

Lignin functionalization and the alkaline delignification rate

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ABSTRACT *The correlation between the amount of dissolved lignin and its content of phenolic hydroxyl groups has been studied in soda, soda-anthraquinone, kraft, and kraft-anthraquinone pulping of spruce wood. Intensive delignification begins after the introduction of a definite amount of phenolic hydroxyl groups into the lignin macromolecule. In the bulk delignification stages in the cooks studied, the rate of dissolution was directly proportional to the rate of the formation of free phenolic hydroxyl groups.*

KEYWORDS

Alkaline pulping
Bibliographies
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Delignification
Functional groups
Hydroxyl groups
Lignin
Phenol groups
Picea
Wood

"Functionalization" pertains to the chemical transformations that must occur for reactions to proceed. Here, in dealing with functionalization, we are concerned with the introduction of functional groups into the lignin macromolecule during the alkaline pulping of wood. By comparing the functional composition, molecular weight, and the quantities of separate types of linkages, or, in a more general sense, by comparing the structures of lignins obtained from wood, black liquors, and pulps, we are able to obtain a general picture of processes that proceed during the interaction of lignin with cooking reagents.

Our purpose in this work was to study the correlation between a quantity of dissolved lignin and its content of functional groups (phenolic, methoxyl, carbonyl) in soda, soda-AQ, kraft, and kraft-AQ pulpings of spruce chips.

Background

Despite a degree of contradiction in experimental data and differences of opinion regarding the mechanisms of lignin interaction with cooking reagents, most researchers acknowledge that the cleavage of alkyl aryl linkages along with the formation of phenolic hydroxyl groups plays a fundamental role in the process of fragmentation and dissolution of lignin. The extensive experimental material on the problems has been summarized in monographs (1-4); therefore, we shall briefly analyze the works of recent years.

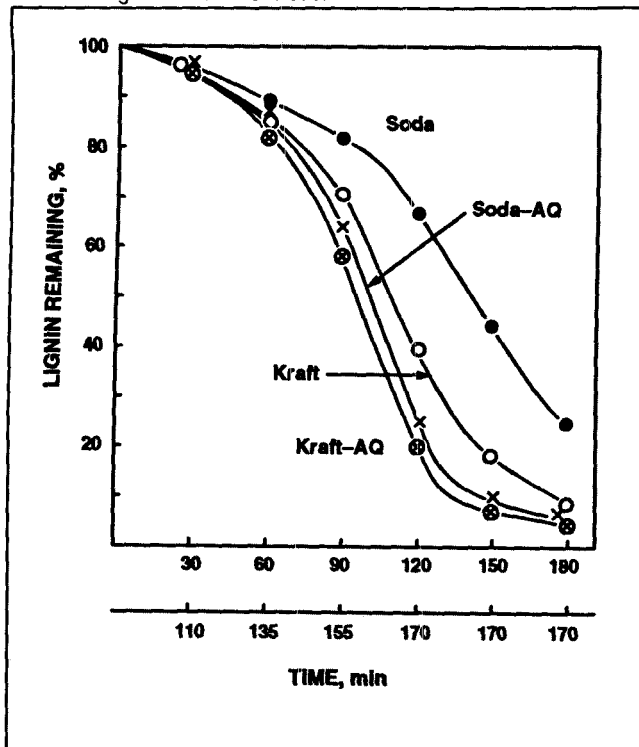
First, in a series of papers, Gellerstedt *et al.* presented the results of studies of lignin withdrawn from black liquors from various stages of pine kraft pulping (5-9). They established that the content of β -alkyl aryl ether linkages during cooking decreased, but the phenolic hydroxyl groups increased, both in dissolved and residual lignins. Toward the end

of the kraft cook, the relative quantity of biphenyl structures in the dissolved lignin increased.

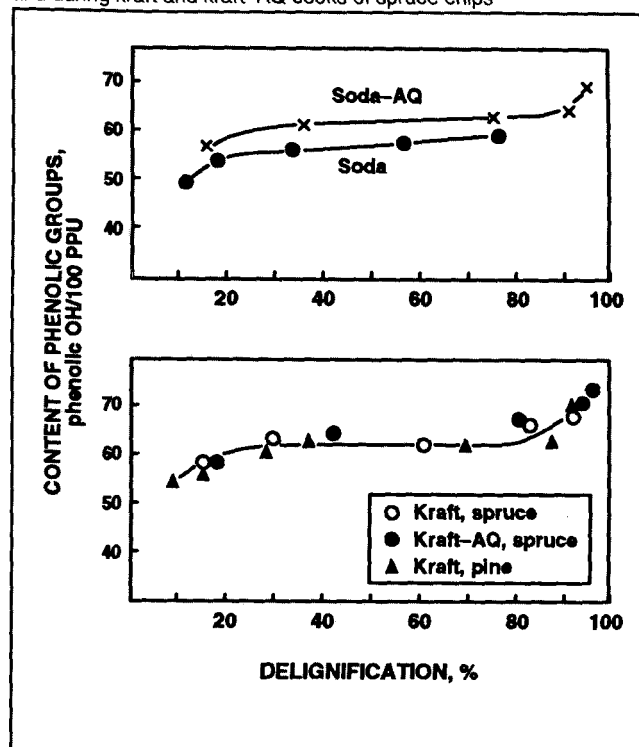
From an evaluation of the experimental data, including data from NMR spectroscopy, liquid chromatography, and elemental analysis, we found that it is not possible to identify any major changes in the chemical structure of the dissolved lignin that could be attributed to the differences in delignification rates at different stages of kraft cooking.

The development of pulp technology employing anthraquinone (AQ) gives an additional incentive for the research on changes of lignin structure under conditions of alkaline cooks. In the first works devoted to the chemistry of soda-AQ pulping, the functional composition of lignin isolated from liquors and its physico-chemical properties were compared (10). It was noted that anthraquinone accelerated the cleavage of β -O-4 alkyl aryl linkages, as reflected by the soda-AQ

1. Delignification curves of spruce chips during soda, soda-AQ, kraft, and kraft-AQ cooks. The percent of lignin remaining is based on the amount of lignin in the initial wood.



2. Relationship between the degree of delignification and the content of phenolic hydroxyl groups in lignin during soda and soda-AQ cooks and during kraft and kraft-AQ cooks of spruce chips



I. Content of phenolic hydroxyl groups in dissolved lignin

Cooking time, min	Phenolic groups per 100 PPU			
	Soda	Soda-AQ	Kraft	Kraft-AQ
60	48.9	56.6	57.4	58.9
90	54.0	61.0	63.8	65.7
120	56.0	62.6	62.4	68.4
150	57.2	64.2	67.7	71.3
180	59.0	69.1	69.8	74.1

II. Content of methoxyl groups in dissolved lignin

Cooking time, min	Methoxyl groups, %			
	Soda	Soda-AQ	Kraft	Kraft-AQ
60	12.31	11.38	11.62	12.69
90	12.96	12.35	12.69	13.08
120	13.12	12.61	12.80	13.16
150	12.96	12.29	13.08	12.88
180	13.25	12.86	13.28	12.97

lignin having a higher content of phenolic groups than soda lignin.

The data of Kosikova *et al.* (11) are at variance with this finding however. Comparing differential spectra of ionization, Kosikova and co-workers established that the content of phenolic groups in soda and soda-AQ lignin were virtually identical.

As spectral analysis (IR and NMR spectroscopy) showed, soda and soda-AQ lignins did not differ significantly in functional composition except for phenolic groups, which were more prevalent in the samples of soda-AQ lignin (12). Bogomolov *et al.* (13) found that the content of phenolic groups in lignins increased according to the following sequence: soda, soda-AQ,

and kraft. This finding is in keeping with the results of Funaoka and Abe (14).

The phenolic hydroxyl groups are important from the standpoint of lignin dissolution during alkaline cooks. As this analysis of literature has shown, the compounds that accelerate alkaline delignification (sodium sulfide and anthraquinone) promote the formation of these phenolic hydroxyl groups.

Although this correlation between lignin dissolution and the formation rates of phenolic hydroxyl groups is fundamentally important, it has not been quantitatively substantiated in a manner that is sufficiently rigorous. The matter of such a correlation

between lignin functionalization and alkaline delignification is important for the solution of a more general problem—the determination of a limit stage of cooking.

Results and discussion

Phenolic hydroxyl groups

Figure 1 shows the curves of delignification during soda, soda-AQ, kraft, and kraft-AQ cookings. These curves are shaped something like an "S", and they reflect initial, bulk, and final stages of the cook, which differ in the lignin dissolution rates. The exception is the curve for soda cooking, in which a final stage is not observed under selected conditions.

Soda and soda-AQ. The duration of the delignification stage depends on the method of cooking. Under the same conditions, a transition from the initial stage to the bulk stage of lignin dissolution is reached in 60–90 min (135–155°C) for soda-AQ cooking and in 90–120 min (155–170°C) for soda cooking (Fig. 1).

Table I presents the changes of phenolic group content in soda and soda-AQ lignins for the same periods of time. The content of phenolic groups grows constantly in lignin that has been dissolved during each type of pulping.

A comparison of data from Fig. 1 and Table I shows that a slight increase in the number of these functional groups is accompanied by a sharp increase in the delignification rate. During the initial part of soda-AQ cook (60 min), for example, lignin contains 56.6 phenolic groups per 100 phenylpropane units (PPU), whereas during the bulk phase (90–120 min), it contains 61.0–62.6 phenolic groups per 100 PPU.

This finding means that the intensive dissolution of lignin begins after the introduction of a certain amount of hydrophilic groups. From literature data, we know that the native lignin (in wood) already contains phenolic hydroxyl groups in small quantities. The lignin of softwood species contains 10–15 phenolic groups per 100 PPU depending on the location (in the middle lamella or cell wall) (8).

Consequently, the number of hydrophilic groups that need to be introduced for the bulk stage of delignification to begin is the difference between the content of phenolic groups in soda-AQ lignin at this stage of the cook and in native spruce lignin. (The mean for the soda-AQ lignin during the bulk phase taking place from 90 min to 120 min is 61.8 phenolic groups per 100 PPU, as Table I shows. The content of phenolic groups in native spruce lignin is 12.5 phenolic groups per 100 PPU. The difference is 49.3 phenolic groups per 100 PPU, and this is the quantity that must be introduced for bulk delignification to begin.) In fact, a specific but undetermined number of phenolic groups corresponds to the functionalization of each second phenylpropane unit of the lignin macromolecule.

As for the content of phenolic groups, soda lignin “lags” the soda-AQ lignin during the whole process of cooking and “acquires” the necessary number of functional groups in approximately 180 min (Table I). In this sense, the difference in the rates of soda and soda-AQ cooks is the difference in the functionalization rates of lignin in each of them (Fig. 1).

Therefore, the degree of lignin functionalization correlates with the degree of wood delignification. This result is presented in the upper graph in Fig. 2, which shows that the high degree of wood delignification (80% or more) can be reached only when the content of phenolic groups in lignin is not less than 61–62 per 100 PPU.

The curves in this graph show that the soda-AQ lignin contains more hydrophilic groups than soda lignin under the same degree of delignification. Consequently, the anthraquinone additive increases both the rate and the completeness of the cleavage of alkyl aryl linkages. In other words, the anthraquinone takes part in the reactions with the linkages that are not cleaved completely when anthraquinone is not available. In regard to the mechanism of lignin reactions with sodium hydroxide and anthraquinone in soda pulping, we should note that the formation of alkaline-resistant enol ethers is a competitive reaction that proceeds along with the cleavage of β -ether linkages in phenolic lignin structures (10).

Kraft and kraft-AQ. The same correlation is observed in the course of kraft cooks as well, as shown in the lower graph in Fig. 2, along with Fig. 1 and Table I. Here, the stage of bulk delignification also begins after the destruction of a certain quantity of interunit lignin linkages that results in the formation of the equivalent quantity of phenolic groups. This quantity is 50 per 100 PPU.

The kraft cook lags the kraft-AQ cook, but it lags less than the soda cook lags the soda-AQ cook, as Fig. 1 and Table I show. The efficiency of β -ether cleavage in the phenolic lignin structures decreases under the influence of cooking reagents according to the following sequence: AQ, Na₂S, and NaOH (15).

The curves are virtually identical for the kraft and kraft-AQ cooks of spruce (Fig. 2). The corresponding points of the kraft cook of pine also

belong to the same curve. [The delignification percentage is the percentage of lignin remaining subtracted from 100%. The locations of points were determined from published data (5, 7).] Therefore, these relationships are of a sufficiently general character for softwood at least.

This lower graph in Fig. 2 also shows that phenolic groups must form beyond a certain quantity for delignification to proceed to a high degree. A horizontal band drawn at 63–65 phenolic hydroxyl groups per 100 PPU would correspond to the bulk delignification. Consequently, this cooking stage proceeds within a narrow interval of values for phenolic group contents.

Functionalization and lignin structure. Why are these values about 64 phenolic hydroxyl groups per 100 PPU, and why are they constant and invariable? Since the main source of the formation of new phenolic groups under alkaline cooking conditions is the cleavage of α - and β -alkyl aryl ether linkages in lignin, we have to analyze data published on the quantity of these linkages. Different researchers who have evaluated the phenolic groups content give the following values for the softwood lignins (per 100 PPU):

- 55 groups (16)
- 55–59 groups (17)
- 61 groups (18, p. 282)
- 63 groups (2, p. 138).

From these data, the maximum value of phenolic groups formed from the destruction of α - and β -alkyl aryl ether linkages should not exceed 63 phenolic hydroxyl groups per 100 PPU.

Considering the quantity of native lignin phenolic groups, we can assume that a small part of alkyl aryl ether linkages $[63 - (64 - 12.5) = 11.5 \text{ per } 100 \text{ PPU, or approximately } 19\%]$ are resistant to the action of cooking reagents and are retained during the whole process of pulping.

Our second question forces us to return to the fundamental problem of lignin structure. The alternative points of view with respect to the size of lignin macromolecule are that the structure is based on:

1. An infinite three-dimensional network
2. A branched molecule of relatively small size (3).

Our results agree more closely with the hypothesis of a branched molecule, especially if we take into account that both the content of phenolic groups (Fig. 2) and the molecular weight distribution of lignin (5, 19) are changed slightly during the bulk delignification. In fact, this hypothesis makes it possible to regard delignification as the process of the functionalization and subsequent dissolution of the lignin macromolecule, for which the molecular weight distribution has been predetermined by the processes in wood cells.

Relationship between the rates of phenolic groups formation and lignin dissolution

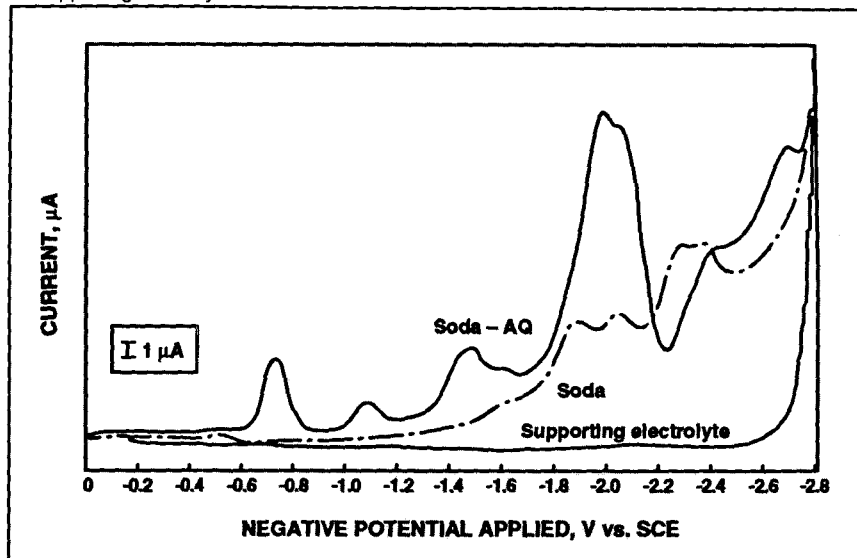
The dependences presented in Figs. 1 and 2 are integral. To find out how the rates of functionalization and wood delignification correlate, we compared the changes of the values within the identified period of time. During kraft bulk delignification, the rate of lignin dissolution and the rate of cleavage of β -aryl ether linkages are almost equal (20). Therefore, the relationship between the average number of phenolic groups formed and the quantity of lignin dissolved in a given period of time is expected to be constant.

In fact, during the bulk delignification stage of pulping, as Fig. 3 shows, the coordinates for the rate of formation of phenolic hydroxyl groups and the rate at which lignin dissolves fall along a straight line. In other words, the greater the rate of lignin functionalization, the greater the rate of delignification.

Note that the points of this line conform to the points of delignification curves (Fig. 1) with ordinate values of 120 min and 150 min for the soda cook and 90 min and 120 min for all the others. The points corresponding to the bulk delignification of pine at 90 min and 125 min also belong to this line. [The location of the points for pine were determined from published data (5, 7).]

The slope of the straight line was calculated by the method of least squares and was found to be equal to 3.7 mmol/g; the correlation coefficient

4. Polarograms of soda-AQ and soda lignins in DMSO with tetrabutylammonium perchlorate as supporting electrolyte



was 0.99. In other words, the dissolution of 1 g of lignin requires the formation of 3.7 mmol phenolic groups, and the rate difference in the cooks is the difference of rates for them to reach this value.

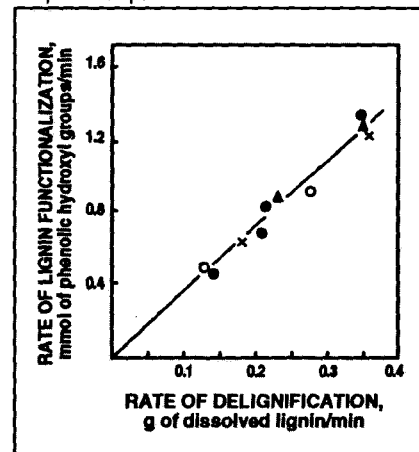
Methoxyl groups

The content of phenolic groups in lignin begins to increase appreciably at high degrees of delignification (more than 80%). In a kraft-AQ cook, the content reaches the value of 74.1 phenolic hydroxyl groups per 100 PPU, which is approximately 10 phenolic groups more than it is on a linear plot (Fig. 2, lower graph).

At first, the cause for this excess appears to be the demethylation of dissolved lignin resulting in the formation of the pyrocatechol structure. However, this hypothesis is not supported by the data in Table II. Toward the end of the cook, the noticeable decrease of methoxyl groups content in the dissolved lignins is not observed.

In search of another source of formation of phenolic groups that is not connected with the destruction of alkyl aryl ether linkages, we paid attention to the data of Gellerstedt and Gustafsson (9). According to these researchers, the content of biphenyl structures with free phenolic groups in the dissolved lignin increases toward the end of the cook. Therefore, if each hundred phenylpropane units at the bulk delignification stage

3. Relationship between the rate of lignin dissolution and the rate of phenolic hydroxyl groups formation in the bulk delignification state of soda, soda-AQ, kraft, and kraft-AQ cooks of spruce chips



contains about 64 phenolic groups, then dissolved toward the end of the cook are those lignin fractions in which there is a phenolic group in each phenylpropane unit. This process is believed to be responsible for the change of the slope of the straight portion of the curve presented in the lower graph in Fig. 2.

Carbonyl groups

Our data have shown that the characteristics of changes in the functional composition of lignin during the soda-AQ and kraft cooks are roughly identical. The changes are in accord with what is known about the mech-

anism of the action of anthraquinone (15), which accelerates the cleavage β -alkyl aryl linkages in the phenolic structures of lignin macromolecule in a manner similar to that of sodium sulfide.

At the same time, Gratzl and co-workers (21-23) found the specific influence of anthraquinone to consist of lignin oxidation. In particular, they found that soda-AQ black liquors differ from black liquors from soda pulping without anthraquinone by having a larger content of vanillin and acetoquaiacone, and the soda-AQ lignin contains more α -carbonyl groups.

The introduction of α -carbonyl groups into the lignin macromolecule is of interest not only because the phenomenon helps in interpreting the action of anthraquinone but also because the introduction of these groups increases the acidity of phenolic groups since the α -carbonyl groups attract electrons. For example, the pK_a of vanillin is 7.40, and that of vanillic alcohol is 9.78 (24). The increase in phenolic groups acidity contributes in turn to the increase of lignin dissolubility. The experimental validation of this possibility is the subject of a separate study; here, we wish to show the specific influence of anthraquinone on the functional composition of lignin.

Figure 4 presents pulse differential polarograms of soda and soda-AQ lignins. (The lignins were from black liquors of cooks carried out for 180 min, and the lignin concentration was 5 mg/mL.) On the basis of polarographic data concerning redox properties of anthraquinone under the same conditions (25), the peak with a potential of -0.73 V can be attributed to the reduction of anthraquinone admixture precipitated together with lignin when black liquors are acidified. The peaks within the range of potentials from -1.0 V to -2.0 V correspond to the reduction of different types of lignin carbonyl groups, with the peaks at the potentials of -1.98 V and -2.06 V belonging to α -carbonyl groups (26-29). The study of the other peaks is in progress.

When comparing the polarograms shown in Fig. 4, one can notice both quantitative and qualitative differences. (Similar differences are observed when kraft and kraft-AQ lignin voltammograms are compared.) The

soda-AQ lignin contains groups with potentials equal to -1.08 V, -1.46 V, -1.98 V, -2.07 V, approximately -2.40 V, and -2.67 V. The corresponding values for soda lignin are -1.87 V, -2.04 V, -2.27 V, and -2.34 V. In other words, several types of reducible functional groups typical for soda-AQ lignin are not available in the soda lignin. On the other hand, the soda lignin also contains α -carbonyl groups, though their quantity is considerably less.

This means that the influence of anthraquinone is exerted in two ways in the alkaline cook. First, anthraquinone initiates reactions that proceed in its presence only (lignin oxidation reactions). Second, it causes an increase in the rates of the processes that proceed anyway during the alkaline cook even without the catalyst, but at the lower rates (cleavage of alkyl aryl linkages of lignin).

Concerning the influence of anthraquinone on the cook, there is a distinct correlation between its redox properties and the acceleration of soda pulping. Over a wide range of anthraquinone derivatives, the catalytic effect increases with the increase of the constant of anthrasemiquinone formation (30-31).

Conclusions

Under the conditions of alkaline cooking, the intensive dissolution of lignin begins after the introduction of a certain amount of phenolic hydroxyl groups. The quantity corresponds to the functionalization of virtually every second phenylpropane unit. There is a relationship between the degree of lignin functionalization and the degree of wood delignification. A high degree of delignification can be reached only when the content of phenolic groups in lignin is equal to more than 62 per 100 PPU.

At the bulk delignification stage of pulpings under study, the rate of lignin dissolution is directly proportional to the rate of formation of phenolic groups. To dissolve 1 g of lignin, the formation of the 3.7 mmol phenolic groups is necessary. The difference observed in delignification rates of alkaline types of cooks is the difference in rates to achieve this value.

In going from bulk delignification to the final stage of a soda-AQ, kraft,

or kraft-AQ cook, an appreciable increase of content of phenolic groups takes place. This increase is not adequately explained in terms of the process of lignin demethylation only.

The action of anthraquinone on alkaline pulping consists of both the influence on the reactions already known (the reactions of lignin oxidation by anthraquinone), and the initiation of reactions whose role is to be found out (the cleavage of alkyl aryl linkages of lignin by NaOH and Na_2S).

Delignification can be regarded as the process of functionalization and the subsequent dissolution of lignin, whose molecular weight distribution has been formed and predetermined by its development in wood cell walls.

Experimental procedures

All cooks of spruce chips (37 g of o.d. wood) were carried out in a series of rotating autoclaves. Every 30 min from the beginning of the cook at 80°C, a couple of autoclave samples, with and without anthraquinone, were withdrawn from the glycerin bath and were quickly cooled. The liquor-wood ratio was 4:1. The temperature was increased from 80°C to 170° for 120 min, and the temperature was held at 170°C for 60 min.

The active alkali charge for the soda and soda-AQ cooks was 18% (as Na_2O). For the kraft and kraft-AQ cooks, it was 15% (25% sulfidity). The quantity of anthraquinone added was 1% on o.d. wood.

Chips were isolated from liquor, were washed with distilled water for several days to achieve a neutral reaction of washing waters, were dried, and were defibrated. The defibrated chips were divided into fractions, and we used the fraction that had been passed through a sieve with holes 0.5 mm in diameter and retained on the sieve with holes 0.25 mm in diameter.

This chip fraction was extracted with alcohol-benzol mixture (1:2) for 7 h. The pulps obtained from final cooking stages were extracted by a similar way.

Klason lignin was determined by the method described by Obolenskaya *et al.* (32). Lignin was isolated by a process of acidification of the black liquors with diluted sulfuric acid to pH 2.0, followed by the sample being

centrifuged, washed repeatedly with water, and dried by P_2O_5 in vacuum.

The free phenolic hydroxyl groups were quantitatively determined by Menzon's method (33) by means of gas chromatography determination of *N*-acetylpyrrolidine, the product of aminolysis of preliminary acetylated lignin samples. The conditions of determination were as follows. The gas chromatograph was a "Crom-5" model (Liaboratorni PRISTROJE, Czechoslovakia), equipped with a flame ionization detector, using a glass column (1.5 m $\times$ 3 mm inside diameter) with 5% silicon OV-17 (stationary phase) on Chromaton-N-AW (0.125–0.160 mm) (solid support) (Chemapol, Czechoslovakia). The rate of carrier gas (He) was 30 mL/min, and the column temperature was 142°C.

The relative standard deviation of phenolic groups determinations (3–5 runs) was 2.76%. For the soda-AQ and kraft-AQ lignins, the anthraquinone content was determined by gas chromatography under the same conditions except for the temperature of analysis, which was 250°C, and an adequate correction was introduced into analytical data. The results are presented in Table III.

The content of methoxyl groups was determined by the modified method of Zeisel (34).

Because of a low content of lignin and its poor precipitation from liquors of cooks that were carried out during 30 min, the determination of functional groups was not performed on these 30-min samples.

Pulse differential polarograms were recorded by a PA-2 polarograph (Liaboratorni PRISTROJE, Czechoslovakia) in DMSO (dimethyl sulfoxide), containing 0.1 mole/L tetrabutylammonium perchlorate as supporting electrolyte, at $25 \pm 0.5^\circ\text{C}$. The measurements were performed in a vessel with a three-electrode arrangement with a saturated calomel electrode (SCE) as the reference electrode at the scan rate of 5 mV/s. The dropping mercury electrode had the controlled drop life of 1 s. A platinum electrode was used as an auxiliary electrode. Oxygen was removed by bubbling argon through the solution for 10 min. □

Literature cited

1. Wood cell wall and its changes under chemical action (in Russian) (V. N. Sergeeva, Ed.), Zinatne, Riga, 1972.
2. Lignins: occurrence, formation, structure, and reactions (in Russian) (K. V. Sarkaenen and C. H. Ludwig, Eds.), Lasnaya Promyshlennost, Moscow, 1975.
3. Shorygina, N. N., Reznikov, V. M., and Elkin, V. V., Reactivity of lignin (in Russian), Nauka, Moscow, 1976.
4. Nikitin, V. M., Theoretical basis of delignification, (in Russian), Lesnaya Promyshlennost, Moscow, 1981.
5. Gellerstedt, G. and Lindfors, E.-L., *Holzforschung* 38: 151(1984).
6. Gellerstedt, G., Lindfors, E.-L., Lapiere, C., and Monties, B., *Svensk Papperstid.* 87(9): R61(1984).
7. Robert, D. R., Bardet, M., Gellerstedt, G., and Lindfors, E.-L., *J. Wood Chem. Technol.* 4(3): 239(1984).
8. Gellerstedt, G. and Lindfors, E.-L., *Svensk Papperstid.* 87(15): R115(1984).
9. Gellerstedt, G. and Gustafsson, K., *J. Wood Chem. Technol.* 7(1): 65(1987).
10. Obst, J. R., Landucci, L. L., and Sanyer, N., *Tappi* 62(1): 55(1979).
11. Kosikova, B., Janson, J., Pekkala, O., and Sagfors, P.-E., *Paperi Puu* 62(4a): 229(1980).
12. Lundquist, K., Simonson, R., and Tingsvik, K., *Paperi Puu* 63(11): 709(1981).
13. Bogomolov, B. D., Gorbunova, O. F., Pyvovarova, V. A., and Butsalenko, V. S., *Khimiya Drevesiny* N 3, 27(1981).
14. Funakoka, M. and Abe, I., *Holzforschung* 39: 223(1985).
15. Shevchenko, S. M. and Deineko, I. P., *Khimiya Drevesiny* N 6, 3(1983).
16. Glasser, W. G., and Glasser, H. R., *Paperi Puu* 63(2): 71(1981).
17. Wegener, G. and Fengel, D., *Das Papier* 37: V22(1983).
18. Grushnikov, O. P. and Elkin, V. V., Achievements and problems of lignin chemistry (in Russian), Nauka, Moscow, 1973.
19. Evstigneyev, E. I., Rusakov, A. E., Shalimova, T. V., and Zacharov, V. I., *Khimiya Drevesiny* N 2, 51(1987).
20. Ljunggren, S., *Svensk Papperstid.* 83(13): 363(1980).
21. Gratzl, J. S., EUCEPA Symposium Proceedings, Helsinki, Finland, Vol. 2, 1980, p. 121.
22. Hise, R. G., Chen, C.-L., and Gratzl, J. S., 1983 International Symposium on Wood and Pulping Chemistry Proceedings, Vol. 2, Japan Paper Association, Tsukuba, Japan, p. 166.
23. Venica, A. D., Chen, C.-L., and Gratzl, J. S., 1989 International Symposium on Wood and Pulping Chemistry Proceedings, TAPPI PRESS, Atlanta, p. 263.
24. Ermakova, M. I., Kiryushina, M. F., and Zarubin, M. Ya., *Khimiya Drevesiny* N 5, 23(1984).
25. Evstigneyev, E. I., Shevchenko, S. M., *Khimiya Drevesiny* N5, 102(1990).

III. Anthraquinone content in dissolved lignin

Cooking time, min	Dissolved lignins, %	
	Soda-AQ	Kraft-AQ
60	7.06	11.43
90	2.85	8.04
120	0.55	2.38
150	0.47	1.30
180	0.25	0.82

26. Evstigneyev, E. I., Bronov, L. V., and Nikitin, V. M., *Lesnoy Zhurnal* N 5, 114(1978).
27. Evstigneyev, E. I., Bronov, L. V., and Nikitin, V. M., *Lesnoy Zhurnal* N 6, 95(1978).
28. Evstigneyev, E. I., Bronov, L. V., and Nikitin, V. M., *Khimiya Drevesiny* N 6, 71(1979).
29. Evstigneyev, E. I., *J. Appl. Chem. (USSR)* 54(2): 265(1981).
30. Evstigneyev, R. I., *Khimiya Drevesiny* N 5, 97(1984).
31. Evstigneyev, R. I. and Shalimova, T. V., *Khimiya Drevesiny* N 1, 50(1985).
32. Obolenskaya, A. V., Shchegolev, V. P., Akim, G. L., Akim, E. L., Kossovich, N. L., and Emelyanova, I. Z., Practical work of wood and pulp chemistry (in Russian), Lesnaya Promyshlennost, Moscow, 1965.
33. Mansson, P., *Holzforschung* 37: 143(1983).
34. Zakis, G. F., Functional analysis of lignin and its derivatives (in Russian), Zinatne, Riga, 1987.

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