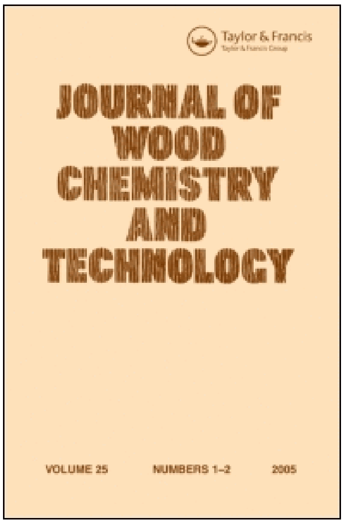

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High Temperature Leaching of Lignin From Unbleached Kraft Pulp Fibers

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HIGH TEMPERATURE LEACHING OF LIGNIN FROM UNBLEACHED KRAFT PULP FIBERS

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ABSTRACT

When an unbleached kraft pulp was suspended in water at various temperatures between 20°C and 90°C the rate of the leaching of lignin from the fiber wall increased with the temperature. From 20°C to 70°C, the change in the intrafiber diffusion coefficient with temperature varied directly as the ratio of the absolute temperature to the viscosity of water, as expected for a diffusion process. Above 70°C, there was a much larger dependence of the diffusion coefficient on temperature than was observed at the lower temperature. The change occurred near the glass transition temperature of the hemicellulose saturated with water, and may have been due to physical changes in the structure of the fiber caused by the thermal softening of the hemicellulose. Even at temperatures of 155°C, the handsheet properties of the pulp were not adversely affected by the leaching process.

INTRODUCTION

When unbleached kraft pulp fibers are suspended in water and gently stirred, soluble lignin macromolecules are leached out of the fiber. In a previous investigation[1] it was shown that the process could be interpreted quantitatively as a diffusion of the macromolecules through the fiber wall into the wash liquid. However, the diffusion coefficient ob-

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served was several orders of magnitude smaller than that corresponding to the range of molecular weights of the dissolved lignin[2]. It was therefore concluded that interaction with the cellulose hydrogel must be the dominant restriction to the diffusion of the lignin macromolecules out of the fiber.

If, indeed, the leaching of lignin from pulp fibers is a diffusion controlled process, then higher temperatures should result in faster leaching from the fiber wall. Moreover, the increase in the rate of diffusion should be proportional to the absolute temperature and inversely proportional to the solvent viscosity according to the Stokes-Einstein equation[3]. The purpose of the work described in the present paper was to test this hypothesis. Unbleached kraft pulp fibers were suspended in water at different temperatures and the leaching of lignin was observed by the technique described previously[1]. The change of the diffusion coefficient with temperature was then compared with the temperature dependence governing the free diffusion of macromolecules in solution. Leaching behaviour at temperatures up to 155°C were investigated and the effect of leaching on the handsheet properties of the fibers was determined.

EXPERIMENTAL

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

Leaching experiments were carried out at various temperatures by means of the procedure and apparatus described earlier[1]. A 9.5 g (dry weight) sample of fibers was stirred gently in 1 L of distilled water and the concentration of lignin leached out of the fiber measured at suitable time intervals. The temperature range was between 20°C and 90°C at 10°C intervals. Because of possible errors due to evaporation experiments were limited to 5 h duration.

The concentration of leachable lignin in the fiber, $C_{sd}(t)$, after a certain time, t and the diffusion coefficient, D were computed as described previously[1,2].

Some experiments were carried out at temperatures above 100°C in a pressure vessel equipped with a stirrer. The conditions were not well enough controlled to allow calculation of the diffusion coefficient and the data were compared with results at lower temperatures by measurement of the concentration, $C_f(t)$ of lignin in the wash liquid after time t.

In order to test whether handsheet properties were affected by the leaching treatment at higher temperatures, a few experiments were done on a scale of kilograms in a pilot digester. Conditions of cooking were the same as those for the 52% yield pulp used in the laboratory experiments.

RESULTS AND DISCUSSION

In Fig. 1 the change in the leachable lignin concentration with time is shown for 20°C, 60°C and 90°C. Curves were based on the diffusion theory described in an earlier paper[1]. It can be seen from Fig. 1 that there is a good correlation between theory and experiment. Similar behaviour was observed at the other temperatures. This agreement suggests that a diffusion mechanism was rate controlling at temperatures between 20°C and 90°C.

From the leachable lignin concentrations in the fiber at 30 minutes, the diffusion coefficients at temperatures between 20°C and 90°C were calculated by means of the equations derived previously[1]. In Fig. 2, the diffusion coefficient is plotted against the temperature. It can be seen

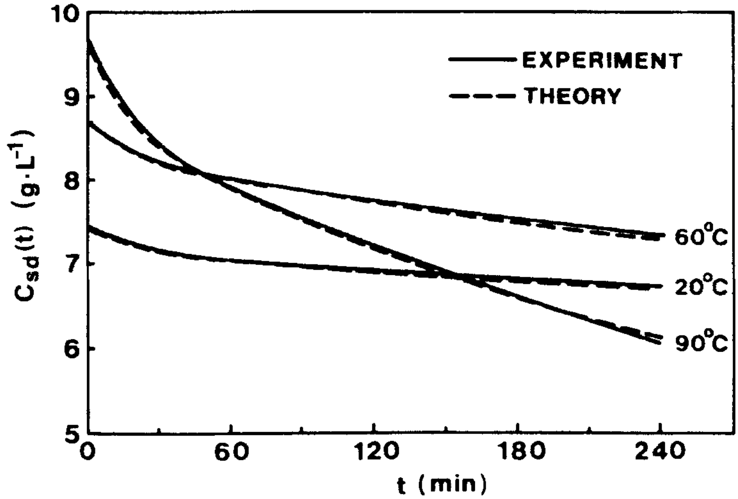

FIGURE 1. Experimentally determined curves of leachable lignin concentration, $C_{sd}(t)$, versus time, t, at 3 temperatures. The theoretically derived curves are included for comparison.

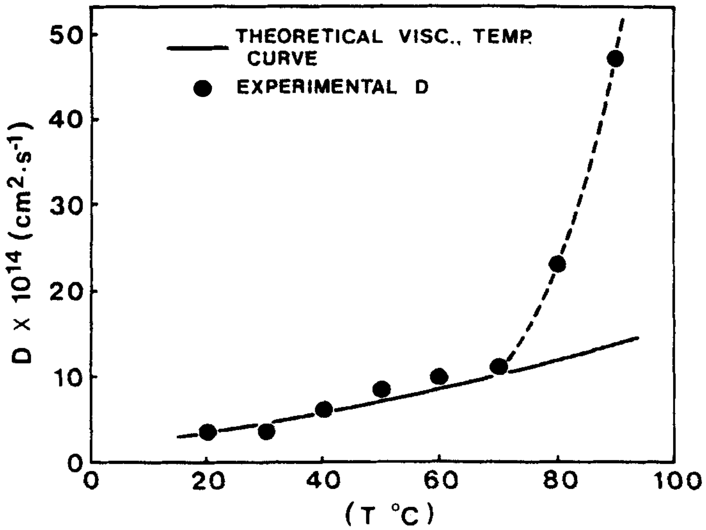

FIGURE 2. Plot of the intrafiber diffusion coefficient, D versus the temperature T. The solid line corresponds to the increase with temperature of D expected from the Stokes-Einstein equation.

that there is a gradual increase in the diffusion coefficient with temperature up to about 70°C, after which D increases much more rapidly.

In free diffusion, the relationship of the diffusion coefficient to the absolute temperature is given by the Stokes-Einstein[3] equation in the form

$$D = \frac{RT}{6\pi \eta r N} \qquad (1)$$

where
D = diffusion coefficient
R = gas constant
T = absolute temperature
r = effective hydrodynamic radius of the macromolecule
η = solvent viscosity
N = Avogadro's number

If it is assumed that r does not change with temperature, we may write

$$D = D_{20} \frac{T \eta_{20}}{\eta \; 293} \qquad (2)$$

where the subscript 20 denotes the value at 20°C.

The solid line in Fig. 2 was calculated by substituting in Eqn. 2 the appropriate values of η, T, and the experimental diffusion coefficient at 20°C. Up to 70°C, the change in the experimentally observed diffusion coefficients correlated well with the change in viscosity and temperature as expected for a diffusion process. Beyond 70°C there is a marked increase in the temperature dependence of D. The origin of this effect is not known. However, it is interesting to note that the activation energy calculated at temperatures $\geq$ 70°C (using the diffusion coefficients), was only 18 kcal $mole^{-1}$ (75 kJ $mole^{-1}$) which is small for the breaking of covalent bonds. Hence, it is likely that a physical effect as opposed to a chemical one is causing the rapid increase of D above 70°C. If the diffusion process is controlled by some structural relationship between the size of the lignin macromolecules and the size of the pores, then small changes in the structure of the fiber could have a large effect on the diffusion coefficient. It is significant that hemicellulose saturated with water undergoes a glass transition at about 55°C[4]. The increased dependence of the diffusion coefficient with temperature above 70°C may be due to physical changes in the structure of the fiber associated with the thermal softening of the hemicellulose in the fiber wall.

In Fig. 3 we have plotted the lignin concentration in the wash liquor versus time for the experiments conducted at temperatures between 20°C and 155°C. It is quite clear that the marked increase in the rate of diffusion shown in Fig. 2 for temperatures higher than 70°C is more pronounced when the leaching is carried out above 100°C. In the experiments at 155°C, it was found that, after 4 hours, over one third of the lignin in the fiber could be removed.

The results of the pilot scale experiments are shown in Table 1. Here times of leaching under pressure were shorter than in the laboratory experiments. The removal of lignin is indicated by the lowering of the kappa number, in some cases over 10 points. Comparison of the weight of the pulp before and after leaching indicated that little or no hemicellulose was removed by the leaching treatment. Handsheet tests on the unbeaten pulps (Table 1) showed that the freeness increased slightly, and the burst and breaking length were slightly lowered while the tear was improved. Brightness increased slightly but the stretch was unchanged. Taken together, the results suggest that leaching of the lignin

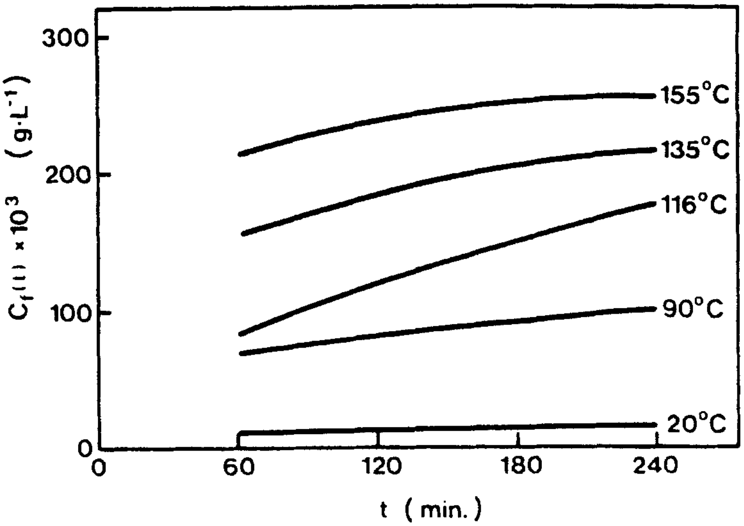

FIGURE 3. $C_f(t)$ versus t for various temperatures of leaching.

TABLE 1.

Handsheet Properties of Unbeaten Pulps Before and After Leaching at Elevated Temperatures

aching Treatment								
Temp. °C	Time min.	Kappa No.	Freeness mL	Burst Index $kPa \cdot m^2/g$	Tear Index $mN \cdot m^2/g$	Breaking Length m	Brightness ISO %	Stretch %
treated		61.2	664	5.2	17.0	7230	22.0	2.2
60	60	55.9	703	4.6	19.2	6480	24.0	2.1
135	20	52.2	698	4.5	19.8	6820	24.0	2.2
135	60	51.1	706	4.5	21.6	6760	23.5	2.1
55	20	51.8	702	4.6	20.6	6680	23.8	2.2
55	60	49.4	698	4.4	21.7	6420	23.1	2.2

out of the fiber lowers the kappa number while producing little change in other pulp properties.

CONCLUDING REMARKS

The results show that the rate of leaching of lignin from unbleached kraft pulp increases with an increase in the temperature. Up to 70°C, the increase in rate is in accordance with the classical laws governing the dependence of the diffusion coefficient on the temperature and viscosity of the liquid. Above 70°C, a very large increase in the rate occurs until, at 155°C, the lignin is leached out of the fiber quickly and in substantial quantities. Apparently only small changes in the strength properties of the pulps are produced by the leaching treatment at high temperatures.

These results may have implications for improved washing practices in kraft mills. If it were possible to install a high temperature (>100°C) leaching stage after the conventional washers, we might achieve a significantly lower kappa number on the pulp going in to the first stage of bleaching. As shown in a subsequent paper, however, the electrolyte concentration in the mill water supply could inhibit significantly the lignin leaching.

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