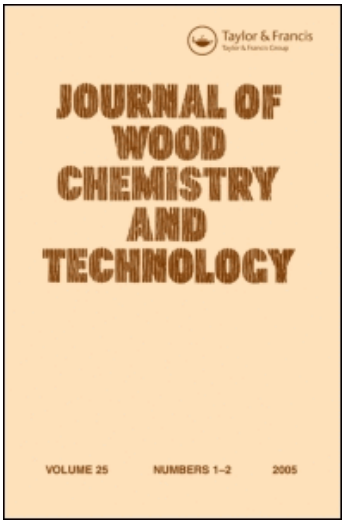

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THE TOPOCHEMISTRY OF DELIGNIFICATION SHOWN BY PULPING MIDDLE LAMELLA AND SECONDARY WALL TISSUE FROM BLACK SPRUCE WOOD

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ABSTRACT

Fractions of tissue from the secondary wall and middle lamella of black spruce wood were pulped by the kraft, acid-sulphite and acid-chlorite methods. In all cases, the delignification of the secondary wall tissue was more rapid than that for the middle lamella tissue. This topochemical effect was largest in kraft pulping. In acid-sulphite pulping the effect was less than in kraft, while in acid-chlorite pulping the effect was smallest. Thus the results confirmed in general the previously reported trends based on microscopic observation. However, in earlier work there was no topochemical difference found in acid-chlorite pulping, even at high delignification. In the present work, the topochemical effect in acid-chlorite pulping increased rapidly above 50% delignification.

INTRODUCTION

Bixler[1] concluded in 1938 that, in the kraft process, the lignin in the middle lamella dissolves faster than that in the secondary wall. Others since then have studied the topochemistry of delignification with varying results[2-5].

In 1967, Procter et al.[6] showed by ultraviolet microscopy that, for both kraft and acid-sulphite pulping, the lignin in the secondary wall dissolved faster than the lignin in the middle lamella. For neutral-sulphite pulping, the topochemical effect was smaller. In 1972, Wood et al.[7] found that there was no topochemical

effect during chlorite pulping. They also related the topochemical effect to the removal of hemicelluloses from the wood and showed that the more the hemicelluloses were removed from the wood early in the cook, the greater was the topochemical effect. These results were supported by the later work of Kerr and Goring[8] who pulped, with acid-chlorite, birch wood from which the hemicelluloses had been removed. They noted that in hemicellulose-free birch there was a topochemical effect, while in normal birch there was no topochemical effect. It was also noted that removal of the hemicelluloses caused larger pores to be formed in the fibre walls during pulping.

Further information about the topochemistry of delignification was obtained by Kerr and Goring[9] when they found that during kraft pulping the lignin of black spruce was removed from the exposed middle lamella as macromolecules of the same size, and at the same rate, as from the middle lamella completely enclosed by tracheid walls. These authors wrote:- "This demonstrates that during the pulping of wood, the primary and secondary walls of the cells do not act as physical barriers to the diffusion of dissolved lignin macromolecules from the middle lamella region."

As mentioned in several previous papers, there are intrinsic problems in the ultraviolet microscopic measurement of lignin concentrations in the various morphological regions of wood[6-9]. The topochemical effects described above may be artifacts created by the methods used. A non-microscopic method of checking the previous results would be useful.

The purpose of the present work was to measure directly the rates of delignification of secondary wall and middle lamella tissue of spruce wood. Whiting et al.[10] have developed a method by means of which fractions rich in middle lamella and secondary wall tissue of wood can be prepared in centigram quantities. Such fractions were treated under the conditions used conventionally in kraft, acid-sulphite and acid-chlorite pulping. Removal of lignin was followed by spectrophotometric analysis of the liquors. Measure-

ments were also made on whole wood. In this manner, data were obtained which permitted an independent check of the topochemical behavior reported previously[6-9].

EXPERIMENTAL

The pulping experiments were performed on three samples of black spruce (Picea mariana (Mill.) B.S.P.) tissue. They were extractive-free black spruce wood flour, secondary wall tissue, and middle lamella tissue, with lignin contents of 27%, 21% and 55% respectively, all prepared as described previously[10]. Each sample was pulped by three different methods.

Kraft

A kraft liquor consisting of 18.7 $g.L^{-1}$ NaOH and 6.7 $g.L^{-1}$ Na_2S was prepared. One to two milligrams of sample were weighed into a glass tube (10 cm x 0.5 cm I.D.). One millilitre of liquor was added and the tube sealed. The tubes were then placed in an oil bath at 160 ± 1° for the desired time. The time required to reach 160°C inside the bomb was less than 5 min. After the desired reaction time the tubes were removed and quenched in cold water. Each tube was opened and the liquor pipetted into a vial containing 9 mL H_2O.

The solution was filtered and the absorbance measured at 280 nm. Further dilutions were made if the absorbance was found to be greater than 0.1. The delignification was calculated using an absorbtivity of 18.7 $L.g^{-1} \cdot cm^{-1}$ [11]. Kraft liquor was cooked for various lengths of time, without the addition of wood material, for use as a blank.

Sulphite

A sulphite liquor was prepared by dissolving 15.6 $g.L^{-1}$ NaOH in water and adjusting the pH to 1.5 with SO_2. One to two milligrams of sample were then treated by procedures identical to those used in kraft pulping except that the temperature was 150 ± 1°C. As in the experiments with kraft, the diluted liquor was filtered and the absorbance measured at 350 nm. The normal wavelength for

lignin absorbance measurements is 280 nm. However, at this wavelength the sulphite liquor absorbed too strongly to allow accurate measurements of a small lignin concentration. At 350 nm the absorbance of sulphite liquor was small compared to the absorbance of lignin and measurements were possible.

To check if 350 nm was a reliable wavelength for lignin analysis, samples of other sulphite lignins were dissolved in the liquor and their absorbtivities measured at 280 nm and 350 nm. Although the absolute absorbtivities for these samples varied from sample to sample, the ratio of $\epsilon_{280}/\epsilon_{350}$ remained constant at 16.8. An average value for the absorbtivity of sulphite lignin at 350 nm was found to be 0.85 $L.g^{-1} \cdot cm^{-1}$. This value was used in the calculation of lignin concentrations in the liquor. Sulphite liquor, cooked for various lengths of time without the addition of wood material, was used as a blank.

Chlorite

Chlorite treatment was done according to the procedure of Wise et al.[12] as adapted by Timell[13], but at a scaled down level. Approximately 5 mg of sample was weighed accurately into 1.5 cm x 12 cm test tubes and 2 mL H_2O added to each. The initial chemical charge was 1.5 mg $NaClO_2$ and 0.5 µL glacial acetic acid. The samples were placed in an oil bath at 70 ± 1°C and stirred regularly. After each hour, 0.1 mL of liquor was withdrawn and fresh chemicals added without the addition of water. The withdrawn samples were placed in vials with 4.9 mL H_2O, filtered, and the absorbance measured at 240 nm. The delignification was calculated from the absorbance using an absorbtivity of 30 $L.g^{-1} \cdot cm^{-1}$ determined by Campbell and McDonald[14]. The same procedure was followed for a blank sample using no wood material.

Each type of sample was pulped three times by each method. The resulting percent delignifications were reproducible to within ± 2%.

RESULTS

The results for the kraft, acid-sulphite, and acid-chlorite pulping experiments are listed in Table 1 and are shown graphi-

TABLE 1

Percent Delignification Values for Pulping of Middle Lamella, Secondary Wall and Whole Wood Fractions of Black Spruce

	% Delignification								
	KRAFT			SULPHITE			CHLORITE		
Time (h)	SW[1]	ML[2]	WW[3]	SW	ML	WW	SW	ML	WW
0.25	82	47	69	-	-	-	-	-	-
0.5	-	56	76	-	-	-	-	-	-
0.75	96	66	84	-	-	-	-	-	-
1.0	-	-	88	6	18	15	18	13	16
1.25	99	-	-	-	-	-	-	-	-
1.5	-	76	95	-	-	-	-	-	-
2.0	-	-	-	48	22	43	40	34	38
2.5	100	82	99	-	-	-	-	-	-
3.0	-	83	-	82	45	75	55	45	49
3.5	-	-	100	-	-	-	-	-	-
4.0	-	88	-	97	64	90	-	-	-
5.0	-	-	-	-	-	-	91	51	83
6.0	-	-	-	100	90	98	-	-	-
7.0	-	-	-	-	-	-	100	57	90

[1] SW: Secondary Wall

[2] ML: Middle Lamella

[3] WW: Whole Wood

cally in Figures 1, 2 and 3, respectively. In all cases the secondary wall lignin was dissolved faster than was the lignin from the middle lamella. The dashed line in each plot was calculated by combining the data for the secondary wall and middle lamella lignins. It has been shown by Fergus et al.[15] that 77% of the lignin in black spruce wood is present in the secondary wall and 23% in the middle lamella region. This proportion was used to calculate what the delignification of the whole wood should be, at a given time during

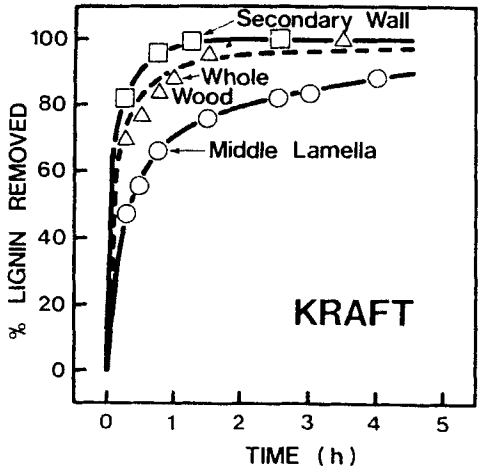

FIGURE 1. Plot of % delignification versus time for kraft pulping of wood tissue fractions. All points are experimental. The dashed line for whole wood was obtained by combining the data for the secondary wall and middle lamella lignins.

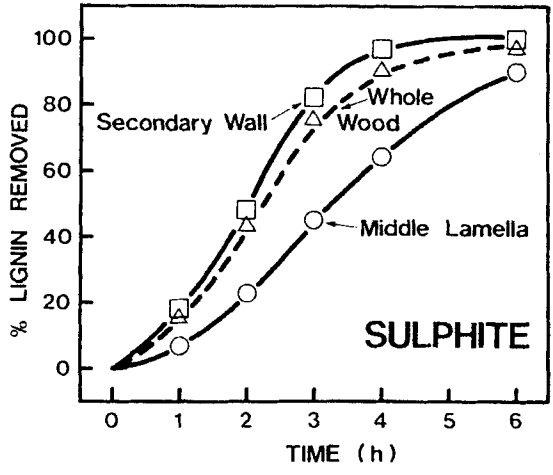

FIGURE 2. Plot of % delignification versus time for acid-sulphite pulping of wood tissue fractions. All points are experimental. The dashed line for whole wood was obtained by combining the data for the secondary wall and middle lamella lignins.

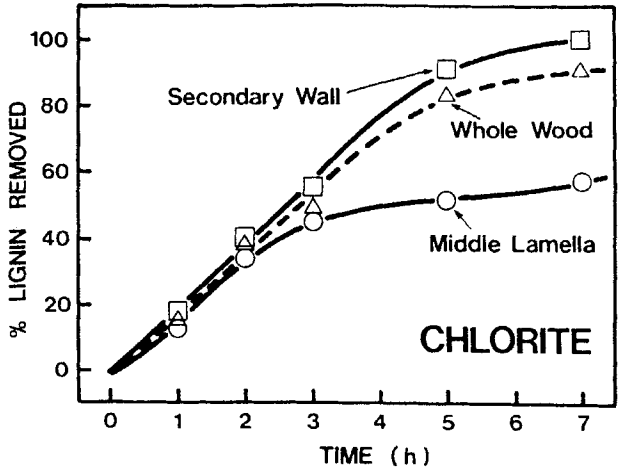

FIGURE 3. Plot of % delignification versus time for acid-chlorite pulping of wood tissue fractions. All points are experimental. The dashed line for whole wood was obtained by combining the data for the secondary wall and middle lamella lignins.

the treatment. The fit of the calculated lines to the experimental points for whole wood is good.

The topochemical effect may also be illustrated by plotting the percent delignification from the middle lamella and secondary wall versus the percent delignification from the whole wood, as in Figure 4. The percent delignification of wood was obtained from the calculated whole wood extraction curves in Figures 1-3. Figure 4 demonstrates that the topochemical effects follow, in general, the trends as reported previously[6,7] (Figure 5). But there are some differences in detail. The most important difference is that in previous acid-chlorite experiments[7] no topochemical effect was noted. However, in this work a small topochemical effect was noted up to about 50% delignification, after which the topochemical effect increased dramatically.

DISCUSSION

Figure 4 clearly demonstrates that the topochemical effect is present in kraft and acid-sulphite pulping, in agreement with the

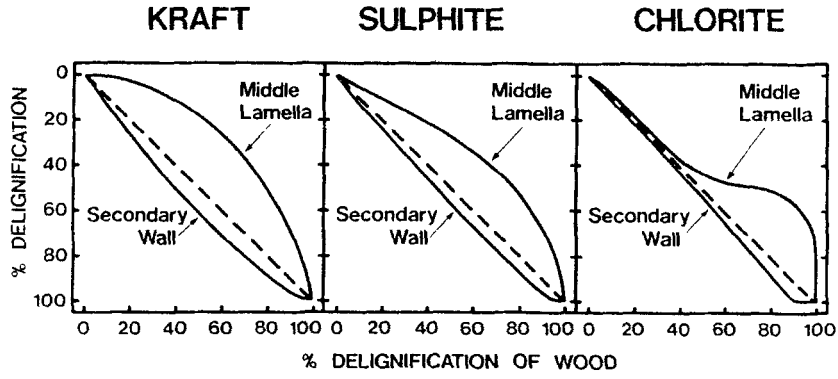

FIGURE 4. Plot of percent lignin removed from the middle lamella and secondary wall of black spruce versus percent lignin removed from the whole wood. The dashed 45° line represents whole wood versus whole wood.

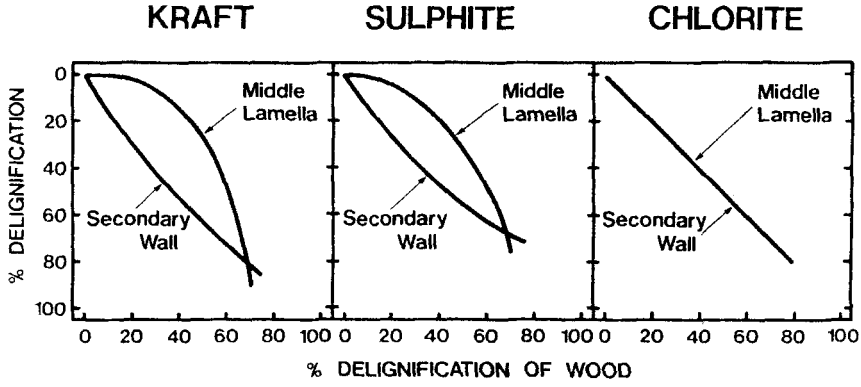

FIGURE 5. Plot of percent lignin removed from the middle lamella and secondary wall of black spruce versus percent lignin removed from the whole wood as determined microscopically[7].

results reported previously[6,7]. The topochemical effect is greater in kraft pulping than in acid-sulphite pulping, also in agreement with previous results[6,7]. The shape of the curves in Figure 4 are almost identical to those presented by Wood et al.[7] at low delignifications (see Figure 5). At higher delignification, significant deviations occur. Wood et al.[7] discussed the difficulties involved in measuring microscopically the lignin content in pulps at high delignifications. The main problem is that the lignin content in the middle lamella is not uniform at high delignification and measurement of the average lignin content is difficult. Also, as the lignin content decreases, the low sensitivity of the microscopic technique leads to large errors. The accuracy of the present method is illustrated by the agreement, even at high delignification, between the calculated and experimentally observed data for whole wood in Figures 1, 2 and 3.

Wood et al.[7] also found that there was no topochemical effect in the delignification of black spruce by chlorite pulping (Figure 5). This observation was supported in the present work since only a small effect was found at delignifications less than fifty percent. However, at high delignifications a large increase in the topochemical effect was noted as shown by the curves for acid-chlorite in Figure 4. Wood et al.[7] found no such effect, probably as a result of the problems encountered in the ultraviolet microscopic method at high delignification.

The reason for the sudden increase in the topochemical effect halfway through an acid-chlorite cook is not known with certainty. However, the effect may be related to the discovery by Ahlgren et al.[16] that above 50% delignification with chlorite, the average pore size in the secondary wall increases. This increase in pore size coincides approximately with a significant removal of hemicelluloses from the cell wall[17]. It is possible, therefore, that the removal of hemicelluloses from the cell wall, at high delignifications, may cause the increase in the topochemical effect observed in chlorite pulping.

Removal of hemicelluloses has also been related to the topochemistry in the kraft and sulphite pulping. Wood et al.[7] estimated the topochemical effect by measuring the area bound by the middle lamella and secondary wall delignification curves in Figure 5 up to 33% delignification. This area, normalized to unity for kraft, was plotted against the percent carbohydrate removed, to give the linear trend shown by the filled points in Figure 6. The data shown in Figure 4 were analyzed in the same manner and these points are also shown in Figure 6. Considering the totally different experimental methods used, we can claim good agreement between the present and previous results.

CONCLUDING REMARKS

Although the reasons for the existence of the topochemical effect are not completely clear, we can make some speculations based on the experimental evidence. There seem to be two factors involved in the dissolution of lignin from the middle lamella and secondary

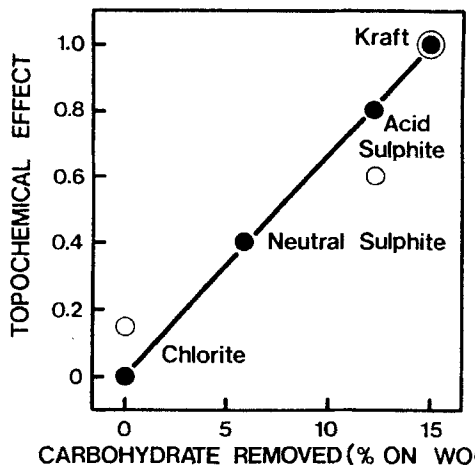

FIGURE 6. Plot of normalized topochemical effect versus percent removal of carbohydrate at 33% delignification of whole wood.
Legend: ● Data presented by Wood et al.[7].
○ Data from present work.

wall of wood. Firstly, there are likely to be inherent chemical differences in the lignin itself in the middle lamella and secondary wall (e.g., the content of phenolic hydroxyl groups[18,19] or the degree of crosslinking[20]). These differences cause the middle lamella lignin to be less reactive than the secondary wall lignin. Secondly, dissolution of hemicelluloses from the secondary wall during pulping increases the size of the pores in the wall and thereby allows the secondary wall lignin to be removed more quickly[8]. Thus, in a process such as kraft, in which the hemicellulose is rapidly removed, the reactive secondary wall lignin is dissolved more rapidly than the unreactive middle lamella lignin. However, when the hemicellulose is retained, as in chlorite, the lignin is "sealed" in the secondary wall and seems to dissolve initially at about the same rate as the middle lamella lignin. Thus, there are both physical and chemical factors involved in topochemical behavior, and the observed topochemistry is the result of an interplay of these factors. It may be possible, eventually, to find ways of treating wood chemically so that the middle lamella dissolves more rapidly than the secondary wall lignin. Such behavior could lead to methods of chemical defibration of wood as yet unexplored.

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