

The frequency of occurrence of each of the quantified acids is given in Fig. 2 as a function of the degree of delignification. For purposes of comparison, the corresponding frequency values obtained earlier from the analysis of residual lignins in kraft pulps are included in the figure. It can be seen that there are distinct changes in the frequency of occurrence of the acids obtained from the flow-through cook lignins as the cook proceeds. These changes coincide rather precisely with the changes taking place with the different acids obtained from residual pulp lignins. For the series of lignins obtained from "normal" kraft cooks, each sample represents the accumulated lignin previously dissolved in the cook. The degradation acids obtained from these lignins do not show the same sharp changes in frequency of occurrence as the

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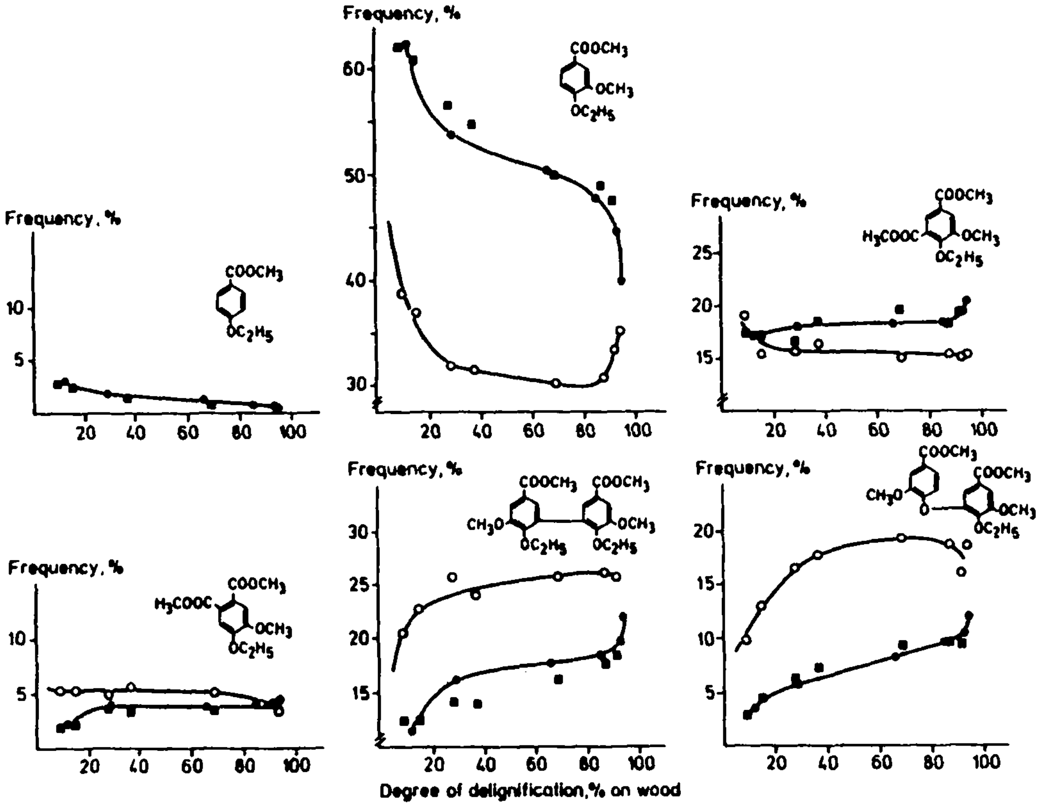

FIGURE 2. Frequency of occurrence of individual degradation acids as a function of the degree of delignification.

● = acids from lignins dissolved in the flow-through cook;

■ = acids from "normal" dissolved kraft lignins;

○ = acids from residual fiber lignin using published data.[5]

acids obtained from the flow-through cook lignins. The same general trends for the individual acids can, however, be distinguished.

Compound 2, the most abundant degradation acid obtained from both the dissolved lignins and from the residual fiber lignin, corresponds to guaiacyl end-groups in lignin. In the beginning of the kraft cook, more than half the phenolic groups are of this type. During the initial delignification phase, in which approximately 20 % of the lignin is dissolved, the number of guaiacyl groups rapidly decreases in the solid phase whereas the lignin going into solution contains a very large (but also in this case decreasing) fraction of such groups. This indicates that, in addition to an alkaline extraction of lignin, some α-aryl and/or β-aryl ether structures are cleaved already in this early part of the cook with the formation of new guaiacyl end-groups. Simultaneously, the residual fiber lignin shows a rapid increase in the frequency of biphenyl structure 6 and the biphenyl ether structure 7. It is obviously much more difficult to get a dissolution of these types of structures into the liquid phase, and throughout the cook they are therefore much more abundant in the residual than in the dissolved lignin.

During the bulk delignification phase, extending to a degree of delignification of approximately 90 % (on wood), the changes in the frequency of occurrence of the various degradation acids are comparatively minor. The number of guaiacyl end-groups in the dissolved lignin, analysed as compound 2, is, however, high throughout, indicating that the β-substituent in phenylpropane-β-aryl ether structures consists to a large extent of guaiacyl structures. This result also supports the view that in order to dissolve a lignin fragment, cleavage of β-aryl ether structures is essential.

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The transition point between bulk and final delignification occurring at approximately 90 % delignification (equal to a kappa number of about 35-40), is clearly accompanied by chemical changes in the structure of both dissolved and residual lignin as shown in Fig. 2. The frequency of occurrence of the various degradation acids changes quite distinctly around this point of delignification and, with one exception, the values obtained for the flow-through cook lignins approach those of the residual lignin. This indicates that the structures of the two types of lignin are becoming more similar to each other towards the end of the cook. Such a conclusion is also supported by analytical data for the number of β-aryl ether structures present in these lignins.[7] It has been found that towards the end of the cook, the number of these structures is almost identical in both the dissolved and residual fiber lignins. The results obtained here as well as those found earlier therefore indicate that the number of chemical reactions in lignin which are decisive for dissolution rapidly decreases when the cook approaches a degree of delignification of approximately 90 %. The major reason for this seems to be a lack of hydrolysable β-aryl ether structures which, although present, may be prevented from being cleaved because of _e.g._ inaccessibility to the cooking chemicals. This lack of reactivity decreases the possibility of creating new free phenolic hydroxyl groups in the lignin. The possibility of dissolving a given lignin fragment thereby also decreases, since the phenolic hydroxyl group is by far the predominant functional group giving water solubility to lignins obtained from alkaline pulping processes.

As discussed above, the degradation acid _4_ may arise from condensed lignin structures in which C-5 positions in aromatic rings have become linked to lignin side-chain carbon atoms or to carbohydrates during the course of the cook. Since the

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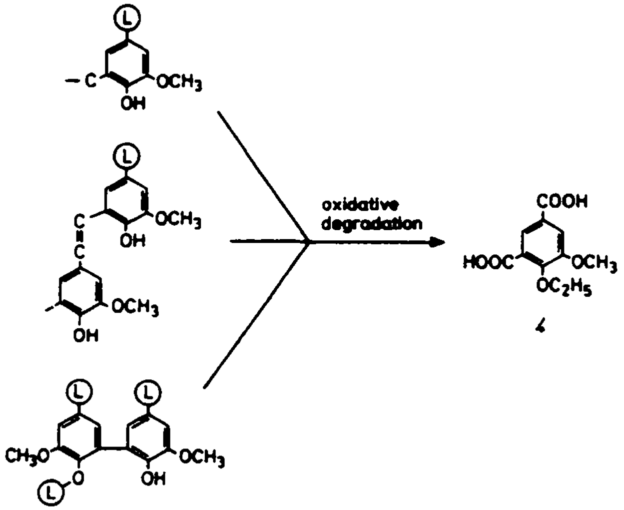

FIGURE 3. Lignin structures giving rise to isohemipinic acid (4) upon oxidative degradation.

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frequency of occurrence of this particular acid does indeed increase in the dissolved lignin towards the end of the cook (Fig. 2), such condensation reactions cannot be excluded. If such reactions take place they may further contribute to the low rate in the final delignification phase. In addition to condensed structures of the type discussed above and to stilbenes originating from phenylcoumaran structures, monophenolic units of the biphenyl type also give rise to the degradation acid 4 in the analytical procedure (Fig. 3). An increase in the amount of biphenyl structures in the lignin (as is observed towards the end of the cook) can therefore also be expected to lead to an increase in the amount of the acid 4, since it is unlikely that all biphenyl structures present carry two free phenolic hydroxyl groups. No definite conclusions concerning the presence or absence of condensation reactions during kraft cooking can therefore be drawn from the results obtained here.

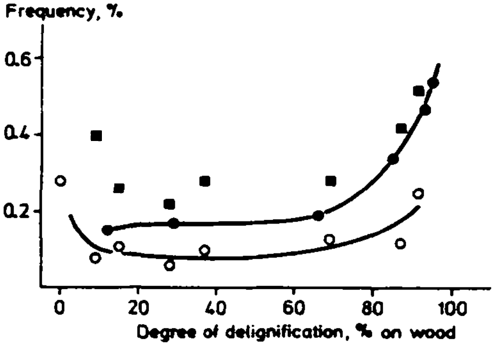

FIGURE 4. Frequency of occurrence of the degradation acid 3 as a function of the degree of delignification.

● = lignin from flow-through cook;

■ = lignin from "normal" kraft cook;

○ = residual fiber lignin using published data.[5]

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Kraft cooking is accompanied by a certain demethylation of aromatic methoxyl groups. This reaction gives rise to malodorous compounds such as methyl mercaptan, dimethyl sulfide and dimethyldisulfide with a concomitant formation of catechol structures. The latter are converted into degradation acid 3 in the analytical procedure employed and the amount of catechol structures can thus be quantified. The results are given in Table 1 and Fig. 4, where it can be seen that in the dissolved lignins, catechol structures strongly increase in relative importance towards the end of the cook. A similar but less pronounced trend is also observed for the residual lignin in the pulp. This result is in accordance with quantitative analyses of the formation of the volatile malodorous compounds formed in kraft cooking, most of which are formed in the later part of the cook.[12]

Among the other degradation acids formed in small amounts from the dissolved lignin, special attention was paid to

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acid 1. This acid is formed from p-hydroxyphenylpropane units in lignin and it has been suggested that such lignin structures are particularly abundant in the middle lamella lignin.[13] In studies of topochemical effects in the delignification during kraft pulping, it has been found that the middle lamella lignin is preferentially dissolved during the later part of the cook, i.e. above a degree of delignification of approximately 50 % (on wood).[14] In this part of the cook, an increase in the amount of the acid 1 should thus be expected, possibly accompanied by the presence of corresponding structures with two or three carboxylic acid groups attached to the same aromatic ring. This was not found to be the case, as demonstrated in Fig. 2. Instead, the frequency of occurrence of acid 1 was found to decrease slowly during the course of the cook and only trace amounts of the corresponding dicarboxylic and tricarboxylic acids were found as analysed by mass spectrometry.

The lignin obtained from a soda cook was found to contain a slightly higher relative amount of guaiacyl end-groups than a kraft lignin obtained at approximately the same degree of delignification. The reason for this is not known, but it could possibly be due to the fact that the soda lignin contains a higher proportion of vinyl ether structures.[7] The latter are preferentially formed from phenolic β-aryl ether structures in the absence of sulfide ions or other nucleophiles. Furthermore, the soda lignin was found to contain appoximately the same relative amount of isohemipinic acid (4) as the kraft lignin samples. This indicates that, if condensation reactions involving C-5 positions in aromatic rings do take place during soda cooking (cf. above), they are of the same magnitude as in kraft cooking. Such reactions cannot therefore explain the differences in the rate of delignification between the two cooking processes.

CONCLUSIONS

The structure of the lignin going into solution in kraft cooking undergoes changes as the cook proceeds, as revealed by oxidative degradation analysis. These changes coincide with the changes earlier observed in similar analyses of residual lignin in kraft pulp fibers. Furthermore, both the transition point between initial and bulk delignification and the transition between bulk and final delignification known to exist in kraft pulping occur at approximately the same degrees of delignification as the chemical changes. The results therefore support the view that chemical reactions in the lignin macromolecule are of significant importance for the lignin dissolution. Among such reactions, a comprehensive cleavage of β-aryl ether structures with a concomitant formation of new phenolic hydroxyl groups is obviously essential. The results obtained further demonstrate that towards the end of the cook the relative amounts of biphenyl and biphenyl ether structures in lignin increase whereas guaiacyl end-groups decrease. This indicates that the lignin going into solution now has a more branched and/or cross-linked structure and that there are fewer hydrolysable β-aryl ether structures. On the other hand, no conclusive evidence for the presence or absence of condensation reactions during cooking has been obtained.

EXPERIMENTAL

The "normal" series of kraft cooks was performed to different pulp yield levels on pine chips (Pinus sylvestris) employing a cooking liquor with 30 % sulfidity and 18 % effective alkali. The soda cook was carried out with a cooking liquor containing 25 % effective alkali. The flow-through cook was carried out as

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described in Ref. 1. All lignin samples were precipitated from the black liquors and purified as described previously.[5]

The oxidative degradation analysis involving ethylation, oxidation with a mixture of potassium permanganate and sodium periodate, oxidation with hydrogen peroxide and methylation was carried out on approximately 30 mg of sample according to the procedure described in Ref. 8. In the ethylation step, a pH of 11 was employed for 24 h. The permanganate oxidation was carried out using purified tert-butanol as the organic solvent. As described before [5], it was always found necessary to add extra portions of solid potassium permanganate and sodium periodate during the course of the reaction (portions of 3 x 25 mg $KMnO_4$ and 3 x 320 mg $NaIO_4$ were used) in order to maintain the purple color of the solution. If this was not carefully done, the yield of oxidation products was found to decrease. The oxidation with hydrogen peroxide was carried out as described before; in the methylation step, diazomethane, prepared from N-methyl-N-nitroso-p-toluenesulfonamide, was introduced together with a stream of nitrogen into a solution containing the aromatic acids.[15]

For quantification purposes, a synthetic mixture containing the (esterified) acids 1,2,3,4,6 was used. The acids 5 and 7 were quantified by assuming similar response factors to acids 4 and 6 respectively. All ester mixtures were separated by gas chromatography on a 30 m DB-1 fused silica capillary column using a temperature program of 5 °C/min from 150 °C to 270 °C and thereafter 270 °C for 7 min. Helium was used as the carrier gas. For the calculations of the frequency of occurrence of the individual degradation acids, an oxidation yield of 60 % per carbon substituent attached to the same aromatic ring was assumed. The mass spectrometric fragmentation pattern was used for structure elucidation of those components in the mixture of esters which were not identified by comparison with authentic materials.

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