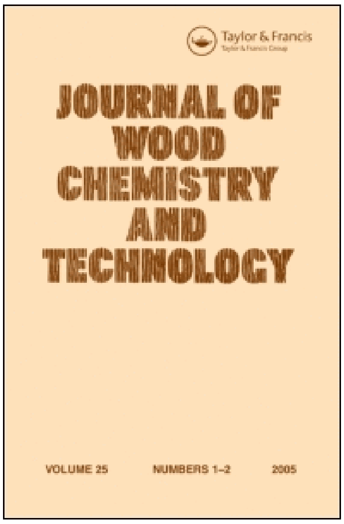

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Barry, R. M. and Bolker, H. I.(1987) 'The Topochemistry of ACID-Sulphite Pulping a Theoretical Analysis Part II', Journal of Wood Chemistry and Technology, 7: 1, 25 — 32
To link to this Article: DOI: 10.1080/02773818708085250
URL: http://dx.doi.org/10.1080/02773818708085250

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 7(1), 25-32 (1987)

THE TOPOCHEMISTRY OF ACID-SULPHITE PULPING
A THEORETICAL ANALYSIS
PART II

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ABSTRACT

Recent results of Whiting and Goring on the acid-sulphite pulping of isolated middle-lamella and secondary-wall tissues of spruce wood have permitted a new theoretical analysis of the topochemistry of delignification. Unlike the previous data obtained by U.V. microscopy of thin wood sections, the new results did not require the postulation of a different reaction rate constant in each morphological region. By assuming only that the crosslink density of the secondary wall was about 0.75 of that of the middle lamella, gel degradation theory provided a good fit to the experimental points. This analysis suggests that the topochemical effect observed in acid-sulphite pulping is determined solely by lignin chemistry. The contrast in the conclusions derived from the two sets of data leads to consideration of which of the data sets is more representative of the topochemistry in the pulping of intact wood.

INTRODUCTION

We have recently demonstrated[1] how the mathematical theory of degelation, using limited assumptions, can provide a good fit to the experimental data[2] on the topochemistry of the acid-sulphite delignification of thin wood sections. Whiting and Goring[3] have since developed a technique which gives almost complete separation

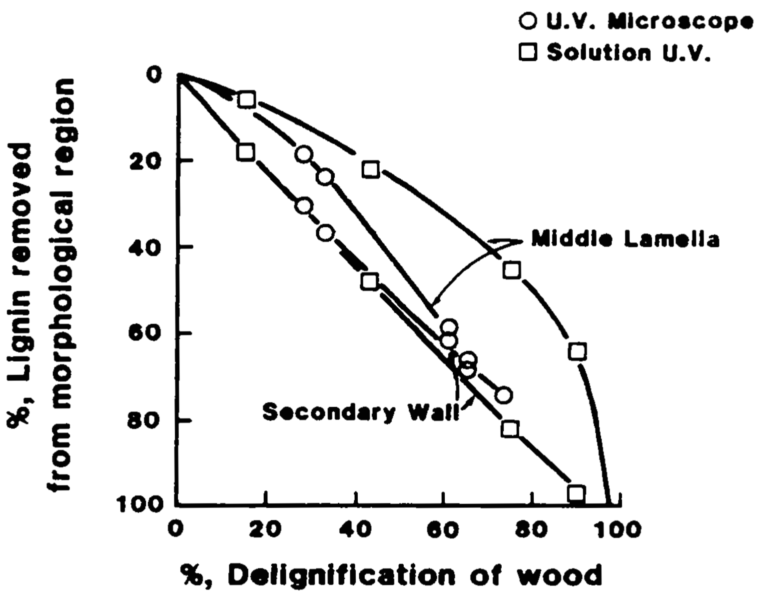

FIGURE 1. Comparison of the topochemical effect measured on isolated tissue fractions[3] and in situ by U.V. microscopy[2].

of middle-lamella and secondary wall tissues, and have pulped each tissue separately. The results differ somewhat from the previous data, particularly at high levels of delignification. The difference is shown in Figure 1, which is a graph of the extent of delignification in the middle lamella, $(w_s)_{ml}$, and secondary wall, $(w_s)_{sw}$, plotted against the extent of delignification in the whole wood, $(w_s)_t$.

Since preliminary calculations suggested that analysis of the new data might permit a simplification of the previous assumptions concerning the structure and reactivity of lignin, a detailed investigation was undertaken.

RESULTS AND DISCUSSION

The theory of Bolker and Brenner[4] proposes that lignin behaves during acid-sulphite delignification as if it were composed of stable chains joined by cleavable benzyl-ether crosslinks. Three parameters define the mathematical expression of the theory: i) the degree of polymerisation of the preformed chains (y), ii) the initial degree of crosslinking (ρ'), and iii) the rate constant of crosslink cleavage (k).

It was found previously[1] that a good fit could be obtained to the experimental data by assuming that y was the same in each morphological region, while ρ' and the rate constant were different. More precisely, it was assumed that the crosslink cleavage was a first order reaction, with its rate determined by crosslink density, but with different rate constants for the reaction in each morphological region. This was expressed mathematically for time, t, by Equation 1 which was rearranged to give Equation 2. The values obtained for ρ'_{sw}/ρ'_{ml} and k_{sw}/k_{ml} were 0.5 and 0.64 respectively.

$$t = \frac{\ln(\rho'_{sw}/\rho_{sw})}{k_{sw}} = \frac{\ln(\rho'_{ml}/\rho_{ml})}{k_{ml}} \qquad (1)$$

$$\ln(\rho'_{sw}/\rho_{sw})/\ln(\rho'_{ml}/\rho_{ml}) = k_{sw}/k_{ml} \qquad (2)$$

It has now been found that the best fit to the new data is given by the same scheme but with changed values of ρ'_{sw}/ρ'_{ml} and k_{sw}/k_{ml}. New values of 0.64 for ρ'_{sw}/ρ'_{ml} and 0.873 for k_{sw}/k_{ml} gave the lowest percentage standard deviation (see Calculations). The excellent match between the experimental data and the theoretical scheme is shown in Figure 2.

These calculations brought the best value for the ratio of k_{sw} to k_{ml} rather close to a value of 1. If the ratio is given the value of 1, then a considerably more exacting theoretical scheme is introduced in which the rate constants for the crosslink cleavage reactions (k_{sw}, k_{ml}) are assumed to be the same in each morphological region. The result from the analysis of this new scheme is illustrated in Figure 3. Although the standard deviation is higher

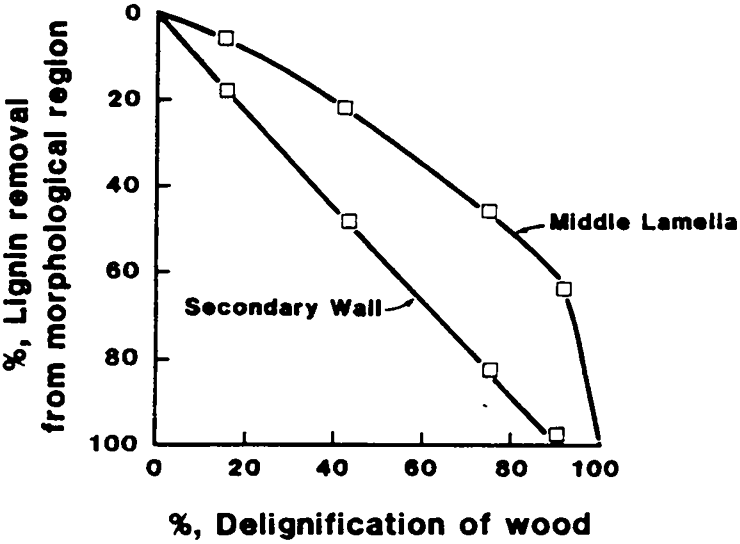

FIGURE 2. The experimental points fit the theoretical curves when $\rho'_{sw}/\rho'_{ml} = 0.64$ and $k_{sw}/k_{ml} = 0.873$ (data from Reference 3).

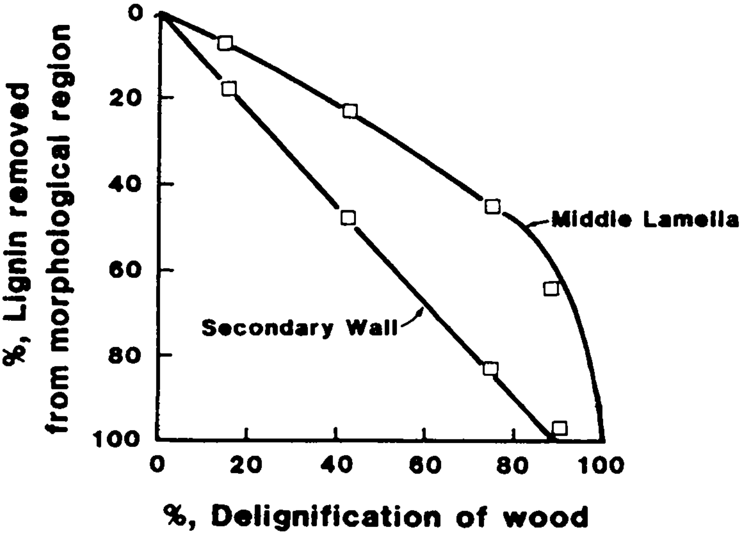

FIGURE 3. The fit to experimental points given when $k_{sw}/k_{ml} = 1$ and $\rho'_{sw}/\rho'_{ml} = 0.764$ (data from Reference 3).

than in the best fit, the match between experiment and theory is good considering the very restrictive assumptions being made. This result contrasts with the analysis of the older data which were very poorly described when k_{sw} was made equal to k_{ml}. The new scheme predicts that the ratio of benzyl-ether crosslinks in the secondary wall and middle lamella, ρ'_{sw}/ρ'_{ml}, is about 0.75.

If Whiting and Goring[3] are correct in saying that their new results are indeed more accurate, rather than simply different, then the new analysis suggests that the topochemical effect exhibited in acid-sulphite pulping is solely dependent on the degrees of crosslinking in the two regions and that the presence or absence of any other wood component does not affect the course of delignification in either the secondary wall or the middle lamella as long as the wood has been saturated with liquor before cooking. An alternative hypothesis, however, is that the isolation of tissue fractions from the wood matrix removes the physical barriers contributing to the topochemical effect, thus leaving only chemical factors to affect the system. If this hypothesis is valid, then the original data constituted a better description of what was occurring during the pulping of intact wood.

CALCULATIONS

TABLE OF SYMBOLS

w_g - extent of delignification
ρ' - initial degree of crosslinking
ρ - crosslink density
y - degree of polymerisation of crosslinked chains
k - rate constant of crosslink cleavage
f - weight fraction of lignin
F - fraction of crosslinks
t - total wood
sw - secondary wall
ml - middle lamella

By taking arbitrary values of ρ'_{sw}/ρ'_{ml}, ρ'_{sw} and ρ'_{ml} were calculated from Equation 3, where $\rho'_t = 0.277^4$, $f_{sw} = 0.762^5$, $f_{ml} = 0.238^5$ and f = weight fraction of lignin.

$$\rho'_{sw} = \rho'_t \;/\; (f_{sw} + f_{ml}\ (\rho'_{ml}/\rho'_{sw}) \qquad (3)$$

$$w_s = [1 - \rho(1 - w_s)]^y \qquad (4)$$

With these values of ρ'_{sw} and ρ'_{ml} and those of ρ_{ml} and ρ_{sw} obtained using Equation 4. , Equation 2 was used to calculate k_{sw}/k_{ml} at each total extent of delignification. Changing the value of ρ'_{sw}/ρ'_{ml} changed the mean value of k_{sw}/k_{ml} and also its relative standard deviation. When ρ'_{sw}/ρ'_{ml} was set to 0.64, the lowest standard deviation of k_{sw}/k_{ml} was obtained. This value of ρ'_{sw}/ρ'_{ml} gave the best fit of theory to experiment.

In the calculation where k_{sw} and k_{ml} were made equal, Equation 1 was simplified to Equation 5, and the mean of the ratios of ρ_{sw}/ρ_{ml} at each extent of delignification was calculated.

$$\rho'_{sw}/\rho'_{ml} = \rho_{sw}/\rho_{ml} \qquad (5)$$

In both schemes, calculating the degree of crosslinking when a given fraction (F) of crosslinks remain permitted determination of $(w_s)_{sw}$ and $(w_s)_{ml}$ from a graph of w_s vs. ρ. By inserting these values into Equation 6, the total degree of delignification $(w_s)_t$ was calculated.

$$(w_s)_t = f_{sw}(w_s)_{sw} + f_{ml}\ (w_s)_{ml} \qquad (6)$$

Figures 2 and 3 are, graphs of $(w_s)_{sw}$ and $(w_s)_{ml}$, respectively, versus $(w_s)_t$.

The last point was excluded from the calculation of the mean because 100% delignification from the secondary wall likely occurred before this result was recorded.

CONCLUDING REMARKS

The analysis in this paper strengthens the evidence for the validity of two concepts. First, it reinforces the concept that lignin is a gel and that degradation of a gel explains many phenomena exhibited during pulping. In acid-sulphite pulping, the fixing of only three parameters, ($y = 18$, $\rho'_{ml} = 0.338$, and $\rho'_{sw} = 0.258$), and the application of a very specific form of gel-degradation theory permits the description of: (1) the relationship between weight-average degree of polymerisation and extent of delignification; (2) the relationship between degree of crosslinking and extent of delignification; and finally (3) the topochemical effect.

Second, the analysis supports the concept that the topochemical effect is largely if not wholly dependent on lignin chemistry during acid sulphite pulping. This conclusion can probably be extended to include the topochemical effect observed in kraft pulping. The latter would be even less likely than acid-sulphite pulping to show interference from the wood hemicelluloses — which are cited[6] as affecting the pore size and hence the rate of diffusion of soluble material from the fibre — because hemicelluloses are rapidly removed during kraft pulping[7]. The difference, then, between the magnitudes of the topochemical effects observed in kraft and acid-sulphite pulping has to be described in terms of differences in chemistry.

Even the topochemical effect observed during acid-chlorite delignification can largely be described in terms of chemistry. The results presented by Whiting and Goring[3] show there is a sudden increase in the topochemical effect halfway through an acid-chlorite cook. This was explained by invoking a surge in secondary wall delignification due to a sudden removal of hemicellulose from the secondary wall. The results of Table 1 from Reference 3, however, show that the rate of removal of lignin from the secondary wall remains constant. Delignification of the middle lamella, on the other hand, almost ceases after 50% lignin removal. This is not what one would expect if hemicellulose were causing the topochemical effect because hemicellulose concentration is highest in the secondary wall. The result obtained is rather what would be expected if the middle lamella lignin were less reactive and less tractable than the secondary wall lignin.

The topochemistry of acid-chlorite delignification may therefore be better accounted for by considering the differing phenolic content and crosslinking densities of the middle-lamella and secondary-wall lignins, differences that have been demonstrated by experimental results[8] and theoretical analysis[1].

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