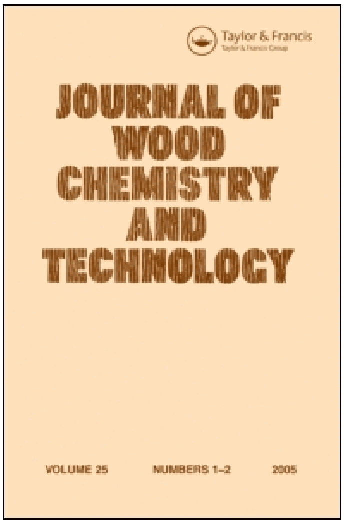

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MOLECULAR WEIGHT OF LIGNIN FRACTIONS LEACHED FROM UNBLEACHED KRAFT PULP FIBERS

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Dedicated to Prof. J.L McCarthy on the Occasion of
his 70th Birthday

ABSTRACT

The molecular weights of lignin fractions leached from an unbleached kraft pulp were found to increase from 230,000 to 410,000 as washing of the pulp proceeded. The free diffusion coefficients for both a spherical and a disk-like conformation were calculated and were found to be seven orders of magnitude higher than the observed intrafiber diffusion coefficient. Also the change in the free diffusion coefficient with molecular weight was far less than the 100-fold polydispersity observed previously. A comparison of the molecular dimensions with the pore size indicated that a flat, disk-like conformation, rather than a spherical conformation, is appropriate for the lignin macromolecule.

INTRODUCTION

In a previous paper[1], we showed that the leaching of lignin macromolecules through the fiber walls of an unbleached kraft pulp suspended in water was diffusion controlled. Two important effects were noted; firstly, a very low rate of diffusion was observed; and secondly, it was necessary to postulate a wide range of diffusion coefficients in order to explain the results obtained for long periods of leaching. We have also shown that the rate of leaching increases with the temperature[2] and decreases at higher concentration of electrolyte[3].

The purpose of the present investigation was to discover whether or not the rate of diffusion of the lignin through the fiber wall could be correlated with the molecular size of the

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soluble lignin macromolecules leached from the fiber. Lignin fractions were collected for various times of leaching. Molecular weights were measured by the short column sedimentation equilibrium technique previously used in this laboratory[4]. In addition, the median pore size in the water swollen fibers was measured by the solute exclusion technique developed by Stone and Scallan[5]. An attempt was then made to relate the small and widely polydisperse diffusion coefficients found previously[1] with the size and shape of the lignin macromolecule.

EXPERIMENTAL

The fiber stock used was an unbleached kraft pulp of 52% yield prepared from black spruce chips as described previously[1].

A 48 g sample (19 g dry weight) of fiber was blended in approximately 900 mL of distilled water for 1 minute, using a Waring blender. The solution was filtered off using a coarse sintered glass filter and the fiber was washed quickly with two 500 mL aliquots of water. The fiber was handpressed after each wash. This procedure served to remove the residual lignin on the surface of the fibers and in the lumens. The fiber was then redispersed in one litre of distilled water. Leaching was carried out at 20°C and 140 rpm in the apparatus described previously[1]. After 20 min, the pulp suspension was filtered and the fiber was washed quickly and handpressed as above. The filtrate for that particular interval was adjusted with NaOH to pH 8 and stored at 4°C. The fiber was then redispersed in one litre of fresh water for the next interval. The process was repeated for 60 min, 100 min, 120 min, and 16 h intervals. The first four intervals were chosen to give approximately equivalent concentrations of soluble leached lignin in the filtrate. It was necessary to repeat the above process eight times in order to build up a quantity of lignin sufficient for the molecular weight determinations.

For ultracentrifugation, the combined filtrates were concentrated in a rotary evaporator at 45°C to a concentration of about 2.5 gL^{-1}. The concentrated samples were filtered through a fine filter to remove the residual debris.

The lignin concentration was determined spectrophotometrically by ultraviolet analysis at 280 nm using an absorbtivity of 18.7 $L\ g^{-1}\ cm^{-1}$.[6,7]

The weight average molecular weight was measured in a Spinco, model E, analytical ultracentrifuge using the short column sedimentation equilibrium technique described previously[2]. The values used for the refractive index increment and the partial specific volume of the kraft lignin were 0.201 mL g^{-1} and 0.663 mL g^{-1} respectively[7].

The median pore size of the fiber was obtained by the solute exclusion technique of Stone and Scallan using dextran molecules of known molecular size as probes[5]. We are grateful to Dr. A.M. Scallan for these measurements.

RESULTS

The molecular weights obtained and their respective time intervals are shown in Table 1. Also given in Table 1 are values for $C_f(t)$, the concentration of leached lignin which would have been found in the wash liquid if the experiment had run continuously. This quantity was obtained by accumulating the total weight of leached lignin up to the end of the particular time interval.

The median pore diameter of the fiber, after being washed for 4 h was found to be 3.6 nm. For the pore size data, no correction was made for the effect of the fibre wall on dextran penetration[8]. The fiber saturation point (FSP) was 1.56 g g^{-1}. The FSP for the same fiber, washed for only 10 min, was 1.60 g g^{-1}.

DISCUSSION

In spite of the scatter of the points, the data in Table 1 show that the molecular weight increases with the quantity of lignin removed.

If a spherical conformation for the lignin macromolecule is assumed, the free diffusion coefficient, D_{free}^{sphere}, can be calculated from

$$d = \left(\frac{6\ M_w v}{\pi\ N}\right)^{1/3} \qquad (1$$

$$D_{free}^{sphere} = \frac{kT}{3\pi\ d\ \eta} \qquad (2)$$

where k ≡ Boltzmann's constant

T ≡ absolute temperature (293° K)

d ≡ effective hydrodynamic diameter of the macromolecule

η ≡ solvent viscosity, (0.01 g s^{-1} cm^{-1} for H_2O at 293° K)

Table 1.

Estimation of the free diffusion coefficients for spherical and disk-like conformations of lignin from the observed molecular weights

Fraction	Wash Time Interval (min)	M_w	$C_f(t)$ x 10^3 (gL^{-1})	d (nm)	D^{sphere}_{free} (cm^2 s^{-1})	Axial Ratio	D^{disk}_{free} (cm^2 s^{-1})
L-1	0 - 20	230,000	7.8	9.2	4.7 x 10^{-7}	6.3	3.6 x 10^{-7}
L-2	20 - 80	320,000	17.2	10.4	4.1 x 10^{-7}	7.5	3.0 x 10^{-7}
L-3	80 - 180	410,000	25.3	11.2	3.8 x 10^{-7}	8.5	2.7 x 10^{-7}
L-4	180 - 300	340,000	33.3	10.6	4.0 x 10^{-7}	7.8	2.9 x 10^{-7}
L-5	300 -1260	410,000	56.0	11.2	3.8 x 10^{-7}	8.5	2.7 x 10^{-7}

M_w ≡ molecular weight

N ≡ Avogadro's number

v ≡ specific volume of the swollen lignin.

The value used for v was 1.1 mL g^{-1}, the specific volume of the swollen fiber wall at 80% delignification[9]. Diffusion coefficients, calculated by means of equations 1 and 2 are given in Table 1. The values decrease slightly over the range of molecular weights of the fractions. However, D_{free}^{sphere} is about seven orders of magnitude higher than the value of 3 x 10^{-14} cm^2 s^{-1} calculated previously[1] for the intrafiber diffusion coefficient from the rate of leaching. Also, the range of D_{free}^{sphere} in Table 1 is much less than the 100-fold polydispersity (1 x 10^{-13} cm^2 s^{-1} to 8 x 10^{-16} cm^2 s^{-1}) found previously[1] for the diffusion of lignin macromolecules through the fiber wall.

Recent work has suggested that lignin macromolecules made soluble during delignification are disk-like in shape, with a constant thickness of approximately 2 nm in the dry state[10]. If such a conformation is assumed for the lignin macromolecules leached out of the fiber, the axial ratios of disk diameter to thickness given in Table 1 are readily computed[10]. Free diffusion coefficients corresponding to the equivalent oblate ellipsoids may then be derived by dividing the free diffusion coefficient of the sphere by the appropriate frictional ratio of the oblate ellipsoid[11].

The free diffusion coefficients corresponding to the disk-like conformation are listed in Table 1. The values of D_{free}^{disk} are somewhat lower than those corresponding to the spherical model. However, the intrafiber diffusion coefficient of 3 x 10^{-14} cm^2 s^{-1}, is still many orders of magnitude lower than the free diffusion coefficients for the disk-like model. Also the change in the free diffusion coefficient with time of leaching is far too small to account for the wide range of polydispersity previously observed in D.[1] It is apparent, therefore, that free diffusion must play a negligible role in transport across the fiber wall and that the interaction of the lignin macromolecules with cellulose hydrogel must be the dominant restriction to the diffusion of lignin out of the fiber.

Comparison of the present data with the earlier results of McNaughton *et al.*[7] shows that the molecular weights of leached lignin fractions are

Table 2.

A comparison of the spherical molecular diameters of lignins, obtained during pulping and leaching, with the pore size data

Lignin Macromolecular Properties			Corresponding Pulp Properties	
Lignin Fraction	M_w	d (nm)	FSP (g/g)	Median Pore Diameter (nm)
CK-7	51,000	5.6	1.56	4.0
L -1	230,000	9.2	1.60	-
L -4	340,000	10.6	1.56	3.6

considerably higher than those for lignins released during pulping. The highest molecular weight obtained by McNaughton et al. was 51,000 for Fraction CK-7. As shown in Table 2 this may be compared with molecular weights of 230,000 and 340,000 obtained for Fractions L-1 and L-4 in Table 1. Note also that in both the pulping and the leaching the degree of delignification was about the same (85% - 88%).

In a study by Ahlgren et al.[12], good agreement was demonstrated between the size of the pores existing in the cell wall, at any stage of pulping, and the spherical molecular size of the lignin liberated at that stage. This type of correlation though, does not hold for leaching. If the fiber saturation points and the median pore sizes of the fibers corresponding to the lignin fractions CK-7, L-1 and L-4 are compared (Table 2) it can be seen that they are similar indicating that the pore size and volume remain constant from the end of the cook up to 4 hours of washing. However, it is interesting to note that if a spherical conformation is assumed for the lignin macromolecule, the molecular diameter, d, increases by a factor of 2 from Fraction CK-7 to Fraction L-4. This suggests that a disk-like conformation is likely since disk-like molecules of uniform thickness, but of different weights, can escape from slit-like pores of identical thickness. These results support the recent suggestions[10,13] that, in fact, soluble lignins are made up of flexible disk-like molecules, a conformation which arises as a result of the lamellar structure of the secondary wall of the wood cell[14].

CONCLUSIONS

The results show that the calculated free diffusion coefficients for spheres or disks cannot account for the low magnitude or the wide polydispersity of the intrafiber diffusion coefficient. Interaction with the cellulose hydrogel must therefore be the dominant restriction to the diffusion of lignin out of the fiber.

In correlating molecular dimensions with pore size measurements a disk-like conformation, as opposed to a spherical conformation, was found to be more appropriate for the soluble lignin macromolecule.

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