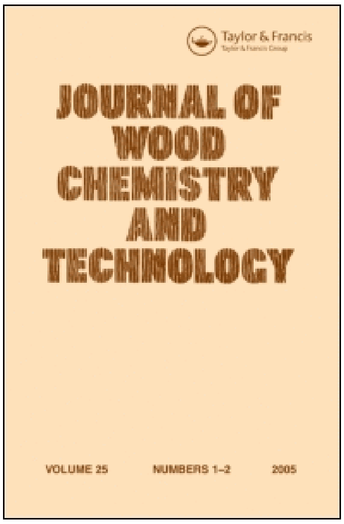


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Factors Affecting Sulphonation of Eastern Black Spruce Wood Chips

C. Heitner[a]; R. P. Beatson[a]; D. Atack[a]
[a] Pulp and Paper Research Institute of Canada, Quebec, Canada

To cite this Article Heitner, C. , Beatson, R. P. and Atack, D.(1982) 'Factors Affecting Sulphonation of Eastern Black Spruce Wood Chips', Journal of Wood Chemistry and Technology, 2: 2, 169 — 185
To link to this Article: DOI: 10.1080/02773818208085128
URL: http://dx.doi.org/10.1080/02773818208085128

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 2(2), 169-185 (1982)

FACTORS AFFECTING SULPHONATION OF EASTERN BLACK SPRUCE WOOD CHIPS

C. Heitner, R.P. Beatson and D. Atack

Pulp and Paper Research Institute of Canada,
570, St. John's Boulevard,
Pointe Claire, Quebec, Canada, H9R 3J9.

ABSTRACT

Eastern black spruce, *Picea mariana*, chips have been treated to high yields, at temperatures from 72° to 150°C with sulphite solutions of pH 7 and total SO_2 concentrations from 0.1 to 1.0 mol L^{-1}. The rate of sulphonation of black spruce chips is directly proportional to the product of concentration of sites available for sulphonation and the total SO_2 concentration. The energy of activation for sulphonation is 62.6 ± 2.3 kJ mol^{-1}. The rate of lignin dissolution at pH 7 is dependent only upon the temperature. High total SO_2 concentrations are necessary for the efficient production of high strength ultra-high yields pulps. It is postulated that sulphonation at pH 7 is governed by a rate limited addition of bisulphite to quinone methide intermediates formed from phenolic lignin units.

INTRODUCTION

Ultra-high yield chemimechanical pulps (CMP) and chemithermomechanical pulps (CTMP), produced by sulphite treatment of wood chips prior to refining, have recently grown in importance especially as replacements for low yield chemical reinforcement pulps in newsprint furnishes [1]. Previous work has shown that the strength properties of handsheets made from these ultra-high yield pulps are dependent on their sulphonate content [2]. As sulphonate contents are increased to values above about 1.0 per cent on O.D. pulp both breaking length and tear index increase rapidly with increasing sulphonate content. Thus, in order to produce strong CTMP and CMP in high yield it is necessary to maximize the sulphonation and minimize the yield losses occurring in the sulphite treatment. This requires a thorough understanding of the factors governing the sulphonation reaction.

Studies on the sulphonation reaction began in the late nineteenth century[3] when it was recognized that lignin combined with sulphur during sulphite pulping. Although early research concentrated on the role of sulphonation in delignification, several parameters important to sulphonation in high yield pulping were delineated. It was shown that about one per cent sulphur on wood was obtained by treating Douglas fir sawdust with acid sulphite at 130° for two hours[4] and by treating spruce sawdust with neutral sulphite, pH 6, for five hours[5]. Further sulphonation, expressed in terms of residual lignin, occurred at a much lower rate. It was also noted[5] that higher bisulphite concentrations gave pulps containing more highly sulphonated lignin.

More detailed results were obtained by Lindgren[6] in a study covering the pH range 4 to 9. In this study it was noted that a rapid sulphonation of spruce sawdust, to a level of 0.75 per cent sulphur on wood, occurred during the first hour to be followed by slow sulphonation, to about one percent sulphur on wood, during the next five hours. Further sulphonation occurred at an extremely low rate.

Similar observations by Mikawa[7] and Nokihara[8] were interpreted in terms of two concurrent reactions between the sulphite solution and lignin, each accounting for 1.9 per cent sulphur on lignin and having rate constants, at 135°C, of 5.4×10^{-2} min^{-1} and 4.7×10^{-3} min^{-1}. The activation energies for the two reactions were determined to be 69.1 and 146 kJ mol^{-1} respectively.

Despite these studies there are crucial gaps in our knowledge and understanding of the sulphonation reactions which need to be filled before the sulphonation of lignin in wood prior to refining can be optimized. Quantitative data on the effect of sulphite concentration, particularly during the initial stages of the sulphonation of wood chips, are required.

A study of the sulphonation of spruce chips at pH 7, over a range of temperature and total SO_2 concentration is described.

EXPERIMENTAL

Preparation of Waferized Chips

Logs of black spruce, *Picea mariana*, obtained from the North Western region of Quebec, were debarked and reduced to waferized chips using a prototype Domtar Axial Feed Waferizer. The chips were screened on an Overstrom Texas

Shaker Screen using a screen plate with 32 mm diameter perforations and 40 per cent open area. Average dimensions of the accepted chips were approximately 18 mm square by 3.6 mm. The chips were stored at about 3°C in polyethylene bags prior to use.

Preparation of Sulphite Cooking Liquors

The sulphite liquor, 1.0 mol L^{-1} in total SO_2, was prepared by dissolving 104g of analytical grade sodium bisulphite and 33.3 g of sodium hydroxide in one litre of deionized water. Liquors with the lower concentrations shown in Table 3, were prepared in a similar manner using the requisite amounts of bisulphite and hydroxide. For all liquors the ratio of total to combined SO_2 was 1.14 giving a pH close to 7.

Treatment of the Chips

a) At temperatures of 120, 140 and 150°C

Approximately 10g OD of waferized chips were thoroughly soaked by repeated evacuation whilst immersed in deionized water over a period of 7 days at room temperature. The soaked chips were transferred to a 250 mL stainless steel bomb and soaked for 24 hours, at room temperature, in 220 mL of cooking liquor. The bomb was immersed in a pre-heated constant temperature bath and the timing begun. The liquor in the bomb reached temperature, as determined by a thermocouple, in approximately 12 minutes.

After treating the chips for predetermined times, up to 100 minutes at 150°C, the bomb was quickly cooled and the chips were removed and washed by repeated soaking in deionized water until no more sulphite was eluted, as determined by a permanganate test. Defibration in a Waring Blendor, followed by further washing with deionized water and drying to constant weight, gave the treated wood in yields between 94 and 99 per cent.

b) At temperatures of 72° and 80°C

The procedures were similar to those used for the higher temperature treatments except that they were conducted for longer times, up to 3000 minutes at 80°C, in glass containers and the cooking liquor was preheated.

Treatment of Methylated Wood Meal

The procedure was similar to that used in chip treatments except that only 0.2 to 0.5 g OD wood meal was used and the time of water soaking was reduced to about 24 h.

Determination of Sulphonate Content of Sulphite Treated Wood

The treated wood was analyzed for sulphur according to CPPA Technical Section Standard Method G28. Assuming the sulphur analyzed exists as the sulphonate group[9], the sulphonate content as SO_3^- could be calculated as,

Sulphonate content of treated wood = sulphur content x 2.5

During the treatments the lignin content drops from 27 to 25 percent with a mean of 26.2 per cent, thus to a good approximation;

Sulphonate content of the lignin (per cent)
= sulphur content of treated wood x 2.5 x 100/per cent lignin on pulp.
= sulphur content x 2.5 x 3.82.

Determination of Lignin Content of Treated Wood

The acid insoluble lignin content of the treated wood was determined by CPPA Technical Section Method G9. The acid soluble lignin in the pulp was determined as described in the Tappi Useful Method UM250.

Analysis of Spent Liquor

Dissolved lignin

The quantity of lignin dissolved during the treatment was estimated by acidifying a sample of the spent liquor with H_2SO_4, and removing the dissolved SO_2 by bubbling air through the solution for 30 minutes. The dissolved lignin was then determined by measurement of the absorption at 205 nm, assuming an absorptivity of 100 L g^{-1} cm^{-1} for sulphonated spruce lignin.

SO_2 concentration

The total and free SO_2 concentrations were determined iodometrically by the method of Palmrose[10].

Methylation of Wood Meal

Black spruce wood meal (40-60 mesh) was extracted with Tetrahydrofuran (THF) under nitrogen for 24 h in a Soxhlet apparatus. Diazomethane (CH_2N_2) was generated as an alcohol-free ether solution from N-methyl-N-nitroso-p-toluenesulfonamide (25 g), and used immediately. Portions of the ice-cold, CH_2N_2 solution (25-50 mL) were added to a thick slurry of wood meal (25 g OD) in THF at 25°C. Evolution of nitrogen was vigorous and the yellow colour was soon discharged. Excess solvent was poured off from the wood meal slurry as the reaction progressed. The reaction slowed noticeably only towards the end of the additions in spite of the large excess of CH_2N_2 (25-30 times the phenolic content of wood [11]). After all colour was discharged from the final addition, the wood meal was filtered, washed with fresh ether and air dried.

Klason lignin content of the methylated wood meal was 28.8%.

Methoxyl content for the extracted wood meal and methylated wood meal were 4.12 and 7.19 per cent respectively.

RESULTS

Sulphonate Content of Sulphite Treated Black Spruce Chips

As shown in Figures 1 and 2, the rate of sulphonation decreases as the reaction proceeds. At higher temperatures and total SO_2 concentrations the reaction rate approaches zero at a sulphonate content of 1.95 per cent on OD treated wood, while at lower temperatures the rate approaches zero at 1.45 per cent sulphonation. Also, the reaction rate increases with increasing total SO_2 concentration and increasing temperature.

Sulphonate Content of Sulphite Treated Black Spruce Methylated Wood Meal

As shown in Figure 3, methylation of spruce wood meal with diazomethane inhibits sulphonation at pH 7 and 140°C with sulphite liquor 1.0 mol L^{-1} in total SO_2. The plateau in sulphonate content for methylated wood meal is only 30 per cent of that for non-methylated wood meal.

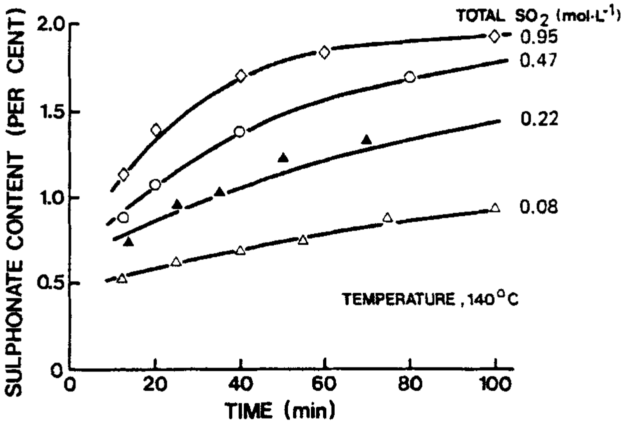


Figure 1. The rate of sulphonation of black spruce chips, at 140° and pH 7, decreases with increasing sulphonate content and decreasing total SO_2 concentration and approaches zero at a sulphonate content of 1.95 per cent on OD treated wood.

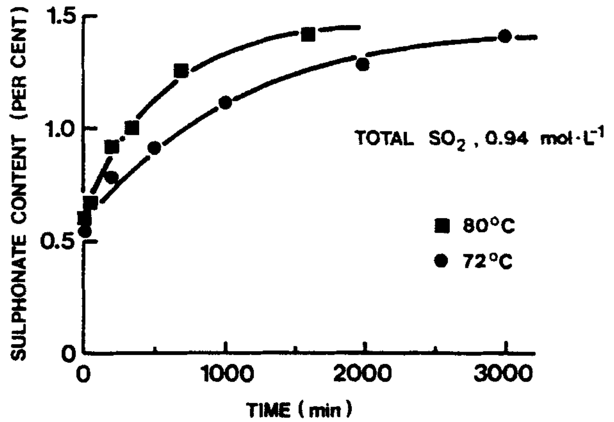


Figure 2. At low temperatures and a total SO_2 concentration of 0.94 mol L^{-1}, the rate of sulphonation approaches zero at sulphonate content of 1.45 per cent on OD treated wood.

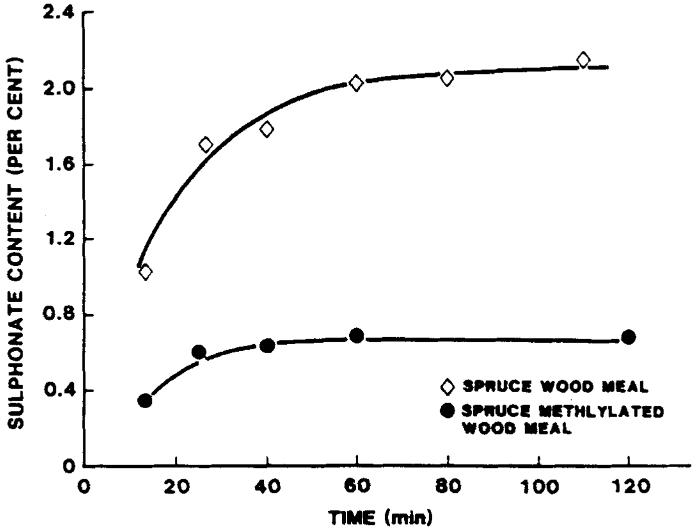


Figure 3. Methylation with diazomethane inhibits sulphonation at 140°C and total SO_2 concentration of 1.0 mol L^{-1}.

Yields and Lignin Contents of Sulphite Treated Black Spruce Chips

Table 1 shows that as the treatment is prolonged more lignin is dissolved in the liquor, the lignin content and yield of treated wood decrease and more soluble lignin is found in the treated wood. At the plateau in sulphonate content, decreases of 1 to 2 per cent in lignin content were observed and the yields of treated wood ranged from 96 per cent at 80°C to 93 per cent at 150°C.

For each temperature shown in Figure 4 the data points cover total SO_2 concentrations from about 0.2 to 1 mol L^{-1} and wood sulphonate contents of 0.70 to 1.95 per cent. Thus, at a given temperature the lignin is dissolved in the liquor at a constant rate which is independent of both sulphite liquor concentration and the sulphonate content of wood. The rate constants given in Table 2 show that the rate of lignin solution increases by about 40 per cent for every 10°C rise.

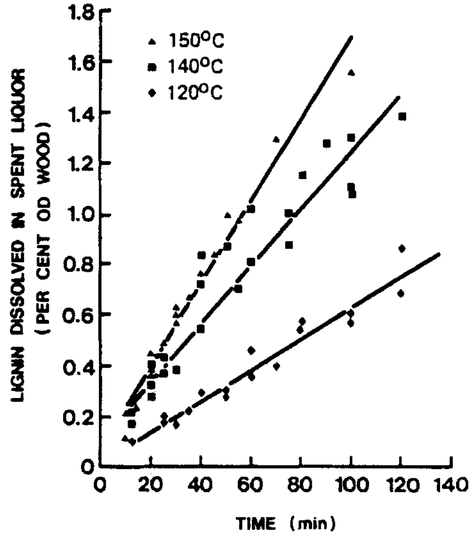


Figure 4. The amount of lignin dissolved is a linear function of time for a range of total SO_2 concentrations and wood sulphonate contents. The rate at which lignin is dissolved increases with increasing temperature.

TABLE 1

The Relationship Between Yield, Dissolved Lignin and Total Lignin During a Typical Treatment of Black Spruce Chips with 1.0 mol L^{-1} Sulphite Solution at 140°C and pH 7.

Duration of Treatments (min)	Yield (%)	Lignin Dissolved (%)	Lignin content Klason (%)	Soluble (%)	Total (%)	Sulphur Content (%)
12	99	0.17	26.5	0.48	27.0	0.44
20	98	0.32	25.8	0.71	26.5	0.56
30	98	0.38	26.1	0.83	26.9	0.63
40	97	0.72	26.1	0.99	27.1	0.66
60	97	1.02	24.7	1.19	25.9	0.76
90	96	1.28	23.6	1.25	24.9	0.78

TABLE 2
The Rate of Lignin Dissolution Increases by about 40 per cent for Each 10°C Increase in Temperature.

Temperature of treatment (°C)	Rate of lignin dissolution (per cent per min.)
150	1.63×10^{-2}
140	1.15×10^{-2}
120	6.03×10^{-3}

ANALYSIS OF RESULTS

The results show that the rate of sulphonation of the wood chips is a function of the extent of sulphonation, the total SO_2 concentration and the temperature.

For a given temperature we may postulate the dependence to take the form

$$\frac{dS}{dt} = k\,(S_P - S)^a\,[SO_2]^b \tag{1}$$

where S_P is the per cent sulphonate at the plateau in the sulphonation reaction

S is the per cent sulphonate at time t, and hence $(S_P - S)$ is a measure of the sites available for sulphonation

$[SO_2]$ is the total SO_2 concentration

a and b are parameters describing the sensitivity of the reaction rate to the extent of sulphonation and total SO_2 concentration respectively.

As sulphite is present in a large excess $[SO_2]$ remains constant and equation 1 becomes

$$\frac{dS}{dt} = k'\,(S_P - S)^a \tag{2}$$

where

$$k' = k\,[SO_2]^b \tag{3}$$

It was found that the data approximated the curve described by the integrated form of Equation 2 with a = 1. This equation is shown below

$$S = S_P - (S_P - S_O)e^{-k't} \tag{4}$$

where S_O is an adjustable parameter which takes into account the sulphur incorporated during impregnation and warm-up. S_P is obtained by extrapolation of experimental data, obtained at high total SO_2 concentrations, to infinite time. Values of k′ and S_O, obtained from plots of ln (S_P — S) versus t, are given in Table 3.

At temperatures of 120 to 150°C the value of S_P is 1.95 per cent and the value of S_O is 0.60 ± 0.10 per cent. High values of S_O occur at 120°C where the fit of the initial sulphonate contents to the equation is poor. At temperatures of 72 and 80°C the value of S_P is lower at 1.45 per cent but S_O remains the same at around 0.60 per cent.

Figure 5 shows plots of k′ versus total SO_2 concentrations for treatments at different temperatures. From these plots it is evident that k′ and the total SO_2 concentration are directly proportional and hence b = 1. Table 4 gives the values of k obtained from the slope of the straight lines and from point values at 72° and 80°C assuming that b also has a value of 1 at these temperatures. As shown

TABLE 3
The Pseudo First Order Rate Constants (k′) for Sulphonation of Waferized Black Spruce Chips at pH 7.

Temperature (°C)	S_P (%)	Total SO_2 Concentration (mol L^{-1})	k′ (x 10^{-2} min^{-1})	S_O (%)
150	1.95	0.96	6.24	0.50
		0.72	4.45	0.63
		0.46	3.09	0.53
		0.22	1.52	0.55
140	1.95	0.95	4.08	0.60
		0.70	2.74	0.60
		0.47	2.01	0.63
		0.22	1.03	0.64
		0.08	0.37	0.48
120	1.95	0.95	1.31	0.75
		0.71	9.76×10^{-1}	0.78
		0.47	5.87×10^{-1}	0.73
		0.21	3.71×10^{-1}	0.63
80	1.45	0.95	2.00×10^{-1}	0.60
72	1.45	0.93	9.23×10^{-2}	0.58

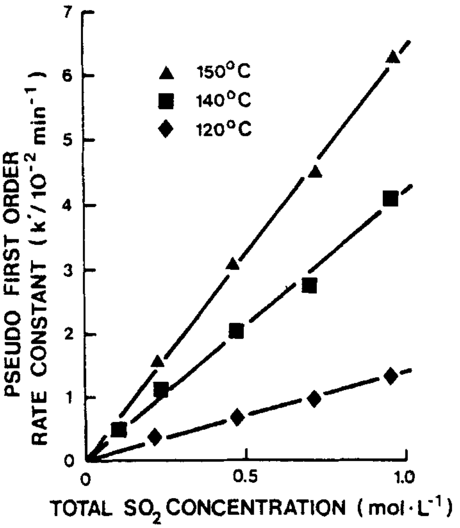


Figure 5. The rate of sulphonation is directly proportional to the total SO_2 concentration.

TABLE 4

The Second Order Rate Constants for Sulphonation of Waferized Black Spruce Chips at pH 7.

Temperature (°C)	k (10^{-2} L mol^{-1} min^{-1})
150	6.44 ± 0.11
140	4.19 ± 0.00
120	1.40 ± 0.04
80	0.211*
72	9.92 x 10^{-2} *

* From measurements at one total SO_2 concentration.

in Figures 1 and 2 there is a good fit of the experimental points to the curves calculated using these second order rate constants.

The dependence of k on temperature, which is evident in Table 4 can be expressed in terms of the Arrhenius Equation

$$\ln k = \ln A - E/RT \qquad (5)$$

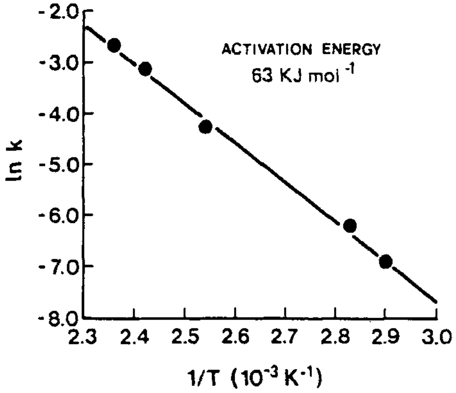


Figure 6. The sulphonation reaction gives a linear Arrhenius plot over the temperature range 72° to 150°C.

where		
	A	is a constant, the frequency factor
	E	is the activation energy
	R	is the gas constant
	T	is the absolute temperature

The plot of ln k versus 1/T shown in Figure 6 is linear in accord with Equation 5 and gives an activation energy of 62.6 ± 2.3 kJ mol^{-1}.

DISCUSSION

The results show that at temperatures of 120° to 150°C it is possible to obtain sulphonate contents of 1.95 per cent on treated wood with yields in excess of 95 per cent. The resulting lignin losses are small, of the order of 2 per cent. This rapid sulphonation prior to significant lignin loss is in accord with the results of Hägglund[5], Lindgren[6], Mikawa[7] and Nokihara[8] on spruce sawdust and spruce wood meal, thus indicating that well impregnated chips behave in a similar manner to the wood meal and sawdust. Also as shown in Table 5 at temperatures of 95°, 120° and 137°C, the values of the second order rate constants calculated from the present data are very close to those obtained by Nokihara[8] for the rapid step in the sulphonation of lignin in spruce wood meal.

TABLE 5
A Comparison of the Rate Constants Obtained in this Study with those of Nokihara[8].

Temperature (°C)	Rate Constant (10^{-3} L mol^{-1} min^{-1}) A Data from this study on spruce chips	 B Calculated from the 'first' order rate constants of Nokihara[8]
95	4.17	4.30
120	16.2	17.5
137	34.4	43.7

The dependence of the rate of sulphonation of spruce chips on the product of the concentration of sites available for sulphonation and the total SO_2 concentration indicates that a single mechanism operates between sulphonate contents of 0.50 to 1.95 per cent and total SO_2 concentrations of 0.1 to 1.0 mol L^{-1}. This is corroberated by the linear Arrhenius plot. The kinetic data indicate that sulphonation of lignin with sodium sulphite at pH 7 is governed by a nucleophilic attack of sulphite on lignin in which the transition state for the rate determining step involves bond formation between the sulphite anion and one lignin site.

Model compound studies[3, 12] have shown that neutral sulphite reacts with lignin propane side chains activated by para phenolic groups or carbonyl groups. Figure 3 shows that methylation of phenolic groups in lignin strongly inhibits neutral sulphonation consistent with activation of neutral sulphonation by para phenolic groups. Spectroscopic studies [13] indicate that about 50 per cent of carbonyls in lignin are alpha to phenyl para alkoxy groups. Neutral sulphonation activated by such carbonyl groups would be inhibited by reduction to unreactive hydroxy groups. However, sodium borohydride reduction of lignin has little effect on sulphonation at pH 6[14]. Therefore, neutral sulphonation of lignin is activated primarily by phenolic groups para to the propane side chain.

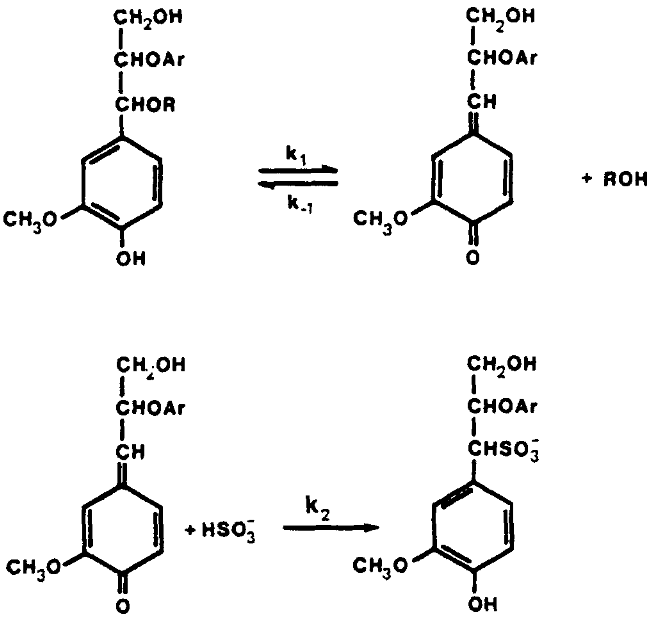
The phenolic hydroxyl content of spruce wood has been reported as 0.10 per lignin C_9 unit [11]. However, it increases to 0.16 per C_9 unit on neutral sulphite treatment to 93 per cent yield [17]. During kinetically observed sulphonations at 80° and 140°C, 0.09 and 0.12 sulphonate groups per C_9 unit were introduced respectively. Thus, there are sufficient phenolic C_9 units to account for the observed sulphonation, provided most of them bear leaving groups in the alpha position. The simplicity of the kinetics suggests that these leaving groups are the same or that any differences in them have little influence on the rate of sulphonation.

Vanillyl alcohol, a model for lignin phenolic C_9 units with the alpha position occupied by a hydroxyl group, reacts rapidly with neutral sulphite[18,19]. In a review[3] it has been implied that this reaction is first order at pH 7, however the experimental evidence [19,20] shows that sulphonation of vanillyl alcohol at pH 7 is second order, being first order in both vanillyl alcohol and sulphite. The reaction is thought to proceed through a quinonemethide intermediate[19]. Sulphonation of lignin in wood could proceed by a similar mechanism as shown in Scheme 1.

Applying the steady state assumption to this mechanism gives the rate equation

$$\text{Rate of sulphonation} = \frac{k_1 k_2}{k_{-1}\,[\mathrm{ROH}] + k_2\,[\mathrm{SO_2}]}\,(S_P - S)\,[\mathrm{SO_2}]$$

If $k_{-1}\,[\mathrm{ROH}] > k_2\,[\mathrm{SO_2}]$ and the addition of water predominates in the pre-equilibrium, this mechanism fits the present observations. Sulphonation would be first order in total SO_2 concentration and independent of the alpha leaving group.



R = H, Alkyl or Aryl

Scheme 1

The lack of dependence of lignin dissolution on total SO_2 concentration could be a result of a diffusion controlled rate, a hydrolytic cleavage totally independent on the sulphonation [21] or lignin release through breakage of alpha aryl ether bonds during formation of the quinonemethide.

The reaction of vanillyl alcohol with neutral sulphite has a rate constant for sulphonation at 90°C of 0.15 min^{-1} [18]. Assuming a total SO_2 concentration of 1 mol L^{-1}, this corresponds to a second order rate constant of 0.15 L mol^{-1} min^{-1}. In the present study the second order rate constant at 90°C is 3.25×10^{-3} L mol^{-1} min^{-1}, 46 times lower than that estimated for vanillyl alcohol. However sulphonation of vanillyl alcohol has an activation energy of 66.5 kJ mol^{-1} which is close to the 62.6 ± 2.3 kJ mol^{-1} found for spruce chips. The similarity in activation energies, but differing rate constants does not preclude a common reaction mechanism because the pre-exponential term, A in the Arrhenius equation is very sensitive to factors such as molecular size, complexity and solvation.

CONCLUSION

The first stage in the sulphonation of spruce wood chips at pH 7 has been shown to be first order in concentration of sulphonatable sites and total SO_2 concentration. The sulphonation reaction has an activation energy of 62.6 ± 2.3 kJ mol^{-1} which corresponds to a 66 per cent rate increase every 10°C rise between the temperatures of 120°C and 150°C that are commonly used for sulphite treatments. As the temperature was increased from 80° to 120°C the number of sites available for sulphonation increased. Lignin was dissolved from the wood chips more rapidly as temperature was increased. However, the rate of lignin dissolution was independent of total SO_2 concentration and the sulphonate content of the wood.

The results indicate that, at pH 7, high sulphonate contents can be obtained at lower temperatures with small lignin losses provided liquors with high sulphite concentrations are used. Higher temperatures also promote high sulphonate levels but at the expense of lower lignin contents and yields. The equations describing the dependence of the sulphonation reaction on temperature, allow the prediction of the sulphonate contents, and hence to some extent the properties of pulps obtained from sulphite treatment of chips, over a wide range of conditions.

The nature of the reaction between lignin and sulphite is thought to involve formation of a quinone methide followed by rate determining bisulphite addition to this intermediate.

ACKNOWLEDGEMENTS

We wish to thank Dr. R.D. Mortimer for the methylated wood meal, Mr. V. Berzins and his staff for sulphur and lignin analyses and Mr. N. Muradali for expert technical assistance.

The basis of this paper was presented at the Ekman-Days 1981, International Symposium on Wood and Pulping Chemistry in Stockholm, June 1981; see symposium proceedings.

REFERENCES

1. D. Atack, C. Heitner, M. Jackson and A. Karnis, Pulp and Paper, 54, (6), 70 (1980).

   M.J. Ford and P.E. Gardner, "Method of Producing Chemi-mechanical Pulps." U.S. Patent 4,116,758, September 1978.

   Y. Lemay, K. Goel, A.M. Ayroud, and B. Beaupré, "Chemi-mechanical Pulp: Yield, Refining and Quality." Prétirés Conference Technologique Estivale, Ste-Adele, Québec, Canada, June 1979.

2. D. Atack, C. Heitner and A. Karnis, Svensk Pappertstidn., 83, (5), 117 (1980).

3. D.W. Glennie, Lignins, p 597-637, K.V. Sarkanen and C.H. Ludwig, (eds.), Wiley Interscience, New York, 1971.

4. F.H. Yorston, "Studies in Sulphite Pulping" Canadian Department of Mines and Resources — Lands, Parks and Forests Branch — Dominion Forest Service Bulletin, 97, (1942).

5. E. Hägglund, The Chemistry of Wood, p 419, Academic Press, 1951.

6. B.O. Lindgren, Acta Chemica Scand., 5, 603 (1951).

7. H. Mikawa, J. Chem. Soc. Japan, Ind. Chem. Sect., 54, 741 (1951).

8. E. Nokihara, J. Agr. Chem. Soc. Japan, 26, 236, (1952).

9. J. Janson and E. Sjöström, Svensk Papperstidn., 69, 107 (1966).

10. G.V. Palmrose, Paper Trade Journal, 100(3), 38 (1935).

11. J.M. Yang and D.A.I. Goring, Can. J. Chem., 53, 2411 (1980).

12. G. Gellerstadt and J. Gierer, Acta Chem. Scand., 24, 1645 (1970).

13. E. Adler and J. Marton, Acta Chem. Scand., 13, 75 (1959).

14. J. Gierer and S. Soderberg, Acta Chem. Scand., 16, 629 (1962).

15. J. Gierer and N-H. Wallin, Acta Chem. Scand., 20, 2059 (1966).

16. R.T.E. Schenk and S. Kaizerman, J. Amer. Chem. Soc., 75, 1636 (1953).

17. J-M. Yang, W.Q. Yean and D.A.I. Goring, Cellul. Chem. Technol,. 15, 337 (1981).

18. N. Migita, H. Mikawa, J. Nonaka and M. Ichino, Kami Pa Gikyoshi, 8(1), 482 (1954).

19. L. Ivnäs and B. Lindberg, Acta Chem. Scand., 15, 1081 (1961).

20. V.M. Reznikov and S.F. Yakubouskii, Khim. Drev., 11, 61 (1972).

21. S. Häggroth, B.O. Lindberg and U. Scædan, Sven.. Papperstidn., 56(17), 669 (1953).