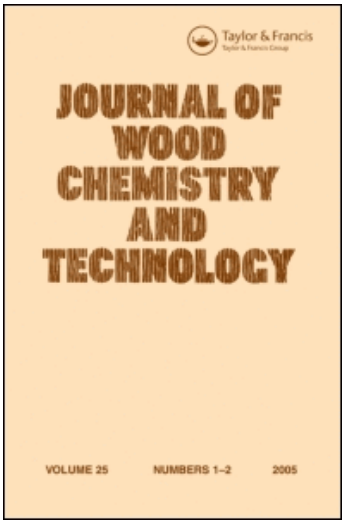

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CHARGE DENSITY OF LIGNIN SAMPLES FROM KRAFT COOKING OF BIRCH WOOD

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ABSTRACT

Black liquor, isolated dissolved lignin and residual lignin samples corresponding to different cooking times were obtained from flow-through kraft cooking of birch wood. Dissolved lignin was isolated from black liquor by acid precipitation and residual lignin was isolated from pulp by acid-dioxane extraction. The average mobility (μ_{av}) of the lignin-containing samples was determined by capillary zone electrophoresis. The lignin samples have a broad mobility distribution that reflects the charge-to-size ratio of the molecules. At pH 12, *i.e.* when lignin is completely dissociated, the μ_{av} of each type of sample increases during the cook, reflecting an increase in charge density of the lignin. For samples corresponding to the initial and beginning of the bulk delignification phases, the μ_{av} decreases in the order dissolved lignin>black liquor>residual lignin. The lower charge density of black liquor compared to dissolved lignin is proposed to be caused by associations between lignin and carbohydrate fragments dissolved in the black liquor. As from the middle of the bulk delignification phase, the μ_{av} of the three series of samples is quite similar. The decrease in mobility on lowering the pH is an indication of the degree of dissociation of the

lignin phenol groups. At pH 10, *i.e.* about the pK_a of lignin, the μ_{av} of black liquor is highest throughout the cook. The relative order of μ_{av} is then black liquor>dissolved lignin≈residual lignin.

INTRODUCTION

In kraft pulping, lignin is removed and individual fibres are liberated. Birch wood and pine wood differ in chemical composition and behave differently during pulping with respect to when defibration occurs, rate of delignification and amount of residual lignin. Birch wood is defibrated when the kappa number of the pulp is 20-25.[1] Although the kappa number is commonly used to describe the degree of delignification, recent studies have shown that as much as 60-80% of the kappa number of unbleached birch kraft pulps is due to non-lignin structures.[2] Usually, the cook is stopped at a kappa number of about 18 since further cooking degrades the pulp and leads to unacceptable loss of yield with only a slight decrease in kappa number.[1,3] The rate of delignification during cooking is higher for birch wood than for pine wood.[4] Although a number of studies have been performed, the reasons for the differences in behaviour between pine and birch are not completely clear. It has been shown that the secondary wall of fibre is delignified faster than in the middle lamella region and in vessels.[5] The lignin in the compound middle lamella of birch wood has been reported to be highly condensed and rich in guaiacyl units.[6] In addition, the ratio syringyl:guaiacyl lignin is higher in the secondary wall than in the middle lamella region of the fibre.[5] Because of this, the rate of delignification was attributed to the chemical structure rather than the availability of the lignin. The faster degradation of syringyl units has also been confirmed by model studies.[7] On the basis of the rate of lignin dissolution, kraft cooking is divided into three phases.[8] From studies on model compounds with guaiacyl units, possible chemical reactions have been correlated to the different delignification phases.[9] The rapid initial delignification phase is diffusion-controlled and includes fragmentation of α- and β-aryl ether bonds in phenolic lignin units. During the bulk delignification phase when the

main part of the lignin is removed, non-phenolic α- and β-aryl ether structures are also degraded.[10] The lower delignification rate during the residual phase is ascribed to cleavage of carbon-carbon bonds. During this phase, condensation reactions may also take place, due to the lower concentration of hydroxide ions.[9]

The phenol groups generated by the cleavage of aryl ether bonds contribute to solubilising lignin fragments into the black liquor. In addition it has been shown that removal of xylan from birch fibres increases the overall rate of delignification, probably by increasing the pore size.[11]

The concentration of phenol groups as well as molecular size of lignin may thus influence the dissolution of lignin fragments into the black liquor. The relation between charged groups and molecular size *i.e.* the charge density, can be studied by capillary zone electrophoresis (CZE). The separation is based on differences in electrophoretic mobility (μ) according to

$$\mu = q/ 6\pi\eta r \qquad [1]$$

where the charge, q, is equal to the charge of an electron times the valence number of the solute molecule. The denominator describes the friction of a molecule with a spherical geometry obeying Stokes law. η is the viscosity of the electrolyte and r is the hydrodynamic radius of the solute.[12] Since the electrophoresis is performed in a free solution, *i.e.* in absence of a stationary phase, it is possible to characterise underivatized isolated lignin samples as well as black liquor using an alkaline electrolyte. Lignin samples have a broad mobility, *i.e.* charge density, distribution. In a previous study it was shown that the mobility distribution of dissolved pine wood kraft lignin gradually shifts towards a higher mobility range during the cook.[13] To make it easier to compare different types of lignin samples, the evaluation was improved by calculating the average mobility (μ_{av}) of the distributions.[14]

In the present study the charge density of birch lignin samples corresponding to different degrees of delignification has been determined by CZE. The results are compared to the charge density of pine lignin from a similar study.

TABLE 1.
Cooking Times, Sample Designation and Kappa Numbers of the Corresponding Pulps. Samples from a Flow-through Kraft Cook of Birch.

Cooking time (min)	Black liquor	Isolated lignin		Kappa number of pulps corresponding to		
		dissolved	residual	Hb	Hd	Hr
30-60	Hb 45	Hd 45				
60-90	Hb 75	Hd 75				
90-120	Hb 105	Hd 105				
120-150	Hb 135	Hd 135				
150-180	Hb 165	Hd 165				
180-210	Hb 195	Hd 195		9.3	9.2	
90			Hr 90			84
150			Hr 150			13
210			Hr 210			9.2

RESULTS AND DISCUSSION

Five flow-through kraft cooks of birch were performed: one to collect black liquor (Hb) for direct characterisation by CZE, one to isolate dissolved lignin from black liquor (Hd) and three to isolate residual lignin from pulp (Hr).

Sample designation and corresponding cooking times and kappa numbers of pulps obtained from the cooks are summarised in Table 1. The transition point between initial and bulk delignification for the cooks in this study is assumed to occur during the 60-90 min interval. The samples obtained between 90-180 min roughly correspond to the bulk delignification phase, and between 180-210 min they correspond to the residual delignification phase. It is noteworthy that the kappa number was reduced to about 9, at a yield of about 47% and viscosity of about 1250 mL/g. The low kappa number is probably due to the flow-through technique, in which dissolved components are continuously removed.

Isolation of Lignin from Black Liquor and Pulp

About 70% of the lignin removed from the pulp was recovered from the black liquor. The residual lignin samples were isolated from the pulps by acid dioxane extraction. This method has been applied to softwood kraft pulps with various lignin contents[15,16] but has previously only been used for isolation of residual lignin from a completed birch kraft cook.[17] The efficiency of the acid dioxane isolation increased with increasing degree of delignification. 65% of the pulp lignin from the Hr 90-pulp and 61% from the Hr 150-pulp were isolated, whereas more than 100% was obtained from the Hr 210-pulp. This shows the difficulties in estimating the lignin content of pulps containing low amounts of lignin by a gravimetric method; the Hr 210 contains less than 0.1% Klason lignin. The carbohydrate content of the Hr 90-sample was 1.3%. The purity with respect to lignin for this sample is also supported by a high methoxyl content,[18] 17.3 OMe/C_{100}. The content of carbohydrates could not be determined for the other Hr samples, due to the small amounts available.

Studies on milled wood lignin have shown that aryl ether bonds are the main cleavage reaction sites during acidolysis.[19] Milled birch wood lignin is also more sensitive to acidolysis than softwood, possibly due to the presence of syringyl units.[20] However, the pulps in the present study were subjected to 0.1 M HCl-dioxane for 2 h whereas 4 h treatment time with 0.2 M HCl-dioxane is used in acidolysis. The α-aryl ether bonds are probably completely cleaved during the milder acidic treatment, whereas the cleavage of β-aryl ether bonds may contribute less to fragmentation. The extent of β-aryl ether cleavage in pulp lignin subjected to similar acid extraction conditions as used in this study has so far not been reported.

Charged Groups and Relative Molecular Weight of Isolated Samples

According to equation 1, both concentration of charged groups and molecular size are of importance when determining the mobility, *i.e.* charge

TABLE 2
Concentration of Phenol and Carboxyl Groups and Number-Average Molecular Weight (M_n) of Isolated Lignin Samples from Kraft Cooking of Birch Wood. Sample Designation According to Table 1.

Sample	Phenol groups	Carboxyl groups	M_n[1]
	mmol/g	mmol/g	(relative to PS)
Hd 45	1.7	0.39	760
Hd 75	2.2	0.41	820
Hd 105	2.3	0.39	830
Hd 135	2.6	0.18	910
Hd 165	2.8	0.16	970
Hd 195	2.5	n.d.[2]	1200
Hr 90	0.86	<0.10	59000
Hr 150	2.3	<0.10	12000
Hr 210	2.5	n.d.[2]	5300

[1] acetylated samples. [2] = not determined.

density of a molecule. The concentrations of phenol and carboxyl groups and the relative molecular weight of the isolated kraft lignin samples are shown in Table 2.

Due to the aryl-ether cleaving reactions during kraft cooking, the concentration of phenol groups in the dissolved lignin samples (Hd) increases until a maximum is reached at the end of the bulk delignification. The lower concentration of phenol groups observed for the sample that corresponds to the end of the cook indicates that these reactions become less frequent. Initially the residual lignin samples (Hr) have lower concentrations of phenol groups compared to the lignin fragments dissolved in the black liquor. As the cook proceeds the difference in phenol concentration between dissolved and residual lignin samples converge and at the end of the cook the concentration is the same.

The concentration of carboxyl groups in all of the analysed samples is very low in comparison with the concentration of phenol groups. This is in accordance

with the non-oxidative conditions prevailing during kraft cooking. Measurable quantities of carboxyl groups are only found in the dissolved lignin samples. The concentration is about constant until the beginning of the bulk delignification phase after which the concentration is about halved. The decrease in carboxyl groups seems to occur when the final temperature is reached, and may be due to decarboxylation. Carboxyl groups in lignin are probably aliphatic in nature.[21,22] 2-guaiacyl acetic acid and 3-guaiacyl propionic acid have been identified in black liquor.[23] A certain contribution from carboxyl groups in carbohydrates is also possible, since guaiacyl compounds substituted with an aliphatic chain with α-hydroxy carboxyl groups also have been identified in black liquor.[24,25] It is possible that similar structures exist in the polymeric lignin fragments as well.

The number average molecular weight (M_n) of acetylated samples was determined relative to polystyrene. Thus the figures can only be used to indicate differences in size between the samples. The M_n of the isolated samples reveal a continuous increase of the size of the dissolved lignin fragments whereas the opposite is true for the lignin remaining in the pulp. All of the residual lignin samples have a higher M_n than the dissolved lignin samples, but the difference becomes smaller at the end of the cook. The high M_n value of the Hr 90-sample may partly be due to condensation reactions between reactive lignin structures during the acid isolation procedure. Acid dioxane extraction as used in this study, has not previously been reported for isolation of residual lignin from highly lignified hardwood pulps. No evidence for condensation has been found for residual lignin isolated from birch kraft pulps obtained at the end of the cook.[17]

Charge Density Distribution at pH 12

In capillary zone electrophoresis (CZE), anions migrate towards the anode but are swept to the cathode by the stronger electroendoosmotic flow (EOF), caused by the migration of hydrated cations adsorbed onto the negatively charged

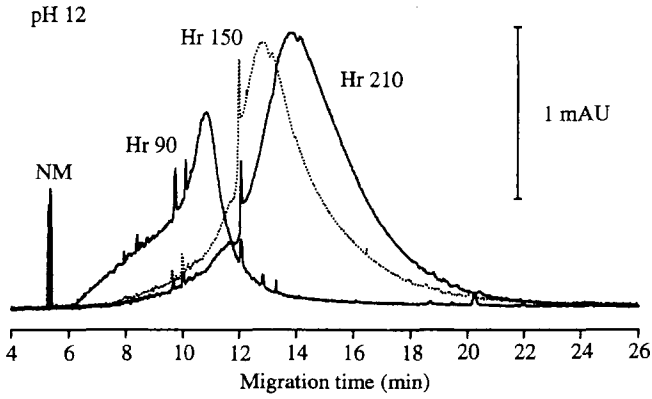

FIGURE 1. Charge density distribution of residual lignin isolated from pulp. The samples correspond to the beginning (Hr 90), the middle (Hr 150) and the end (Hr 210) of a kraft cook of birch. Capillary, 0.72 m x 50 μm I.D., applied voltage 20 kV; electrolyte, 0.1 M glycine-sodium hydroxide, pH 12; temperature 30 °C; detection 254 nm.

silica surface. The magnitude of EOF is measured by adding a neutral molecule (NM) to the samples. An increase in migration time of the lignin samples in this study reflects an increase in the mobility. In general, the peak widths of anions increase with migration time because of the decrease in observed velocity. All of the electropherograms in this study were corrected for this as previously described.[14]

The phenol groups in softwood lignins are extensively dissociated at pH 12.[26-28] This may also be true for birch wood kraft lignins since guaiacyl and syringyl monomers with the same side chain have nearly the same pK_a-value.[29] Electropherograms of isolated residual and dissolved lignin samples corresponding to different parts of the cook are shown in Figure 1 and Figure 2, respectively. The distributions of the residual lignin samples are fairly smooth. The dissolved lignin samples have some well-discernible peaks superimposed on their distributions. As the cook proceeds, the distributions are shifted towards longer migration times *i.e.* the charge density becomes higher in both the residual

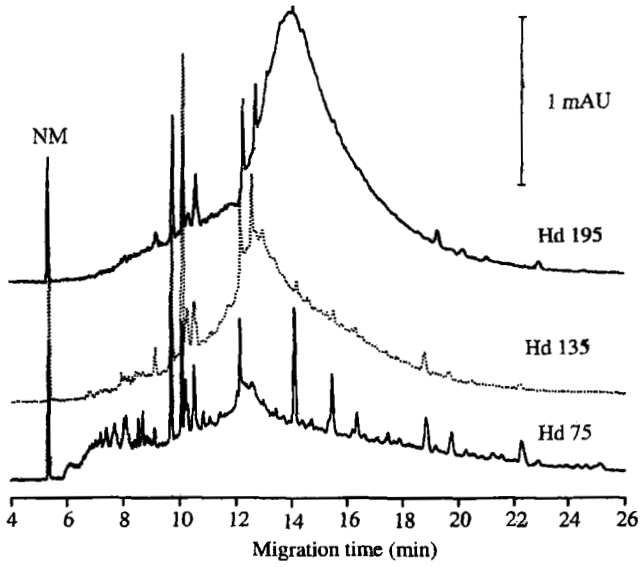

FIGURE 2. Charge density distribution of dissolved lignin isolated from black liquor collected in the beginning (Hd 75), in the middle (Hd 135) and at the end (Hd 195) of a kraft cook of birch. Conditions as in Figure 1.

and dissolved lignin. Since the sample concentrations are equal, the increase in detector response reflects a change in the lignin structure during cooking. However, the low detector response of the Hr 90 sample is also due to the much higher M_n (Table 2) implying a higher viscosity (η) of the sample solution compared to the other residual lignin samples. The relation between injected volume (V) and η is described by the Poiseuille equation

$$V = \Delta P \pi r^4 t / 8 \eta L \qquad [2]$$

where ΔP is the pressure drop across the capillary, r is the internal radius of the capillary, t is the injection time and L is the capillary length. Thus the injected volume decreases with increasing viscosity of the sample solution. It should be

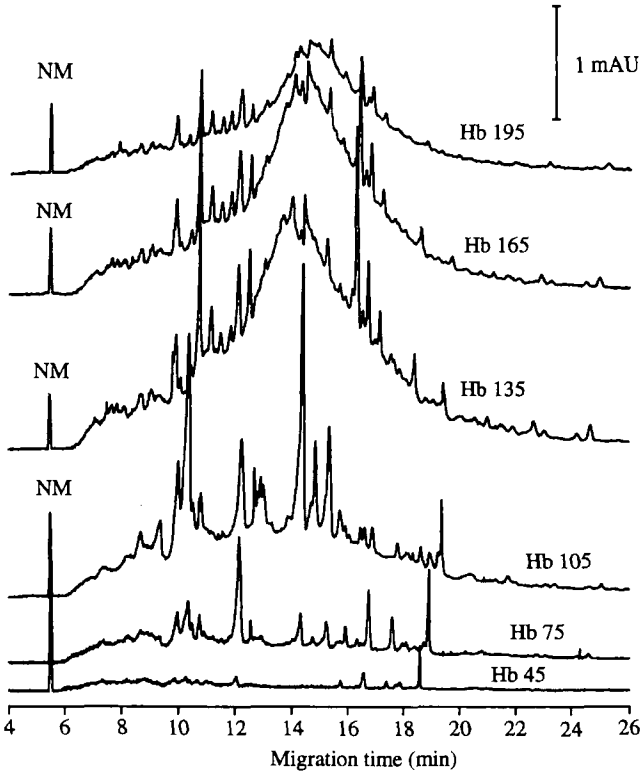

FIGURE 3. Charge density distribution of black liquor collected during a kraft cook of birch. Conditions as in Figure 1.

emphasised that this does not, however, influence the interpretation of the mobility distribution. The Hr 90 has a narrow distribution compared to its dissolved lignin counterpart, Hd 75. This indicates that the charge density of residual lignin fragments is more uniform than the dissolved lignin at the beginning of the bulk delignification.

As in the isolated dissolved lignin, black liquor (Hb) has a broad charge density distribution at pH 12, Figure 3. These samples were diluted equally prior to characterisation and thus the difference in detector response is primarily due to

different concentrations of lignin in the black liquor. The large number of sharp peaks detected over the entire distribution indicates that these peaks are low molecular weight components having phenol and possibly carboxyl groups.

Average Charge Density at pH 12

Due to the different profiles it is difficult to estimate and compare the mobility of the distributions. To ease comparison between lignin-containing samples, the centre of gravity (t_g) of the distributions were determined as previously described.[14] The common equation that relates migration time with mobility was then used to calculate the average mobility (μ_{av}) of the distributions

$$\mu_{av} = \ell L/U\ (1/t_g - 1/t_{NM}) \qquad [3]$$

ℓ is the length to detector, L is the total length of the capillary, U is the applied voltage and t_{NM} is the migration time of the neutral marker. Lignin samples only contain anions and thus the μ_{av} will be negative. Since this study only concerns the magnitude of the mobility, the $|\mu_{av}|$ is reported.

The μ_{av} at pH 12 of residual lignin, dissolved lignin and residual lignin samples is shown in Figure 4. The 95% confidence limits of the mean were calculated from triplicates. The data points of black liquor and dissolved lignin samples are plotted at the mean collection time for each range, Table 1. The charge density of the residual lignin is low in the beginning of the cook but increases during the bulk delignification phase and becomes equal to those of the other samples later in the cook. The dissolved lignin has the highest charge density of the different sample types during the first part of the cook. The μ_{av} remains about the same for the dissolved lignin samples until in the middle of the bulk delignification phase when it increases slightly. The charge density of the black liquor samples has the same trend as that of the dissolved lignin samples although it is lower for the former. As suggested for black liquor collected from a similar kraft cooking of softwood,[13] the lower charge density may be due to

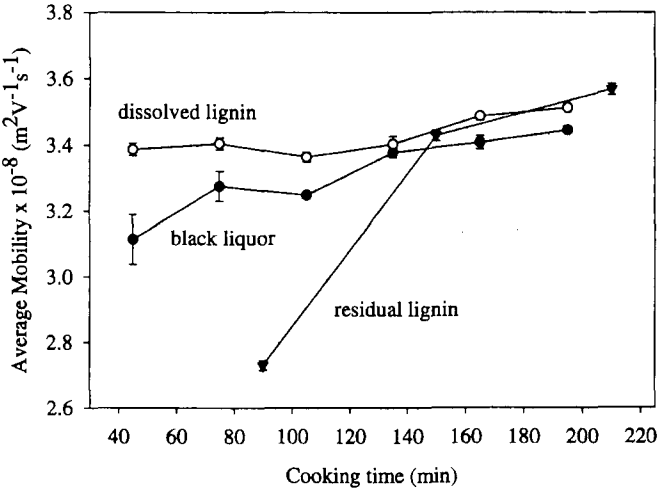

FIGURE 4. Average mobility (μ_{av}) at pH 12 of black liquor and isolated lignin samples corresponding to different cooking times. μ_{av} was calculated according to equation 2. The error bars correspond to the 95% confidence limits of the mean (n=3).

associations with other dissolved molecules, probably carbohydrate fragments. The greatest difference in charge density between black liquor and its isolated lignin counterpart is in the beginning of the cook, when hemicellulose fragments are dissolved into the black liquor.

Limited solubility of lignin fragments is one suggested explanation for the declining delignification rate at the end of kraft cooking of birch.[17,30] Since the charge density is about the same for residual lignin and the lignin removed from the pulp, the declining rate of delignification does not seem to be explained by a limited solubility of the residual birch lignin.

The Influence of pH on Mobility

At pH 10, the mobility of the lignin sample is lower than at pH 12, because

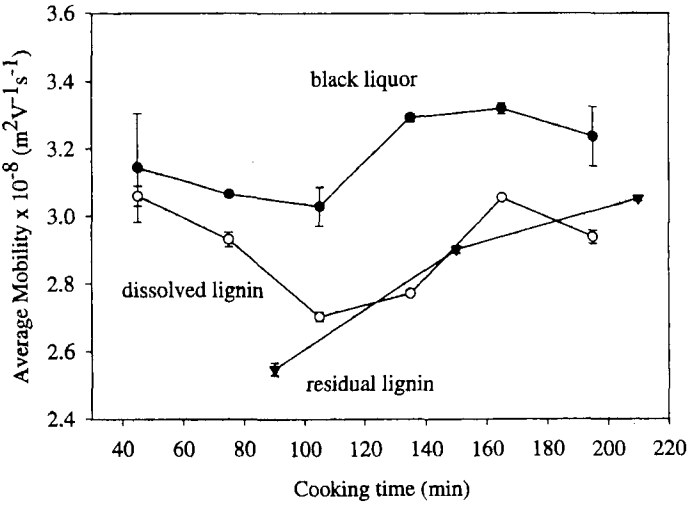

FIGURE 5. Average mobility (μ_{av}) at pH 10 of black liquor and isolated lignin samples corresponding to different cooking times. μ_{av} was calculated according to equation 2. The error bars correspond to the 95% confidence limits of the mean (n=3).

of the lower charge density. The difference in mobility may also give an indication about the relative average acidity of the isolated lignin samples. The pK_a of lignin-related phenol groups varies over a wide range depending on substitution.[29] Differences in the average pK_a of lignin fragments may influence their solubility and thus dissolution from the fibre. If the relative acidities of the phenol groups were the same throughout the cook, the shape of the μ_{av}-graph should be retained. As revealed in Figure 5, this is not the case. In particular, the shape of the μ_{av}-graph for the dissolved lignin and the black liquor samples is changed when lowering the pH of the electrolyte. At pH 10, the relation between the μ_{av} is Hb>Hd≈Hr, *i.e.* different from that at pH 12. This means that the black liquor samples contain lignin fragments of much higher charge density than the dissolved lignin samples at pH 10. The modest decrease in mobility of the Hb samples indicate the presence of acid groups being completely dissociated even at

pH 10. Such groups may be carboxylic acids in dissolved carbohydrates being associated to dissolved lignin fragments. During the isolation of lignin from black liquor, such highly polar components are removed. The changes in μ_{av} is largest for the Hd samples corresponding to the middle of the cook, indicating the presence of phenol groups of relatively low acidity.

Comparison with Kraft Lignin Samples from Pine Wood

The changes in mobility measured at pH 12 of the different sample types during flow-through kraft cooking are similar for birch and pine wood lignin. For pine wood lignin samples, the μ_{av} increases with increasing delignification. The relative charge density differed significantly in the order dissolved lignin>black liquor>residual lignin, except at the end of the cook when the charge densities of black liquor and residual lignin were about the same.[13] In contrast, for samples derived from kraft cooking of birch wood, the charge density of the residual lignin is equal to that of the dissolved lignin at the end of the cook. This indicates that the solubility of the birch wood pulp lignin is sufficiently high and is thus not the limiting factor for dissolution.

The birch wood residual lignin isolated from the beginning of the cook has a much lower charge density than the corresponding pine wood lignin. At this stage of the cook the syringyl units still remain in the pulp lignin. These structures have been reported to be more etherified than guaiacyl units.[31] Accordingly, the concentration of free phenol groups in the present study was lower in comparison to the residual lignin in softwood kraft pulp at similar cooking times. Also, the difference in relative acidity between the birch lignin samples seems to be greater than for the corresponding pine lignin samples.

CONCLUSIONS

From mobility measurements of isolated lignin samples and black liquor

the following conclusions can be drawn.

- The charge density of birch wood kraft lignin increases during the cook. The largest increase is observed for the residual lignin during the first part of the bulk delignification. At the end of the cook, the charge density of the residual lignin is about the same as that of dissolved lignin, indicating that the solubility is sufficient for the pulp lignin to be dissolved.
- The differences in mobility of the black liquor compared to the isolated dissolved lignin may be due to associations between lignin fragments and carbohydrates in the black liquor.
- The relative acidity of the isolated lignin samples is changed during the cook, especially for the dissolved lignin corresponding to the middle of the cook. This indicates that the lignin fragments removed during this stage have phenol groups of relatively low acidity.
- The difference in delignification rate between kraft pulping of birch wood and pine wood cannot be explained by differences in the charge densities of the studied samples.

These conclusions need to be confirmed using other isolation methods for residual lignin, since the applied method may influence the charge density of the pulp lignin.

EXPERIMENTAL

Materials

All chemicals were of analytical grade. For the capillary electrophoresis characterisations, 100 mM glycine electrolytes were prepared by mixing appropriate volumes of 100 mM stock solutions of sodium hydroxide and glycine to a final pH of 10.0 or 12.0, respectively, measured at room temperature. The final solutions were kept under nitrogen and were used within five days.

Cooking Conditions and Sample Preparations

Five flow-through kraft cooks of birch wood were performed; cooking times and sample designation according to Table 1. Cooking conditions and isolation procedures for the dissolved and residual lignin samples are described in a previous publication.[18] Nitrogen was added to the collected black liquor fractions to prevent oxidation. The Hb samples (black liquor) were diluted by an equal volume of deionized water and characterised by capillary electrophoresis within two hours. The dissolved lignin samples (Hd) were isolated from black liquor by acid precipitation according to Gellerstedt and Lindfors.[15]

The isolated dissolved and residual lignin samples, respectively, were dissolved in the pH 12-electrolyte over night (under nitrogen) and diluted by an equal volume of deionized water to a final concentration of 4.0 mg/L. All sample solutions and electrolytes were filtered through a 0.45 μm filter (Chrompack, Acro disc LC 13) prior to CZE characterisation.

Analysis

Pulp viscosity was determined according to SCAN-CM 15:88 and kappa numbers of the pulps were determined according to SCAN-C 1:77. Klason lignin of wood and pulps was determined after swelling the pulp in 72% sulphuric acid at 30 °C for 1 h, followed by dilution to 3% and hydrolysis at 125 °C, 1.4 bar for 1 h. Klason lignin was used to estimate the recovery of dissolved lignin and the efficiency of the residual lignin isolation.

Quantification of Phenol and Carboxyl Groups

Phenol group determinations of the isolated lignin samples were carried out by aminolysis according to the procedure described by Månsson[32]. This

method also provided the acetylated samples for characterisation by size-exclusion chromatography. Carboxyl groups were determined by quantitative ^{1}H-NMR, as described in Ref. 14. The RSD of the carboxyl group determination was 10% and the minimum detectable concentration (MDC) was 0.1 mmol/g.

Size-exclusion Chromatography

The SEC system consisted of a Rheodyne 7125 injector, a Waters 510 pump, a set of three columns connected in series, 10^4Å, 500Å, 100Å, (ultrastyragel, Waters) and a flow rate of 1 mL/min was used. 40 µg of acetylated lignin dissolved in THF was characterised at room temperature using THF as mobile phase. The solutes were detected by a Waters 410 refractive index detector. Polystyrene (PS) standards in the range 580 D to 350 kD (Polymer Laboratories Ltd., UK) were used to calibrate the SEC-systems. Data acquisition and calculations were carried out using Baseline software (Waters).

Capillary Electrophoresis

CZE was performed on an Applied Biosystem 270A-HT instrument with a 72 cm x 50 µm I.D. fused silica capillary. The sample vials were filled with 50 µl of each sample solution and 5 µl of n-C_{14}, giving a layer to prevent oxidation. To minimise evaporation, the sample compartment was kept at a constant temperature of 7 °C. The samples were introduced by vacuum for 1.5 s preceded by 0.5 s injection of pyridine (0.1% v/v) as neutral marker. A voltage of 20 kV was applied and the temperature of the separation compartment was kept at 30 °C. Detection was carried out at 254 nm 50 cm from the injection site. Electropherograms were registered and calculations were performed using the ELDSPRO Labdata system (Chromatography Data Systems AB, Kungshög, Sweden).

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REFERENCES

1. R. Aurell, Svensk Papperstidn., 66(23), 978 (1963). *In Swedish.*
2. J. Li, in Towards an accurate determination of lignin in chemical pulps, PhD thesis, Royal Institute of Technology, Stockholm, Sweden, 1999, p. 61.
3. M. Söderqvist Lindblad and L. Olm, SCAN Forsk rapport 600 (1992). *In Swedish.*
4. L. Edwards, S.-E. Norberg and A. Teder, Svensk Papperstidn., 77(3), 95 (1974).
5. B.J. Fergus and D.A.I. Goring, Pulp Paper Mag. Can., 70, T314 (1969).
6. G. Meshitsuka and J. Nakano, in Proceedings of the 3rd International Symposium on Wood and Pulping Chemistry, Vancover, Canada, 26-30 August 1985, p. 103.
7. R. Kondo, Y. Tsutsumi and H. Imamura, Holzforschung, 41(2), 83 (1987).
8. P. Axegård, S. Nordén and A. Teder, Svensk Papperstidn., 81(4), 97 (1978). *In Swedish.*
9. J. Gierer, Wood Sci. Technol., 14, 241 (1980).
10. S. Ljunggren, Svensk Papperstidn., 83(13), 363 (1980).

11. A.J. Kerr and D.A.I. Goring, Can. J. Chem., 53, 952 (1975).

12. S.F.Y. Li, in Capillary Electrophoresis. Principles, Practice and Applications, p. 203, Elsevier Science Publishers B.V., Amsterdam, Netherlands, 1992.

13. E. Sjöholm, N.-O. Nilvebrant and A. Colmsjö, J. Wood Chem. Technol., 13(4), 529 (1993).

14. E. Sjöholm, E. Norman, S. Moe and A. Colmsjö. Submitted to J. Wood Chem. Technol. (1999).

15. G. Gellerstedt and E.-L. Lindfors, Holzforschung, 38, 151 (1984).

16. Z.-H. Jiang and D.S. Argyropoulos, J. Pulp Paper Sci., 25(1), 25 (1999).

17. G. Gellerstedt, J. Pranda and E.-L. Lindfors, J. Wood Chem. Technol., 14(4), 467 (1994).

18. E. Sjöholm, K. Gustafsson and A. Colmsjö, J. Liq. Chromatogr. Relat. Technol., 22(11), 1663 (1999).

19. K. Lundquist and R. Lundgren, Acta Chem. Scand., 26, 2005 (1972).

20. K. Lundquist, Acta Chem. Scand., 27, 2597 (1973).

21. K.H. Ekman and J.J. Lindberg, Pap. Puu, 42(1), 21 (1960).

22. J. Marton and E. Adler, Tappi, 46(2), 92 (1963).

23. T. Enkvist, Pap. Puu, 43(11), 657 (1961).

24. L. Löwendahl, G. Petersson and O. Samuelson, Svensk Papperstidn., 81(12), 392 (1978).

25. J. Gierer and S. Wännström, Holzforschung, 38(4), 181 (1984).

26. J.J. Lindberg, Finska Kemists. Medd., 68(1), 5 (1959). In German.

27. G.B. Shtreis and V.M. Nikitin, Zh. Prikl. Khim., 40(8), 1814 (1967). *In Russian.*

27. D.L. Woerner and J.L. McCarthy, in Proceedings of the 4th International Symposium on Wood and Pulping Chemistry, Paris, France, 27-30 April 1987, Vol. 1, p. 71.

29. M. Ragnar, C.T. Lindgren and N.-O. Nilvebrant, in Proceedings of the 10th International Symposium on Wood and Pulping Chemistry, Yokohama, Japan, 7-10 June 1999, Vol. 2 p. 154.

28. G. Gellerstedt, K. Gustafsson and R.A. Northey, Nordic Pulp Paper Res. J., 2, 87 (1988).

29. Y.-Z. Lai and M. Funaoka, J. Wood Chem. Technol., 13(1), 43 (1993).

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