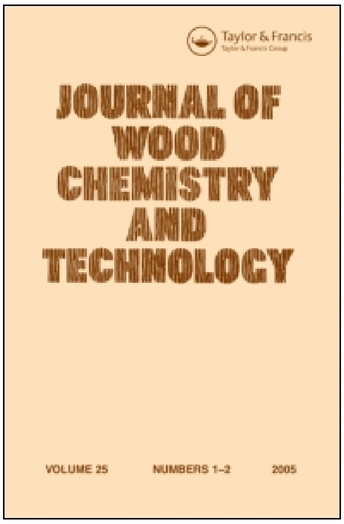

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Sulphonation of Eastern Black Spruce Chips, Part II

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SULPHONATION OF EASTERN BLACK SPRUCE CHIPS, PART II.[1]

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ABSTRACT

Eastern black spruce, *Picea mariana*, chips have been treated to high yields, at temperatures from 120° to 150°C, with sodium bisulphite solutions of pH 4 and total SO_2 concentrations from 0.23 to 1.92 mol L^{-1}. The rate of sulphonation depends on the concentration of sites available for sulphonation and total SO_2 concentration to the power of 0.4; it increases by approximately 70 percent for each 10°C temperature rise. It is postulated that sulphonation at pH 4 occurs by two mechanisms, one which is dependent on total SO_2 concentration and involves a quinonemethide intermediate and one which is independent of total SO_2 concentration and involves a carbonium ion intermediate.

The rates of yield loss and lignin loss are dependent only on temperature and approximately double for each 10°C temperature increase. High total SO_2 concentrations are necessary for efficient production of high strength ultra-high yield pulps from black spruce chips when treated with sodium bisulphite solutions.

INTRODUCTION

Ultra-high yield pulps are being used to replace more expensive, low yield reinforcement pulps in newsprint furnishes[2]. Semi-bleached kraft has been replaced by chemimechanical pulp produced by treatment of softwood chips to 90 per cent yield with

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sodium sulphite-bisulphite solutions at pH 7 to 8[3]. Unbleached sulphite pulp has been replaced by chemimechanical pulp produced by treatment of softwood chips to 85 per cent yield with sodium bisulphite solutions at pH 4 to 4.5[4]. The strength of paper made from these ultra-high yield chemimechanical pulps increases as the sulphonate content of the treated chips is increased from 1 to 2 per cent. A better understanding of the factors governing sulphonation and yield loss during sulphite treatment should assist in maximizing pulp strength while maintaining high yield.

In part I of this study of sulphonation of spruce chips it was shown that sulphonation at pH 7 depends on the concentration of active sites and the total SO_2 concentration[5]. Sulphonation is thought to occur by nucleophilic sulphite attack on quinone-methides formed from phenolic units in lignin. Dissolution of lignin was found to be independent of total SO_2 concentration.

This paper describes a study of the effects of total SO_2 concentration and temperature on sulphonation, yield and lignin losses when black spruce chips are treated at pH 4 with sodium bisulphite liquors.

RESULTS AND DISCUSSION

Sulphonate Content of Bisulphite Treated Black Spruce Chips

Treatment of waferized black spruce chips with bisulphite solutions, pH 4, at temperatures of 120° to 150°C for 12.5 to 200 minutes gives sulphonate contents, based on OD wood, from 0.23 to 2.6 per cent. Figure 1 shows typically that at 140°C the sulphonation rate decreases as the reaction proceeds, but increases as some function of total SO_2 concentration. At lower temperatures sulphonation is slower, as seen in Figure 2. The rate of sulphonation may be written quite generally as a function of the sulphonate content at time t, multiplied by the total SO_2 concentration to the power b, as seen in Equation 1.

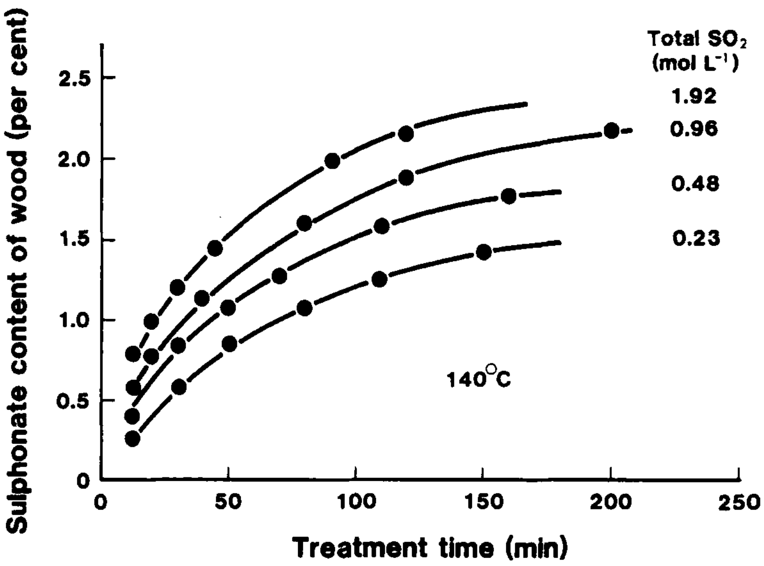


FIGURE 1. The rate of sulphonation of black spruce with sodium bisulphite at 140°C increases with increasing total SO_2 concentration.

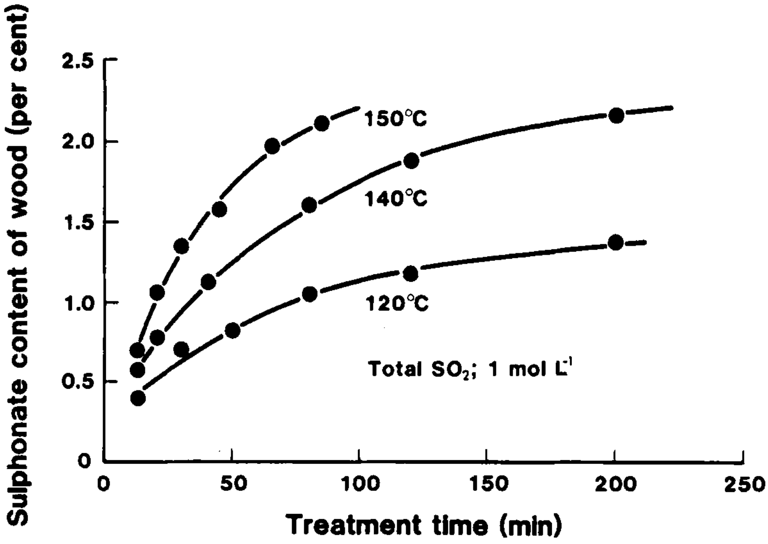


FIGURE 2. The rate of sulphonation of black spruce chips with 1 mol L^{-1} bisulphite liquors increases with increasing temperature.

$$\text{Rate of sulphonation} = f(S) \times [SO_2]^b \qquad (1)$$

where S is the sulphonate content of treated wood at time t

$[SO_2]$ is the total SO_2 concentration

b is the parameter describing the sensitivity to SO_2 concentration

A non-linear regression fit of data obtained at 140°C to Equation 1 indicated that the rate of sulphonation at pH 4 depends on the total SO_2 concentration to the power 0.39 ± 0.3. This is in contrast to sulphonation at pH 7 where the rate has a first order dependence on total SO_2 concentration.

The dependence of black spruce sulphonation on total SO_2 concentration to the power of 0.39 may be the result of lignin in the wood being sulphonated by two mechanisms, one mechanism first order and the other zero order in total SO_2 concentration. Provided these reactions occur at different lignin sites and an excess of sulphite is present, the sulphonate content of the lignin at any time would be given by the sum of the sulphonate contents incorporated by the two mechanisms, as shown in Equation 2.

$$\text{Sulphonate content of lignin} = S_1^{\infty} - (S_1^{\infty} - S_1^{0})e^{-k_1 [SO_2] t} + S_2^{\infty} - (S_2^{\infty} - S_2^{0})e^{-k_2 t} \qquad (2)$$

where S_1^{∞}, S_2^{∞} are the maximum sulphonate contents at infinite time

S_1^{0}, S_2^{0} are the sulphonate contents at time zero, and reflect the sulphonate groups incorporated during impregnation.

k_1, k_2 are the second and first order rate constants respectively

t is time

Equation 2 simplifies to Equation 3.

$$\text{Sulphonate content of lignin} = A - Be^{-k_1[SO_2]t} - Ce^{-k_2t} \quad (3)$$

where $A = S_1^{\infty} + S_2^{\infty}$
$B = S_1^{\infty} - S_1^{o}$
$C = S_2^{\infty} - S_2^{o}$

A non-linear regression fit of the data obtained at 140°C to Equation 3 has a R^2 value of 0.990 and standard deviation of the residuals of 0.23 per cent. The values of the parameters are given in Table 1. Also, Table 1 shows the values of the parameters obtained by fitting data obtained at 120° and 150°C to Equation 3, assuming A is constant at the value found at 140°C. Since B plus C approximates A at all three temperatures, S_1^o and S_2^o must be close to zero, and thus B and C reflect the maximum sulphonate contents attainable through the SO_2 dependent and independent reactions respectively. As can be seen from the standard deviation of the residuals and the values of R^2, the data at all

TABLE 1
The parameters obtained from non-linear regression fits of the data to Equation 3.

	Temperature		
	120°C	140°C	150°C
A (per cent)	10.2	10.2±0.3	10.2
B (per cent)	6.7±0.8	6.1±0.3	6.2±0.9
C (per cent)	2.6±0.8	3.3±0.2	4.3±1.0
k_1 (10^{-3} L mol^{-1}min^{-1})	1.8±0.6	9.5±1.1	22.0±4.0
k_2 (10^{-2} min^{-1})	1.4±0.7	1.9±0.3	3.4±1.2
R^2	0.953	0.990	0.984
Standard deviation of the residuals	0.33	0.23	0.33

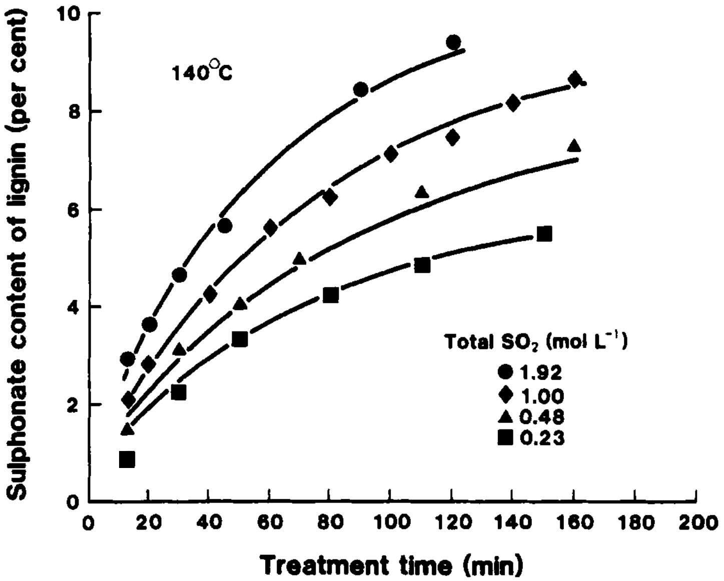
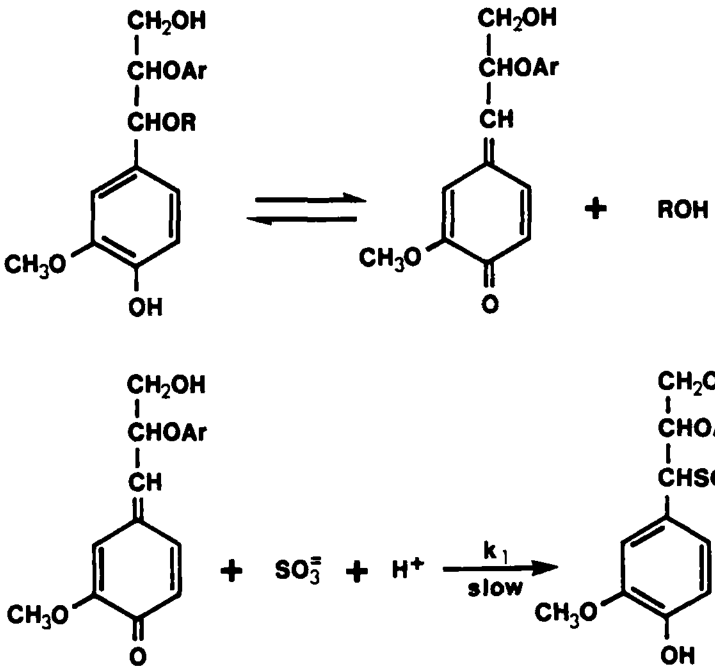


FIGURE 3. At 140°C, the sulphonate content of lignin in black spruce increases with increasing total SO_2 concentration in accordance with simultaneous SO_2 dependent and SO_2 independent sulphonation reactions. Lines are calculated from Equation 3 and data points are experimental.

three temperatures fit Equation 3 well. The quality of the fit is illustrated in Figure 3, where the lines calculated from Equation 3 are displayed along with experimental data points.

The reaction which is first order in total SO_2 is probably the same reaction that is operative during sulphonation at pH 7[5,6] involving quinonemethide formation from phenolic lignin units followed by slow sulphite attack, as shown in Scheme 1. The number of sites that are sulphonated by this mechanism at pH 4 corresponds to about 0.15 per C_9 unit of lignin which is close to the value of 0.16 per C_9 unit found for sulphonation at pH 7. The rate constant for this reaction at 140°C is 4.4 times lower at pH 4 than at pH 7, and is consistent with a shift of the equilibrium



R = H, Alkyl or Aryl

Scheme 1

from sulphite to the less nucleophilic bisulphite anion at lower pH. The possibility of quinonemethide formation from phenolic lignin units under the conditions used in this study has been demonstrated by investigations of the self-condensation reactions of vanillyl alcohol[7]. At and below pH 4 vanillyl alcohol forms condensation products through the alpha carbonium ion but at and above pH 5 condensation products are formed through the quinonemethide. At 120°C to 150°C the pH of bisulphite liquors is close to 5[8] and under such conditions phenolic lignin units should form quinonemethides which then can be sulphonated.

Sulphonation via this route can be inhibited by blocking quinonemethide formation through methylation of phenolic lignin units with diazomethane. Figure 4, shows that the sulphonation is indeed greatly inhibited by methylation. Further analysis of the sulphonation that still occurs gives a maximum attainable sulphonate content of 3.1 per cent on lignin with a rate constant of 1.95 x 10^{-2} min^{-1} in excellent agreement with the values of 3.3 per cent and 1.9 x 10^{-2} min^{-1} predicted for the total SO_2 independent reaction by the non-linear regression fit.

The sulphonation attributable to the reaction independent of total SO_2 concentration is significant at pH 4 but not at pH 7 and thus, must involve a rate determining acid catalyzed formation of a readily sulphonatable intermediate. It has previously been suggested that the lignin sites sulphonated under acidic conditions are non-phenolic β-arylether units. Units bearing α-alkoxy[9], α-hydroxy and α-aryloxy groups[6] have been proposed. The most likely site for acid catalyzed sulphonation at pH 4, based on previous studies, is the alpha position of the non-phenolic α-hydroxy β-arylether units[10].

Treatment of wood with diazomethane should increase the content of such units in wood by methylation of phenolic groups which in turn should lead to an increase in the maximum degree of sulphonation, C, occuring by the SO_2 independent route. This increase will correspond to the content of phenolic α-hydroxy β-arylethers in the lignin in wood. No such increase was observed in the present study. Thus if non-phenolic α-hydroxy β-arylether units are indeed the site of sulphonation by the acid catalyzed route at pH 4, then the content of their phenolic counterparts in wood must be very low.

The kinetic analysis shows that sulphonation via the carbonium ion occurs at a distinctly different site from sulphonation via the quinonemethide. This also implies that native lignin contains a very small amount of phenolic α-hydroxy β-arylether

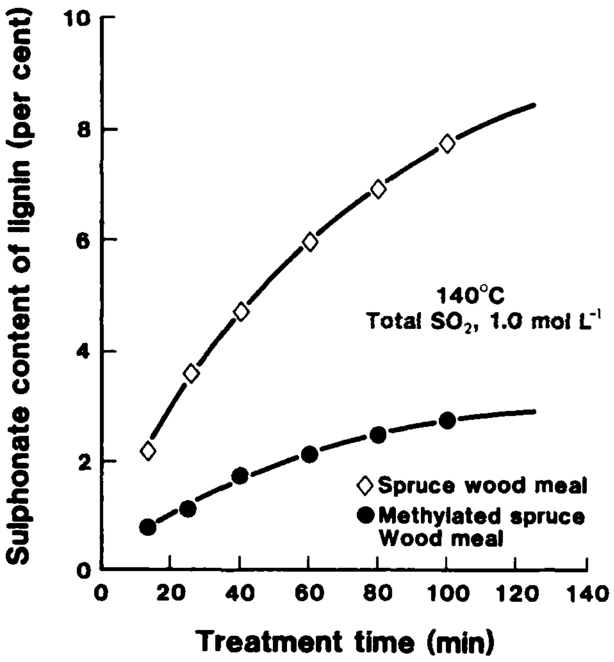
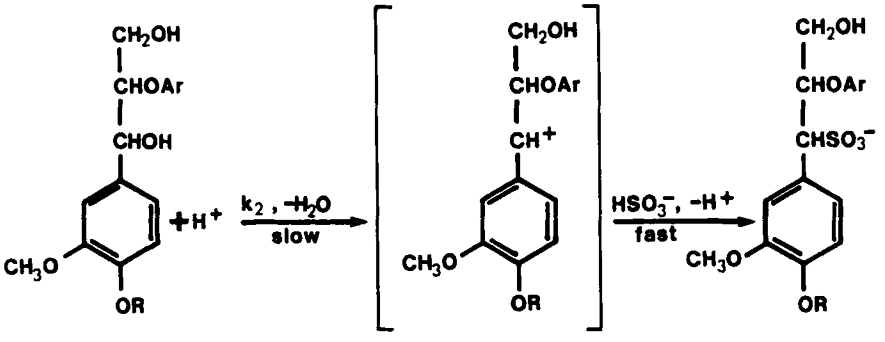


FIGURE 4. Methylation of spruce wood meal inhibits sulphonation of phenolic lignin units at 140°C with 1 mol L^{-1} sodium bisulphite.

units, since these units bear both an α-hydroxy group capable of being sulphonated via the carbonium ion mechanism and the free phenol, required for sulphonation via the quinonemethide.

The content of phenolic α-hydroxy β-arylether groups in milled wood lignin is about 0.06 per C_9 unit[11]. However their content in lignin in wood is probably much lower since a large increase in the phenolic content of lignin is known to occur during its isolation from spruce[12,13]. Moreover, this increase in phenolic content probably results from breakage of the labile alpha bond in phenolic α-aryloxy β-arylethers which would result in formation of phenolic α-hydroxy β-arylethers along with the new phenolic sites.



R = alkyl or aryl

Scheme 2

The mechanism for sulphonation at non-phenolic α-hydroxy β-arylether groups is shown in Scheme 2. The rate of this reaction would be independent of total SO_2 concentration if the rate determining step was formation of the carbonium ion.

The temperature dependence of the rate constants, k_1 and k_2, for both sulphonation pathways reflects not only the effect of normal rate enhancement according to the Arrhenius equation, but also the increase of pH and sulphite anion concentration in the sodium bisulphite solutions with increasing temperature[8]. The net effect is that the rate constant, k_1, for the reaction involving sulphite anions, increases by a factor of 2.3 for each 10°C rise in temperature. This is somewhat higher that the corresponding factor of 1.7 found for the second order rate constant at pH 7. The rate constant, k_2, for the acid catalyzed reaction increases by a factor of 1.3 for each 10°C temperature rise.

Yields and Lignin Contents of Sulphite Treated Black Spruce Chips

Yield decreases linearly with time at constant temperature and is independent of sulphite liquor concentration as seen in

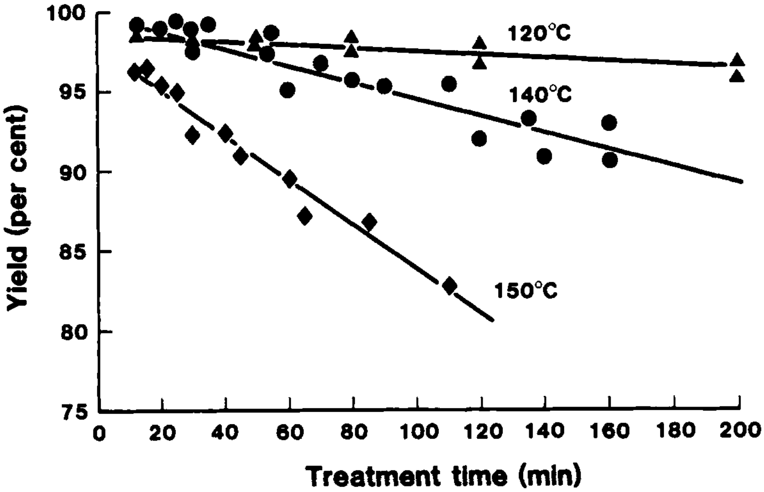


FIGURE 5. Yield decreases linearly with time at constant temperature and is independent of total SO_2 concentration. The rate of yield loss increases 2.3 times for every 10°C temperature rise. At each temperature data points cover a range of total SO_2 concentrations.

Figure 5. At 120°C, yield loss is low. The rate of loss increases by about 2.3 times for every 10°C temperature rise attaining 1.4 per cent for each 10 minutes of treatment at 150°C.

Table 2 shows for 1.46 mol L^{-1} sodium bisulphite liquors at 140°C that as treatment is prolonged more lignin is dissolved in the cooking liquor, lignin content of the treated wood decreases and the amount of soluble lignin increases.

For each temperature shown in Figure 6 lignin dissolves in the cooking liquor at a constant rate which is found to be independent of both sulphite liquor concentration and the sulphonate content of the wood. The rate of lignin dissolution increases by about 90 per cent for each 10°C rise in temperature as seen in Table 3.

Figure 7 shows that the same effects control the total quantity of lignin removed during treatment and subsequent exhaustive

TABLE 2

The relationship between yield, dissolved lignin and total lignin during a typical treatment of black spruce with 1.46 mol L^{-1} bisulphite solution at 140°C and pH 4.0.

Duration of treatments (min)	Yield (%)	Lignin dissolved in liquor based on untreated wood (%)	Lignin content of treated wood Klason (%)	Soluble (%)	Total (%)	Sulphur content (%)
12.5	99.4	0.16	26.3	0.3	26.6	0.27
25	99.2	0.41	25.9	0.5	26.4	0.41
35	99.1	0.65	25.3	0.6	25.9	0.50
55	98.2	1.19	24.2	0.7	24.9	0.59
90	95.2	2.00	23.5	1.3	24.8	0.74
135	93.1	3.07	20.2	2.6	22.8	0.83

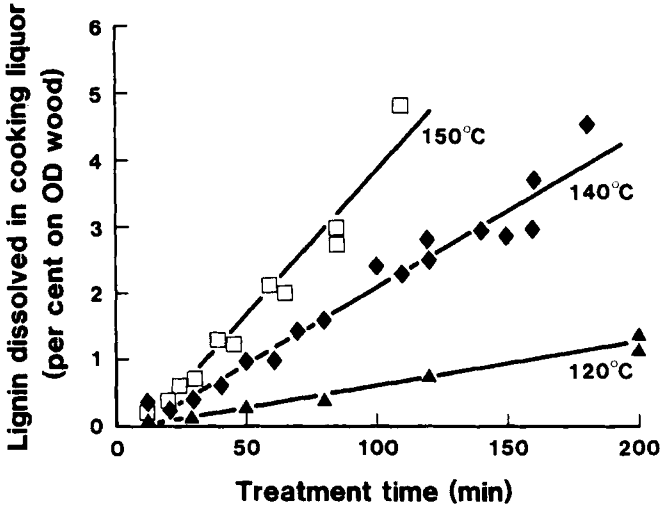


FIGURE 6. Lignin is dissolved in the cooking liquor at a constant rate, independent of total SO_2 concentration, at a given temperature. The rate of lignin dissolution increases about 90 per cent for each 10°C rise in temperature. At each temperature data points cover a range of total SO_2 concentrations.

TABLE 3

The rate of lignin removal increased by 80 to 90 per cent for each 10°C temperature rise.

Temperature of treatment (°C)	Rate of lignin* dissolution into cooking liquor (10^{-2} per cent $\min^{-1}$)	Rate of total* lignin loss (10^{-2} per cent $\min^{-1}$)
120	0.64±0.03	1.16±0.27
140	2.31±0.07	3.20±0.37
150	4.39±0.24	7.14±0.61

* Based on untreated wood

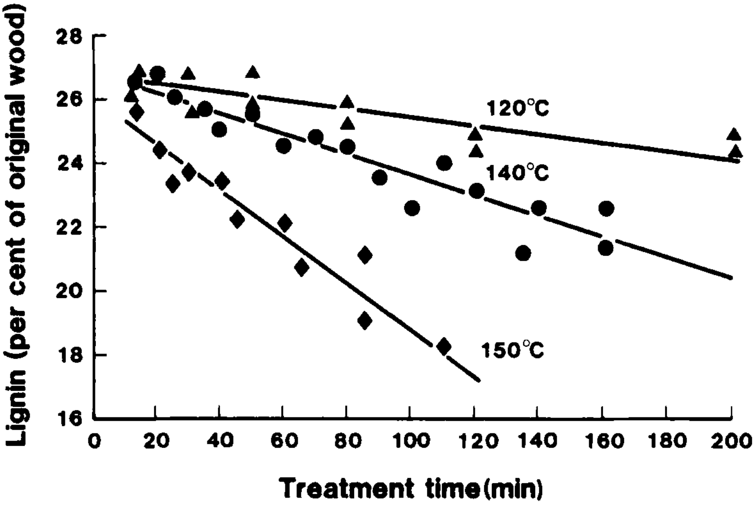


FIGURE 7. The total amount of lignin removed by sulphite treatment and washing is a linear function of time and is independent of total SO_2 concentration. The rate of lignin removal increases about 80 per cent for each 10°C temperature rise. At each temperature data points cover a range of total SO_2 concentrations.

washing. Again, there is no discernable effect of total SO_2 concentration and, at least during the first 100 minutes, lignin loss is approximately linear with time with a rate that increases by about 83 per cent for each 10°C temperature rise. As can be seen from Table 3, about 40 per cent of the lignin released by treatment is removed from the waferized chips during washing.

Lignin release by a rate determining step independent of the sulphonation reaction is consistent with it occuring in the first step of the mechanisms shown in Schemes 1 and 2[14]. Other plausible explanations are that lignin is released by hydrolytic cleavage elsewhere in the lignin polymer[15] or that the rate of lignin release is determined by a diffusion controlled process.

CONCLUSIONS

During sulphite treatment of black spruce chips at pH 4, sulphonate groups are incorporated into the lignin by two mechanisms, one dependent and the other independent of total SO_2 concentration. This results in the rate of sulphonation being a function of total SO_2 concentration to the power of 0.4. The total SO_2 dependent mechanism is thought to be the same as that governing sulphonation at pH 7 and to involve formation of a quinonemethide followed by the rate determining sulphite attack. The sulphonation route which is independent of total SO_2 concentration is thought to involve the rate determining acid catalyzed formation of a carbonium ion, probably at the alpha position of non-phenolic α-hydroxy β-arylether units, followed by rapid sulphite addition.

The rates of yield and lignin loss are independent of total SO_2 concentration and approximately double for each 10°C temperature rise. About 60 per cent of the lignin released by treatment is dissolved in the cooking liquor and the remaining 40 per cent is released from the chips during washing.

The results show that high total SO_2 concentrations promote sulphonation but do not affect yield. Increasing temperature increases sulphonation rates but decreases yield. Thus, in order to obtain chemimechanical pulps with high sulphonate contents in high yield by treatment with sodium base bisulphite liquors, high total SO_2 concentrations must be used. However, it should be remembered that sulphonation at pH 4 is less dependent on total SO_2 concentration than at pH 7 and thus the rate enhancement obtained by increasing total SO_2 concentration is smaller at lower pH.

The equations describing the kinetics of sulphonation and delignification allow the prediction of the sulphonate contents of treated wood and hence to some extent the properties of the resulting chemimechanical pulps.

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 Cooking Liquors

The cooking liquors were prepared by dissolving reagent grade sodium bisulphite in deionized water to give total SO_2 concentrations from 0.23 to 1.92 mol L^{-1}.

Treatment of the Chips

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 preheated constant temperature bath and the timing begun. The liquor in the bomb reached the bath temperature, as determined by a thermocouple, in approximately 12 minutes.

After treating the chips for predetermined times, up to 110 minutes at 150°C and up to 200 minutes at 120°C, the bomb was quickly cooled and the chips were removed. The chips were 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 84 and 100 per cent.

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 by Tappi Useful Method UM250.

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[16] the sulphonate content as SO_3^-, in wood could be calculated as,

Sulphonate content of treated wood = sulphur content x 2.5

Sulphonate content as SO_3^- on lignin = Sulphur content of treated wood x 2.5 x 100/per cent lignin in treated wood.

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[17].

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-tolouene-sulfonamide (25g), and used immediately. Portions of 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. After each addition the slurry was stirred until most of the yellow colour disappeared. This took 1 to 2 h initially but slowed to 1 to 2 days towards completion of the reaction. Excess solvent was poured off from the wood meal slurry as the reaction progressed. After all colour was discharged following the final addition, the wood meal was filtered, washed with fresh ether and air dried.

Methoxyl content for the extracted wood meal and methylated wood meal were 4.12 and 7.94 per cent respectively.

ACKNOWLEDGEMENTS

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