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Investigation of lignins from soda and soda/anthraquinone cooking of spruce wood

SUMMARY

Lignins isolated from spent liquors from soda and soda/anthraquinone cooks of spruce wood were examined. ^1H NMR spectroscopy demonstrated that β -O-4 structures disappeared more rapidly and that phenolic groups were liberated to a larger extent when anthraquinone was present in the pulping liquor. Units with glycerol side chains could be detected in the lignins from soda cooks. The IR spectra and molecular weight distributions of all the lignin samples were found to be very similar.

TIIVISTELMÄ

(*Kuusihakkeen sooda- ja sooda/antrakini-
keittojen ligniinitutkimukset*)

Kuusihakkeen sooda- ja sooda/antrakini-
keittojen jätelemistä eristettyjä ligniinejä on tutkittu. ^1H NMR-spektroskopian avulla on osoitettu, että antrakiniolisäys nopeuttaa β -O-4 rakenteen häviämistä ja lisää fenoliryhmien vapautumista. Soodakeittojen ligniineistä on löydetty glyserolisivuketjuja. Sekä

IR-spektrien että molekyyllipainojakautumien on todettu olevan hyvin samankaltaiset kaikilla ligniininäytteillä.

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The beneficial effect of an addition of anthraquinone to pulping liquors on the rate of delignification and on the stabilisation of carbohydrates has been the subject of several recent papers (see, e.g., 1, 2). Anthraquinone (AQ) is reduced by the carbohydrates to anthrahydroquinone (AHQ) (2—4; see also 5). AHQ interferes with the alkaline reactions of the lignin and accelerates its degradation. Alkaline lignin reactions in the presence of the AQ/AHQ system have primarily been elucidated by studies of model compounds (4, 6—8) and only to a limited extent by studies of alkali lignins (6, 9, 10).

In the present investigation alkali lignins from soda and soda/AQ cooks of spruce wood were examined, primarily by spectral methods. The cooking conditions were those used by Basta and Samuelson (11). The experiments were run for 90 min and 250 min. A 90-min cook with AQ added resulted in approximately the same degree of delignification (kappa number 30) as did a 250-min soda cook (11). Since a discussion of the results requires it as background, a review of some important reactions of lignin during alkaline pulping is given below.

SOME IMPORTANT REACTIONS OF LIGNIN DURING ALKALINE PULPING

The β -O-4 structures (1) constitute the major type of structural element in lignins. Scheme 1 summarises the main reactions of β -O-4 structures during soda cooking (for reviews, see 12, 13). It is notable that the cleavage of β -ether bonds with the formation of units with glycerol side chains (2) is a slow reaction and that enol ethers of type 5 are comparatively stable during the cooking conditions. The β -5 structures (6) constitute a second important type of structural elements. Soda cooking of phenolic β -5 structures produces stilbenes (7); non-phenolic β -5 structures are unaffected (12, 13).

Anthraquinone present in the cooking liquor is reduced by carbohydrates to anthrahydroquinone, which exists in the cooking liquor as the dianion (AHQ^{2-}). This undergoes a nucleophilic addition to quinone methides formed from phenolic β -O-4 structures during the alkaline treatment. The adduct decomposes with simultaneous cleavage of the β -ether bond, formation of a coniferyl alcohol unit, and regeneration of anthra-

quinone (Scheme 3) (4, 6—8). Coniferyl alcohol units undergo a complex series of conversions in the alkaline pulping liquor (12, 13).

RESULTS AND DISCUSSION

The methoxyl content of all the lignin samples investigated was found to be about 14.8 % (± 0.2 %). This figure is close to that generally found for alkali lignins and indicates a high purity of the lignin samples isolated.

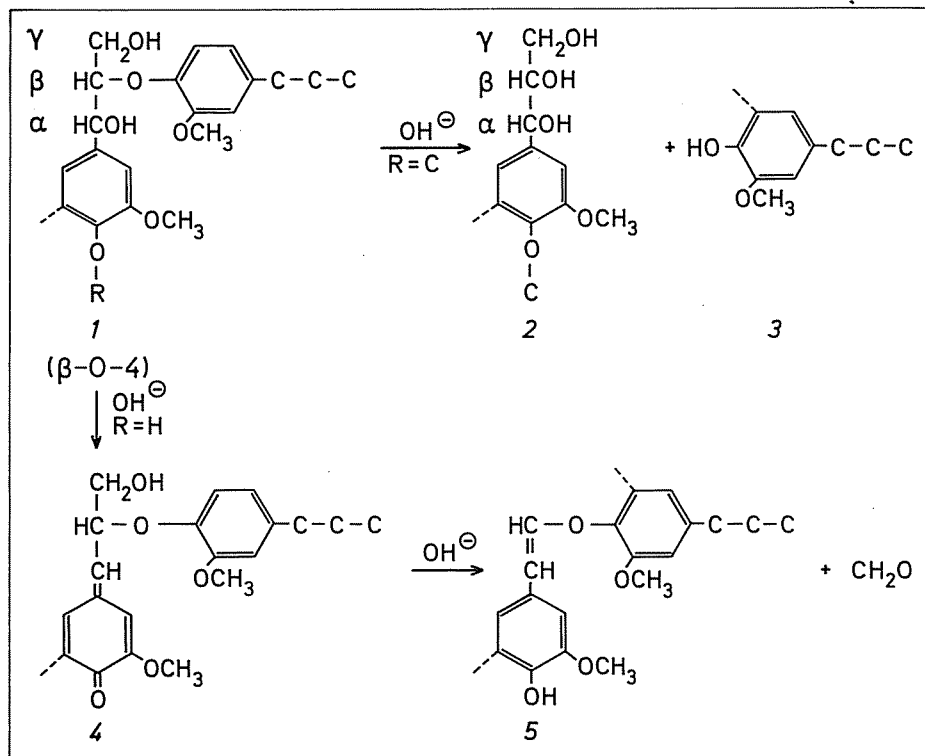
The lignin samples were examined by GPC on Sephadex LH 60, using DMF-acetic acid (200:1) as eluent. (This eluent was found to eliminate the anomalies observed (14) on GPC with the Sephadex LH 60/DMF system). The molecular weight distributions were found to be similar for all the lignin samples examined (Fig. 1). Calibration with compounds of known molecular weight showed that materials with a molecular weight of about 1000 were eluted at $K'_d \approx 0.7$. Thus, it could be concluded from the GPC curves (Fig. 1) that only a very small proportion of the alkali lignins had a molecular weight of less than 1000. All the lignins exhibited very similar IR spectra which were essen-

tially identical with the IR spectrum of kraft lignin (15). This was particularly true of the lignin from the 90-min soda cook. The appearance of the spectrum of the lignin from the 90-min soda/AQ cook deviated slightly in the shape of a peak at 1725 cm^{-1} ($\text{C}=\text{O}$ stretching). The spectra of lignins from the 250-min cooks exhibited a somewhat more distinct 1725 cm^{-1} peak, but were otherwise practically identical with the spectra of lignins from the 90-min cooks.

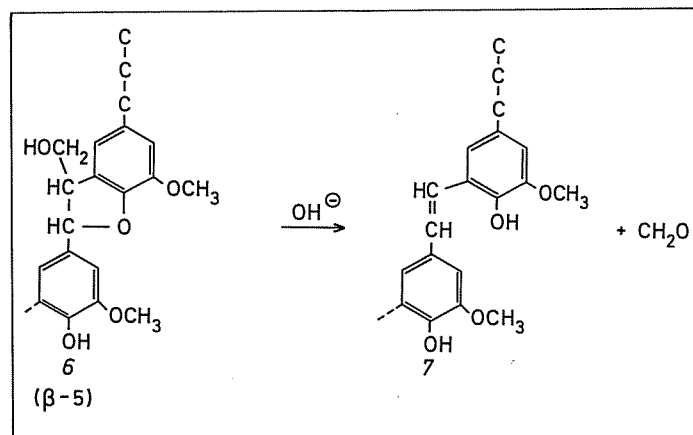
All the ^1H NMR spectra of alkali lignins (Figs. 2 and 3) have essentially the same appearance. Compared with the spectrum of milled wood lignin, the alkali lignin spectra are rather featureless. This can be explained by the very complex structure of alkali lignins caused by a wide variety of reactions occurring during the alkaline treatment. The assignment and intensities of the predominating peaks are given in Table 1. These peaks are very broad and obviously include signals from various types of protons. The assignments refer to the types of protons which primarily cause the peaks. We found it advantageous to discuss the spectra in terms of peak positions and peak intensities (Table 1) in combination with data obtained from difference spectra (Figs. 4 and 5, Table 2).

A comparison of the ^1H NMR spectral properties of soda and soda/AQ lignin from 250-min cooks demonstrates that clearly larger amounts of phenol groups are liberated when AQ is present in the cooking liquor (Fig. 3, Table 1). Regarding phenol groups in the lignins from 90 min cooks, the difference spectrum in Fig. 4 suggests (judging from estimations of peak areas) larger amounts of phenol groups in soda/AQ lignin than in soda lignin, while the peak intensities (Table 1) indicate the reverse. The phenol acetate peak is comparatively sharp in the soda lignin spectrum (Fig. 2; cf. Fig. 4), and this causes the probably false result derived from peak intensities. It is apparent from Fig. 4 and Table 2 (minimum at $\delta\ 2.00$) and Table 1 that an AQ addition causes a rapid decrease in alcohol groups. Fig. 5 and Table 2 (minimum at $\delta\ 2.01$) show that a decrease in alcohol groups is also affected by prolonged soda cooking.

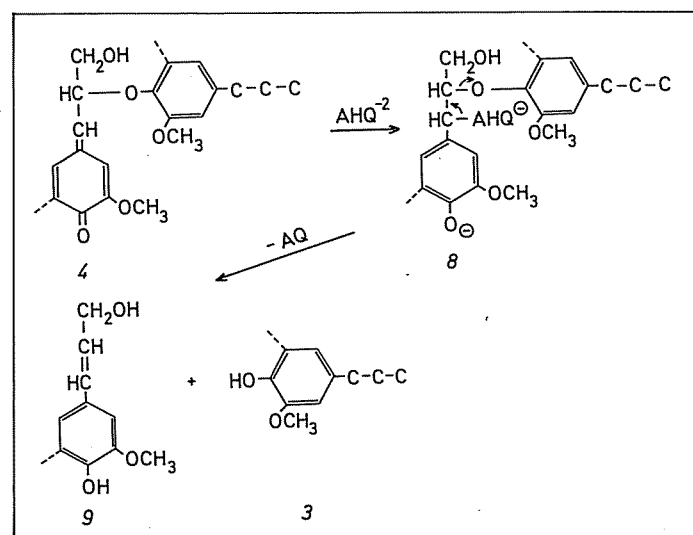
The liberation of larger amounts of phenol groups on soda/AQ cooking is consistent with the reactions in Schemes 1 and 3. Thus, the formation of alkali-stable enol ethers of type 5 during soda cooking is replaced in the presence of AQ by the reaction sequence in Scheme 3, which involves a formation of units with a phenol group (3). The rapid



Scheme 1.



Scheme 2.



Scheme 3.

decrease in alcohol groups is presumably also associated with the reactions in Scheme 3, together with subsequent conversions of coniferyl alcohol units (9) involving losses of alcohol groups (12, 13). The fact that phenolic groups are liberated to a smaller extent during soda cooking favours the formation of units with glycerol side chains (2) (Scheme 1). Such units could be detected in the soda lignin preparations by ^1H NMR spectroscopy (see below).

Soda cooking results in a slow hydrolysis of methyl aryl ethers in lignin units (16). This is probably the reason for the minimum at δ 3.84 in Fig. 5. As could be expected, the corresponding peak is negligible in Fig. 4.

The spectrum of soda lignin from the 90-min cook exhibits a number of small peaks in the range of δ 3–7. Signals at δ 6.03 (H_α) and 4.70 (H_β) can be ascribed to residual β -O-4 structures (1) (17). Peaks at δ 4.22 (H_γ) and an inflection at 5.94 (H_α) can be attributed to signals from side chain protons in arylglycerol units (2) (18). The corresponding peaks are hardly discernible or absent in the spectra of soda/AQ lignins. Small peaks at δ 4.22 and 5.94 appear in the spec-

Table 1. Positions, intensities, and assignments of the major peaks in ^1H NMR spectra of acetylated alkali lignins from NaOH and NaOH/AQ cooks.

δ values (rel. intensities are given in parentheses)				Assignment
NaOH 90 min	NaOH 250 min	NaOH/AQ 90 min	NaOH/AQ 250 min	
2.04 (95)	2.04 (91)	2.04 (82)	2.04 (88)	CH_3COO -alkyl
2.30 (86)	2.29 (86)	2.29 (84)	2.28 (95)	CH_3COO -aryl
3.82 (100)	3.83 (100)	3.83 (100)	3.82 (100)	CH_3O -
6.95 (45)	6.94 (42)	6.93 (39)	6.90 (40)	Aromatic protons
		6.99 (39)		

Table 2. Positions of some prominent peaks in the difference spectra shown in Figs. 4 and 5. (Pairs of δ values are given in some cases when two peaks are located close to each other).

^1H NMR [NaOH/AQ (90 min)]- ^1H NMR [NaOH (90 min)] δ values		^1H NMR [NaOH (250 min)]- ^1H NMR [NaOH (90 min)] δ values	
maxima	minima	maxima	minima
2.26	2.00	2.20	2.01
2.35	2.30		2.30
3.94	3.82		3.84
	4.69		4.28
	5.53, 5.45		4.65, 4.70
	6.03		5.56
	6.95		6.05
6.69		6.69	7.01
	7.27 (CHCl_3)		7.27 (CHCl_3)

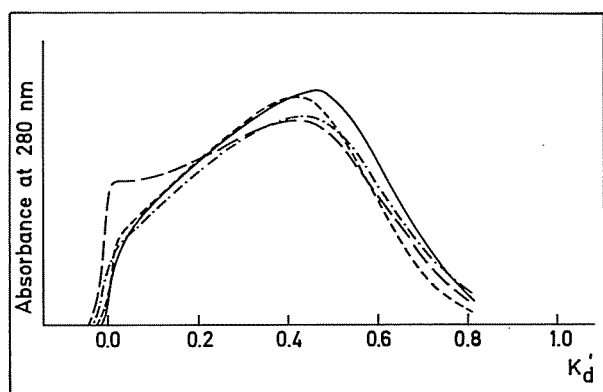


Fig. 1. GPC curves of lignins from 90-min NaOH (---), 90-min NaOH/AQ (—), 250-min NaOH (···), and 250-min NaOH/AQ (-·-·) cooks of spruce wood. $K_d = 1$ corresponds to the elution volume of acetone and $K_d = 0$ corresponds to the elution volume of a lignin carbohydrate complex from spruce, which was found to be excluded from the gel.

trum of lignin from the 250-min soda cook and suggest the presence of minor amounts of units with glycerol side chains. The occurrence of arylglycerol units (2) and residual β -O-4 structures (1) is in agreement with a prevalence of the reactions in Scheme 1 during soda cooking.

Structural differences reflected in the ^1H NMR spectra of soda and soda/AQ lignins are in line with what could be expected from the reactions in Schemes 1–3. However, the differences are

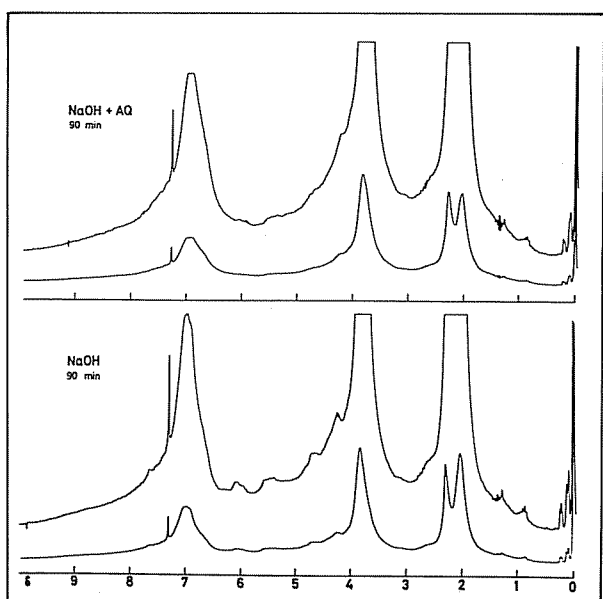


Fig. 2. ^1H NMR spectra of acetates of alkali lignins from 90 min cooks.

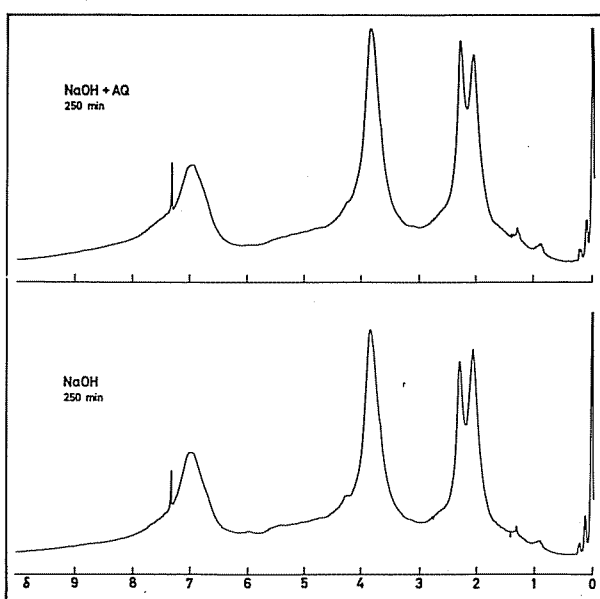


Fig. 3. ^1H NMR spectra of acetates of alkali lignins from 250 min cooks.

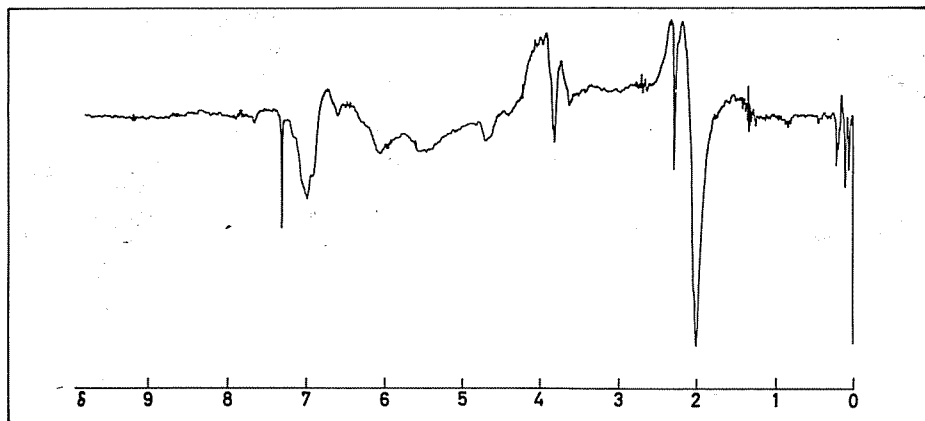


Fig. 4. Difference spectrum obtained by subtraction of the ^1H NMR spectrum of acetylated lignin from 90-min soda cooking (Fig. 2) from the corresponding spectrum of acetylated lignin from 90-min soda/AQ cooking (Fig. 2).

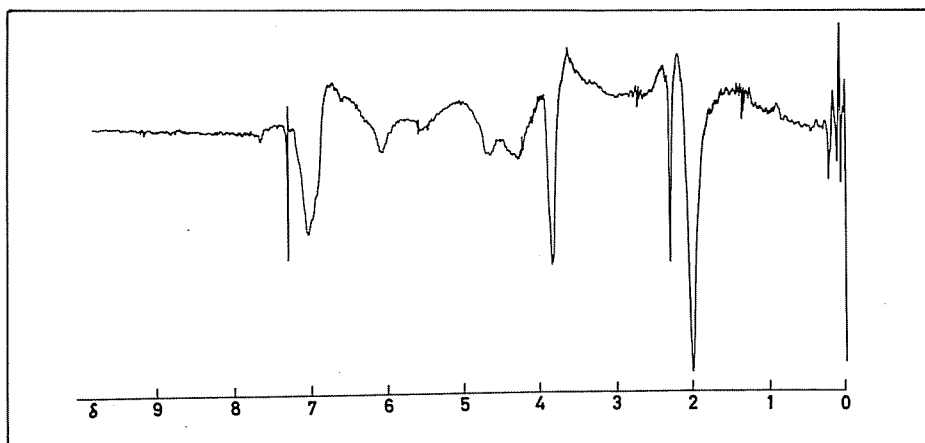


Fig. 5. Difference spectrum obtained by subtraction of the ^1H NMR spectrum of acetylated lignin from 90-min soda cooking (Fig. 2) from the corresponding spectrum of acetylated lignin from 250 min soda cooking (Fig. 3).

rather small and an overall impression from the spectra is a far-reaching structural similarity between soda and soda/AQ lignins. Since AQ dramatically accelerates delignifications larger structural differences could be expected in the final lignin products (e.g. lignins from 250-min cooks). The reason for this discrepancy is presently unknown.

EXPERIMENTAL

Analyses

^1H NMR spectra were recorded on a Bruker WH 270 instrument at 270 MHz, using deuteriochloroform as solvent (internal reference, TMS). IR spectra were recorded on a Perkin Elmer 197 instrument. Molecular weight distributions were examined by gel permeation chromatography (GPC) on Sephadex LH

60, using DMF-acetic acid (200:1) as eluent.

Cooking procedure

Wood meal from spruce (10 g was pulped with 70 ml of 1 molar NaOH (or 1 molar NaOH with anthraquinone (AQ) added in an amount corresponding to 0.5 % of the dry wood meal) at 170 °C for 90 min and 250 min according to the procedure described in ref. 11.

Isolation of lignins from cooking liquors

The pulp was filtered off from the cooking liquor and washed with 1 M NaOH (75 ml) and water (30 ml). The filtrate and washing were combined and acidified to pH 2 with 2 molar hydrochloric acid. The mixture was ex-

tracted twice with 480 ml of dioxane-chloroform (1:1) and, subsequently, 240 ml of dioxane-chloroform (1:1). The combined extracts were dried over Na_2SO_4 and the solvents removed by film evaporation. The residue was dissolved in 50 ml of chloroform-dioxane (1:1) and the solution dropped into magnetically stirred ether (1 litre). The precipitated lignin was centrifuged off, washed with 3×200 ml of ether, and dried *in vacuo* over P_2O_5 .

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REFERENCES

- Holton, H. H., Soda additive softwood pulping: a major new process, *Pulp Paper Can.* 78 (1977): T218.
- Löwendahl, L. and Samuelson, O., Carbohydrate stabilization during soda pulping with addition of anthraquinone, *Tappi* 61 (1978): 2, 19.
- Ruoho, K. and Sjöström, E., Improved stabilization of carbohydrates by the oxygen-quinone system, *Tappi* 61 (1978): 7, 88.
- Landucci, L. L., Quinones in alkaline pulping. Characterization of an anthrahydroquinone-quinone methide intermediate, *Tappi* 63 (1980): 7, 95.
- Fleming, B. I., Kubes, G. J., MacLeod, J. M. and Bolker, H. I., Soda pulping with anthraquinone, a mechanism, *Tappi* 61 (1978): 6, 43.
- Obst, J. R., Landucci, L. L. and Sanyer, N., Quinones in alkaline pulping. β

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- Ether cleavage of free phenolic units in lignin, *Tappi* 62 (1979): 1, 55.
7. *Aminoff, H., Brunow, G., Miksche, G. E. and Poppius, K.*. A mechanism for the delignifying effect of anthraquinone in soda pulping. *Paperi ja Puu — Papper o. Trä 61* (1979): 6—7, 441.
 8. *Gierer, J., Lindeberg, O. and Norén, I.*. Alkaline delignification in the presence of anthraquinone/anthrahydroquinone. *Holzforschung* 33 (1979): 213.
 9. *Farrington, A., Nelson, P. F. and Vanderhoek, N.*. The effect of anthraquinone on the alkaline degradation of lignin: Gel filtration studies. *Appita* 32 (1979): 300.
 10. *Kosiková, B., Janson, J., Pekkala, O. and Sjöfors, P.-E.*. The effect of anthraquinone on the reactivity of pulp components. *Paperi ja Puu — Papper o. Trä 62* (1980): 4a, 229.
 11. *Basta, J. and Samuelson, O.*, Sodium hydroxide cooking with addition of anthraquinone. *Svensk Papperstidn.* 81 (1978): 285.
 12. *Brunow, G. and Miksche, G. E.*. Some reactions of lignin in kraft and polysulfide pulping. *Appl. Polymer Symposia* 28 (1976): 1157.
 13. *Gierer, J.*, Chemical aspects of kraft pulping. *Wood Sci. Technol.* 14 (1980): 24.
 14. *Connors, W. I., Sarkanen, S. and McCarthy, J. L.*. Gel chromatography and association complexes of lignin. *Holzforschung* 34 (1980): 80.
 15. *Lundquist, K. and Kirk, T. K.*. Fractionation-purification of an industrial kraft lignin. *Tappi* 63 (1980): 1, 80.
 16. *Sarkanen, K. V., Chirkin, S. and Hrutfiord, B. F.*. Base-catalyzed hydrolysis of aromatic ether linkages in lignin. i. The rate of hydrolysis of methoxyl groups by sodium hydroxide. *Tappi* 46 (1963): 6, 375.
 17. *Lundqvist, K.*. NMR studies of lignins. 4. Investigation of spruce lignin by ¹H-NMR spectroscopy. *Acta Chem. Scand. B* 34 (1980): 21.
 18. *Lundqvist, K.*. NMR studies of lignins. ¹H NMR spectroscopic data for lignin model compounds. *Acta Chem. Scand. B* 33 (1979): 418.

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