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### Viscosities of Unbleached Alkaline Pulps. II. The G-Factor

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VISCOSITIES OF UNBLEACHED ALKALINE PULPS. II.  
THE G-FACTOR

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ABSTRACT

The activation energy for the loss of pulp viscosity (cellulose chain cleavage) during soda-AQ pulping was found to be the same as in kraft cooking:  $179 \pm 4$  kJ/mol. Calculations based on literature data gave a value of 175 kJ/mol for soda pulping. The agreement confirms previous findings that reducing additives do not affect pulp viscosity ( $\eta$ ). When high sodium hydroxide charges are employed, straight-line plots of  $1/\eta$  versus cooking time at maximum temperature are obtained. A "G-factor" is proposed to combine cooking time and temperature into a single variable, similar in concept to Vroom's H-factor, for calculating the effect on pulp viscosity of widely varying cooking cycles.

INTRODUCTION

In a previous publication<sup>1</sup> we concluded that the viscosities of unbleached alkaline pulps from black spruce, made at a cooking temperature of 170°C, depended only on the alkalinity of the liquor and the cooking time. The viscosities were independent of the

presence of anthraquinone or sulphide ion in the cooking liquor. To investigate the kinetics of the viscosity loss, we have now examined more closely the effects of alkalinity, cooking temperature, and time.

## RESULTS AND DISCUSSION

### Reciprocal-viscosity plots

In the experiments described below, a high liquor-to-wood ratio was used to maintain a large reservoir of hydroxide ion so that its concentration would not change appreciably during cooking (see conditions and results in Table I). We then found it possible to plot  $1/\eta$  ( $\eta$  = viscosity of 0.5% cuene solutions) versus cooking time at maximum temperature and, for each alkali concentration, obtain a straight line with a high correlation coefficient,  $r$  (Fig. 1). The reciprocal-viscosity term relates to the number of cellulose chains per unit weight of pulp<sup>2</sup>, so that the slopes,  $d(1/\eta)/dt$ , of the lines in Figure 1 indicate the rate of chain cleavage ( $k_{vis}$ ). Plotting the slopes against the initial hydroxide ion concentrations,  $[OH^-]_0$ , gave a straight line (Fig. 2) indicating that for kraft pulping, cellulose chain cleavage is first order in hydroxide ion. Similar results (not shown) were obtained for soda-AQ pulping.

Graphs of reciprocal viscosity versus time have been used to express the viscosity loss of cellulose undergoing acid hydrolysis<sup>3,4</sup> or pyrolysis<sup>5</sup>, and we have also found that the results of Lai<sup>6,7</sup> et al. for viscosity loss of cotton hydrocellulose during alkaline hydrolysis can be plotted in this way to give straight lines. Direct plots of viscosity against time produce hyperbolae which can be misleading<sup>3,4</sup>. The reciprocal-viscosity versus time relationship is readily derived by considering the random scission of a long chain polymer (see kinetic model).

### The Effect of Temperature

Figure 3 presents the kraft data from Table II plotted to show that at constant alkali charge, straight-line plots of  $1/\eta$  versus

Table I. Pulping of Black Spruce with Varied Alkali Charge

Type of cook <sup>a)</sup>	Conditions				Results		
	Effective Alkali Concentration, as Na <sub>2</sub> O % on o.d. wood	Liquor-to-wood ratio	Time at temp., min	H-factor x 10 <sup>3</sup>	Kappa Number	Viscosity, mPa.s	
Kraft pulping at 30% sulphidity	102	17	60:1	65	1.1	74.5	60.5
				84	1.4	50.6	42.2
				104	1.7	36.7	36.5
	82	34	24:1	130	2.1	26.7	30.7
				66	1.1	23.3	27.0
				85	1.4	16.8	19.9
	204	51	40:1	104	1.7	12.9	14.3
				129	2.1	11.8	12.1
				65	1.1	14.4	12.2
	272	68	40:1	85	1.4	10.8	8.2
				104	1.7	8.9	7.1
				130	2.1	7.8	5.7
66				1.1	9.5	6.8	
83				1.4	7.3	5.1	
102				1.7	6.6	4.3	
Soda-AQ pulping with 0.25% AQ on o.d. wood	120	20	60:1	65	1.1	95.3	30.3
				84	1.4	79.3	27.5
				104	1.7	63.1	26.7
	97	40	24:1	130	2.1	47.3	23.2
				66	1.1	42.0	17.0
				85	1.4	29.5	13.8
	240	60	40:1	104	1.7	23.6	11.5
				129	2.1	17.2	9.1
				65	1.1	28.2	9.0
	320	80	40:1	83	1.4	18.6	7.0
				104	1.7	14.7	5.9
				130	2.1	11.7	4.9
			64	1.1	22.0	4.5	
			83	1.4	15.2	3.7	
			102	1.7	11.5	3.2	
			127	2.1	8.5	2.9	

a) 90 minutes rise to the maximum cooking temperature of 170°C  
 b) 0.5% cuene (TAPPI Standard Method T-230).

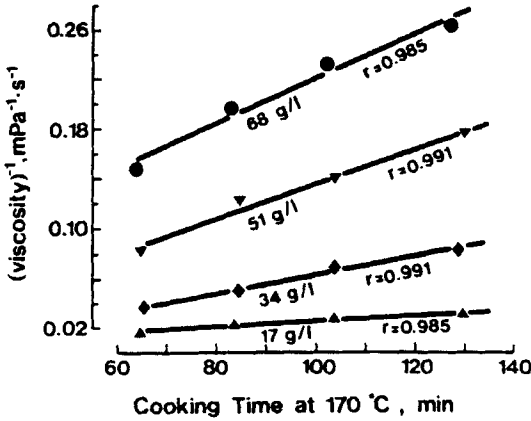


Figure 1. Reciprocal viscosities (0.5% cuene) of unbleached black spruce kraft pulps are plotted against time at maximum temperature. All cooks were done at 170°C but at different effective alkali concentrations which are indicated (as g/l Na<sub>2</sub>O) on the graph.

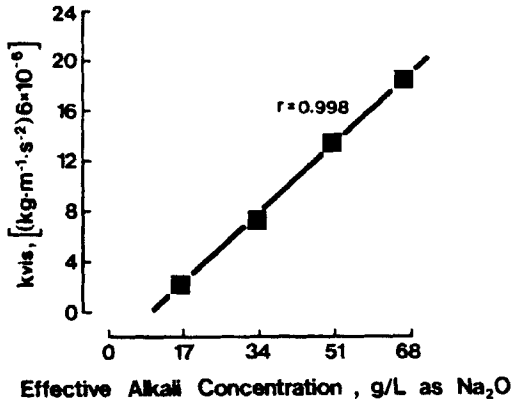


Figure 2. The slopes ( $k_{vis}$ ) of the lines in Fig. 1 plotted against the effective alkali concentration.

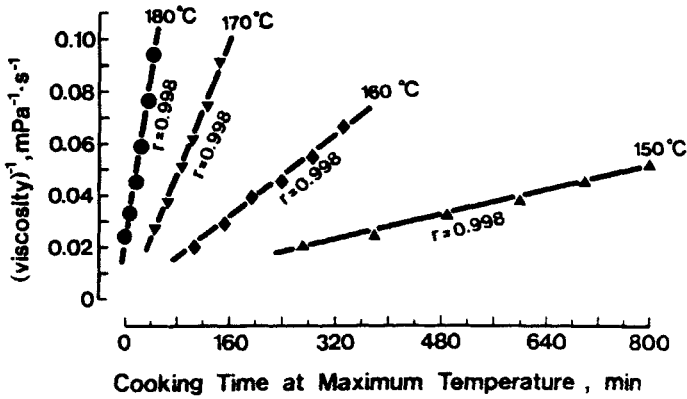


Figure 3. Reciprocal viscosities (0.5% cuene) of unbleached black spruce kraft pulps are plotted against time at four different maximum temperatures. All cooks were done at an effective alkali concentration of 34 g/L (as Na<sub>2</sub>O).

time were obtained, with a different slope for each cooking temperature. Similar results (not shown) were obtained for soda-AQ pulping.

The slopes represent the specific rates,  $k_{vis}$ , of the chain cleavage reaction, and their significance derives from the Arrhenius equation (eq. 1) which relates a reaction rate,  $k$ , to the absolute temperature,  $T$ , and the activation energy,  $E_a$ , of the reaction;  $A$  and  $R$  are constants.

For viscosity loss as a function of temperature (alkali charge held constant), the Arrhenius equation can be rewritten as equation 2, where the  $k_{vis}$  values are the slopes of the lines in Figure 3, and  $E_{a,vis}$  represents the activation energy for viscosity loss.

$$k = A \cdot e^{-\frac{E_a}{RT}} \tag{1}$$

$$k_{vis} = A_{vis} \cdot e^{-\frac{E_{a,vis}}{RT}} \tag{2}$$

TABLE II - Alkaline Pulping of Black Spruce at Different Cooking Temperatures

PULPING CONDITIONS			RESULTS			
Maximum Cooking Temp., °C	Time at max. Cooking Temp., min	H-factor	KRAFT <sup>a)</sup>		SODA-AQ <sup>b)</sup>	
			Kappa Number	Viscosity, mPa.s	Kappa Number	Viscosity, <sup>c)</sup> mPa.s
150	272	800	34.7	47.6	63.9	24.6
	381	1100	21.6	38.8	46.8	20.7
	490	1400	16.5	30.5	35.9	19.4
	599	1700	13.1	25.5	27.1	16.8
	708	2000	11.8	21.6	22.3	13.9
	816	2300	10.2	18.8	20.4	13.2
160	108	800	35.8	45.0	58.5	24.4
	152	1100	22.1	33.5	39.9	18.8
	196	1400	16.4	25.0	31.1	16.6
	241	1700	13.6	21.5	24.4	14.3
	286	2000	11.5	17.9	20.5	13.1
	333	2300	9.8	14.8	16.2	11.5
170	46	800	38.7	37.1	62.9	22.0
	66	1100	22.0	26.7	43.4	17.8
	86	1400	16.2	19.6	29.7	14.4
	105	1700	12.6	16.1	23.1	12.4
	125	2000	10.9	13.3	19.5	10.5
	145	2300	8.8	11.0	16.4	9.0
180	0	800	45.9	39.8	62.3	19.8
	9	1100	27.2	29.3	47.5	15.0
	18	1400	19.2	21.6	30.0	11.4
	24	1700	13.9	16.5	24.0	10.0
	35	2000	11.9	13.0	18.2	8.5
	44	2300	10.3	10.5	14.2	7.2

- a) Constant conditions: kraft: 81.8% E.A. as Na<sub>2</sub>O on o.d. wood  
34.0 g/L as Na<sub>2</sub>O  
24:1 liquor-to-wood ratio  
30% sulphidity:  
Time to temperature = 90 min
- b) Constant conditions: soda-AQ: 96.5% E.A. as Na<sub>2</sub>O on o.d. wood  
40 g/L as Na<sub>2</sub>O:  
24:1 liquor-wood ratio  
0.25% AQ on o.d. wood  
Time to temperature = 90 min

c) 0.5% cuene (TAPPI Standard Method T-230)

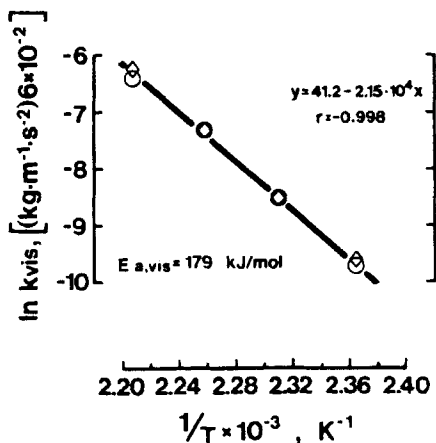


Figure 4. Kraft (circles) and soda-AQ (diamonds) cooks of black spruce yield the same Arrhenius plot for viscosity loss during alkaline pulping. The kraft points are the logarithms of the slopes ( $k_{vis}$ ) of the lines shown in Fig. 3. The slope of this graph gives the activation energy for viscosity loss,  $E_{a,vis}$ , as 179 kJ/mol.

A co-variance analysis showed that the soda-AQ and kraft data points of the Arrhenius plot were not significantly different. We therefore plotted all the results together (Fig. 4) and obtained an activation energy of  $179 \pm 4$  kJ/mol (42.8 kcal/mol) for viscosity loss in soda-AQ and kraft pulping.

### The G-factor

As derived for application to the kinetics of delignification, Vroom's H-factor<sup>8</sup> can be defined according to Equation 3, where  $k_{lig}(373)$  is the delignification rate at 100°C (373 K). Now, by analogy with the H-factor, we can define the G-factor for viscosity loss as a means of expressing the effect of cooking time and temperature in a single variable (equation 4).

$$H = \frac{1}{k_{lig}(373)} \int_0^t k_{lig}(T) \cdot dt \quad (3)$$



TABLE III - Relative rate of cuene viscosity loss ( $k'_{vis}$ )  
for alkaline pulping<sup>a</sup>)

Temperature, °C	Relative Rate	Temperature, °C	Relative Rate	Temperature, °C	Relative Rate
100	1	130	73	160	2960
101	1	131	84	161	3320
102	1	132	95	162	3720
103	2	133	109	163	4170
104	2	134	124	164	4670
105	2	135	141	165	5220
106	2	136	160	166	5840
107	3	137	182	167	6530
108	3	138	207	168	7300
109	4	139	235	169	8150
110	4	140	267	170	9100
111	5	141	303	171	10200
112	6	142	343	172	11300
113	7	143	389	173	12600
114	8	144	440	174	14100
115	9	145	498	175	15600
116	11	146	563	176	17400
117	12	147	636	177	19400
118	14	148	718	178	21600
119	16	149	811	179	26000
120	19	150	915	180	29600
121	22	151	1030	181	32800
122	25	152	1160	182	40300
123	28	153	1310	183	44700
124	33	154	1470	184	49500
125	37	155	1660	185	54800
126	43	156	1860	186	60100
127	49	157	2090	187	64800
128	56	158	2350	188	69700
129	64	159	2640	189	72700

a) The calculation of these rates is described in the Experimental section. For comparison, the relative delignification rates used in the H<sup>-</sup>-factor calculation<sup>8</sup> are as follows: 1 (100°C), 25 (130°C), 165 (150°C), 401 (160°C), 927 (170°C) 2042 (180°C).

$$G = \frac{1}{k_{vis(373)}} \int_0^t k_{vis(T)} \cdot dt \quad (4)$$

Following Vroom's approach, the next step is to calculate the ratio of  $k_{vis(T)}$  to  $k_{vis(373)}$  to obtain the relative rate constant

$k'_{vis}(T)$ . The value of this constant at various temperatures is given in Table III, and the calculation is described in the experimental section. The footnote to the table shows that, as a consequence of its high activation energy, viscosity loss accelerates more rapidly than delignification as temperature increases. Therefore, only in the case of isothermal pulping (no rise-to-temperature) would a linear relationship exist between G and H.

Using the relative rates given in Table III, the G-factor of any temperature rise profile (e.g., Fig. 5) can be calculated by adding up the accumulated "G" over 15 minute segments as described by Vroom<sup>8</sup> for the H-factor. A sample calculation is given in Table IV. Regardless of the combinations of cooking times and temperatures, cooking cycles which give equal G-factors would be expected to produce unbleached pulps of the same viscosity (other parameters being held constant).

#### Verification of the G-factor

Three tests were applied to verify the G-factor.

1. Basta and Samuelson<sup>9</sup> have used high alkali charges for the soda pulping of Scandinavian spruce, and we could check the activation energy for viscosity loss in soda pulping by replotting data taken from their figures. We obtained well-correlated  $1/\eta$  versus time plots at 4 hydroxide ion concentrations (Fig. 6a) and 3 temperatures (Fig. 7a). Once again, viscosity loss was first-order in hydroxide ion (Fig. 6b), and the Arrhenius plot (Fig. 7b) yielded an  $E_{a,vis}$  of 175 kJ/mol (41.8 kcal/mol). Within experimental error, this is the same as the value obtained for soda-AQ and kraft pulping.

The data given in reference 9 are intrinsic viscosities (I.V.) values, but the reciprocal viscosity versus time graphs are nonetheless linear. When we converted cuene viscosities (Tables I and II) into intrinsic viscosities<sup>10,11</sup>, the data

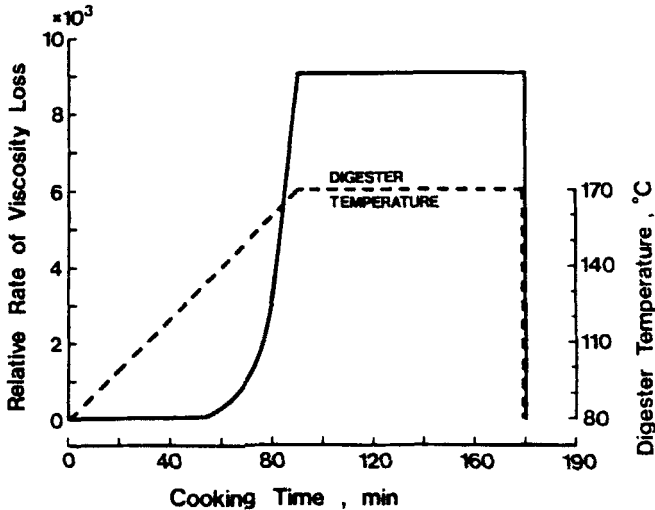


Figure 5. The relative rate of viscosity loss during a cooking cycle. The area under the relative rate curve (solid line) is the total "G- factor" accumulated.

fitted equally well into a reciprocal viscosity-time plot. This was surprising because the cuene viscosity - intrinsic viscosity relationship is non-linear; the explanation is that reciprocal cuene viscosity versus reciprocal I.V. plots are linear ( $r = 0.998$ ) over the viscosity range encompassed by this work. Thus, intrinsic and TAPPI cuene viscosities can be treated equally well by reciprocal viscosity plots.

2. A second test was to see if cooks done at high alkali charge to the same G-factor but at different temperatures and different times would indeed produce pulps of the same viscosity. The results are shown in Table V. Pulping at  $172^\circ$  and  $160^\circ$  to constant G-factor gave viscosity values which were constant within the experimental error of the test, whereas the kappa numbers were completely different (the H-factors were not identical).
3. All the cooking reported here has been done with very high alkali charges to maintain fixed hydroxide ion concentrations

TABLE IV - Calculation of G-factor for a typical alkaline cook<sup>a)</sup>

Time from start, h	Temperature, °C	Relative rate of viscosity loss	Average x Rate	Time Interval	G-factor Increment <sup>b)</sup>
0.00	20.0	0			
0.25	45.5	0			
0.50	71.0	0			
0.75	96.5	0			
1.00	122.0	25	12.5 x	0.25 =	3
1.25	147.5	718	371.5 x	0.25 =	93
1.50	170.0	9100	4910 x	0.25 =	1228
3.16	170.0	9100	9100 x	1.67 =	15200
Total "G" factor =					16524c)

a) Conditions: Cooking time to maximum temperature . . . . . 90 minutes  
 Cooking time at maximum temperature . . . . . 100 minutes  
 Maximum cooking temperature . . . . . 170°C

b) G-factor increment = Average rate x time interval

c) The corresponding H-factor is 1700

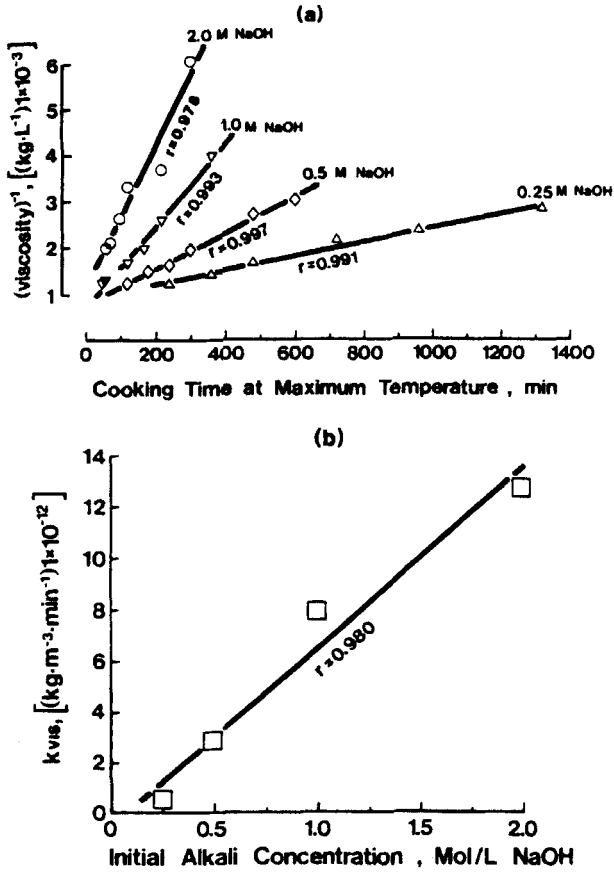


Figure 6. (a) Plots of reciprocal viscosity versus cooking time for soda pulping of Scandinavian spruce at 170°C with different alkali concentrations (data taken from ref. 9). (b) The slopes of the lines in (a) plotted against the alkali concentration.

during pulping. Nevertheless, the correlation of G-factor with viscosity should still exist at low alkali charges, if we assume that the decline of the effective alkali follows a similar pattern in each cook. Figure 8 shows viscosity data reported by Hart and Strapp<sup>12</sup> for the kraft pulping of spruce with various alkali charges, plotted against G-factors calculated from the relative rates given in Table III. All but one of the data

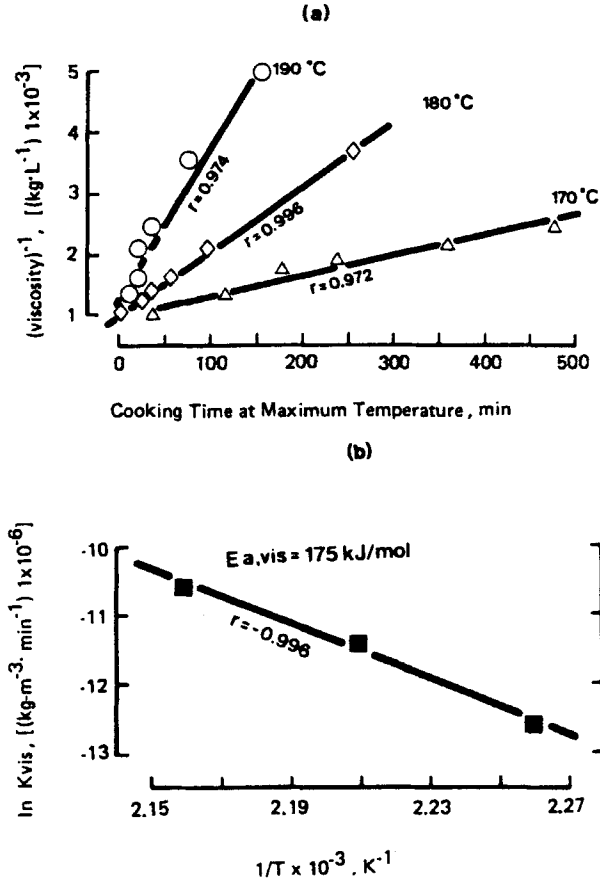


Figure 7. (a) Reciprocal viscosity versus cooking time plots for soda pulping of Scandinavian spruce in 1M sodium hydroxide at different temperatures<sup>9</sup>. (b) The Arrhenius plot derived from (a). The slope yields  $E_{a,vis} = 175$  kJ/mol.

points fall on smooth curves for each alkali level. Thus, regardless of the cooking temperature (160°, 170° or 180°C), the results of all cooks at the same alkalinity fall on the same G-factor curve.

A Kinetic Model

The development of the G-factor was based on the discovery that at constant hydroxide ion concentration, a straight line is

TABLE V. Experiments showing that cooking to same G-factor (8,945) leads to the same viscosity

Pulping Process	Maximum Cooking Temp., °C	Cooking Time at Maximum Temp., min	"H" factor	Viscosity, 0.5% cuene, mpa.s	Kappa No.
Kraft	172	40	843	32	28
	160	174	1220	30	16
Soda-AQ	172	40	843	29	78
	160	174	1220	30	51

a) Effective Alkali Charge: 82% as Na<sub>2</sub>O on o.d. wood

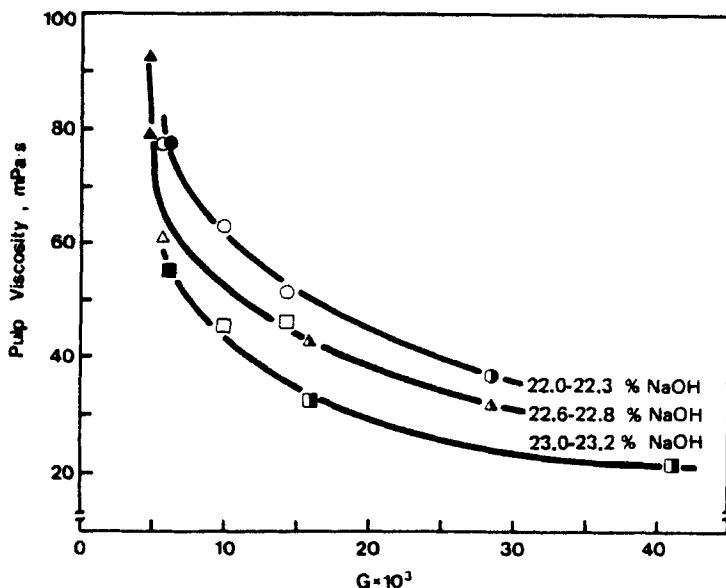


Figure 8. Viscosity data taken from ref. 12 are plotted against  $G$ -factor. Open symbols indicate cooks done at  $170^\circ$ , solid symbols  $160^\circ$ , and half-solid symbols  $180^\circ$ . The initial charges of effective alkali (as NaOH on o.d. wood) are indicated for each curve.

obtained on plotting  $1/\eta$  versus time at maximum temperature. This enabled us to show that viscosity loss is first-order in hydroxide ion, and to calculate the activation energy. We now present a kinetic model which can explain these observations.

The hydrolytic cleavage of any glycosidic bond in a linear polysaccharide chain yields two polymer chains each having a lower molecular weight than the original. Therefore, the molar concentration of carbohydrates increases with time. Assuming that the reaction is of a bimolecular type, where a hydroxide ion, directly or indirectly, attacks a glycosidic bond, the rate equation for hydrolytic cleavage may be expressed as equation 5, where  $[C]$  and  $[OH^-]$  are the molar concentrations of carbohydrate and hydroxide



ion,  $t$  is time and  $k'$  is the bimolecular rate constant.  $[\text{Gly}]$  is a molar concentration term for glycosidic bonds as defined in equation 6.

Because the number of glycosidic bonds is very large, their concentration hardly alters during pulping<sup>13</sup>. This can be visualized by considering a monodisperse cellulose sample of DP 2000. If we break one glycosidic link anywhere in each molecular chain, the number-average DP is thus reduced to 1000, but the number of glycosidic links is only decreased by 1/1999th or 0.05%.

Therefore, in equation 5,  $[\text{Gly}]$  can be replaced by a constant. In addition, at very high hydroxide ion charges as used in our work,  $[\text{OH}^-]$  is constant. This leads to a zero-order rate equation (eq. 7), which, when integrated with respect to time, yields equation 8, where  $C_0$  refers to the initial concentration of carbohydrate.

$$\frac{d[C]}{dt} = k' [\text{Gly}][\text{OH}^-] \quad (5)$$

$$[\text{Gly}] = \frac{\text{conc. of glycosidically bonded monomers}}{\text{MW of monomer}} \quad (6)$$

$$\frac{d[C]}{dt} = k' [\text{Gly}][\text{OH}^-] = k \quad (7)$$

$$[C] - [C_0] = kt \quad (8)$$

In cellulose, the number of glycosidic bonds is very close to the number of monomer units, so equation 6 can be simplified as shown in equation 9, which, when substituted in equation 10 (a definition of  $[C]$ ) gives a new expression (equation 11) relating  $[C]$  to  $[\text{Gly}]$  and  $\overline{DP}_w^*$ . Combining equations 8 and 11 yields equation 12, in which  $\overline{DP}_{w(t)}$  and  $\overline{DP}_{w(o)}$  are the weight-average degrees

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\* For high molecular weight polymers the ratio of  $\overline{DP}_n$  to  $\overline{DP}_w$  is 1:2 (14).

of polymerization at time  $t$  and time zero, respectively. Equation 12 relates the zero-order rate constant,  $k$ , to the degree of polymerization of the polysaccharide, and is similar to an equation obtained in a different way by Vink<sup>15</sup> who considered the random scission of a long-chain polymer.

$$[\text{Gly}] = \frac{\text{conc. of glycosidically bonded monomers}}{\text{MW of monomer}} = \frac{\text{conc. of polysaccharide}}{\text{MW of monomer}} \quad (9)$$

$$[C] = \frac{\text{conc. of polysaccharide, g/l}}{\text{MW of monomer} \cdot \overline{\text{DP}}_n} \quad (10)$$

$$[C]_t = \frac{2[\text{Gly}]_t}{\overline{\text{DP}}_w(t)} \quad (11)$$

$$\frac{1}{\overline{\text{DP}}_w(t)} - \frac{1}{\overline{\text{DP}}_w(0)} = \frac{kt}{[\text{Gly}]} \quad (12)$$

Equation 13 shows<sup>15</sup> how  $\overline{\text{DP}}_w$  values relate to intrinsic viscosity,  $[\eta]$ . The exponent  $\alpha$  has usually been given a value of somewhat less than 1 (e.g. 0.905)<sup>16</sup> although occasionally it has been set at unity<sup>17</sup>. For pulping purposes, unity is an acceptable approximation because the errors incurred in considering the DP-value proportional to the intrinsic viscosity are counterbalanced, to some extent, by the effects of neglecting glucose units removed by peeling.

By substituting for  $\overline{\text{DP}}_w(t)$  and  $\overline{\text{DP}}_w(0)$  in equation 12 we obtain an equation (eq. 14) showing how pulp viscosity varies with time. The expression  $0.75 k/[\text{Gly}]$  is equivalent to the observed rate constant for viscosity loss,  $k_{\text{vis}}$ . The expression for  $k_{\text{vis}}$  is related to the second-order rate constant by substituting from eq. 7 to give equation 15. Equation 14 explains the experimental facts given in Figure 1, while Figure 2 is explained by Eq. 15 which shows that the slopes ( $k_{\text{vis}}$ ) of Figure 1 are proportional to the hydroxide ion concentration.

$$DP_w^\alpha = 0.75[\eta] \quad (13)$$

$$\frac{1}{[\eta_t]} - \frac{1}{[\eta_o]} = \frac{0.75kt}{[\text{Gly}]} = k_{\text{vis}} \cdot t \quad (14)$$

$$k_{\text{vis}} = 0.75 k'[\text{OH}^-] \quad (15)$$

The Arrhenius-type temperature dependence of  $k_{\text{vis}}$  (Fig. 4) is explained by the temperature dependence of the bimolecular rate constant  $k'$ . In the heating-up process, the value of this constant is a function of time, and equations 8 and 14 become equations 16 and 17, respectively, where the time-dependence of  $k$  is given by the temperature program. Equation 17 shows that when the hydroxide ion concentration is constant, processes having the same G-factor (eq. 4) should yield pulps of equal viscosities.

$$[C] - [C_o] = \int_0^t k(t) \cdot dt \quad (16)$$

$$\frac{1}{[\eta_t]} - \frac{1}{[\eta_o]} = \int_0^t k_{\text{vis}}(t) \cdot dt \quad (17)$$

### CONCLUSIONS

The observation that kraft, soda, and soda-AQ pulping all exhibit (within experimental error) the same activation energy for viscosity loss confirms and extends our previous finding<sup>1</sup> that sulphide and anthraquinone additives do not affect pulp viscosity. Under the same restrictions required for the H-factor (constant wood species and alkali charge), cooking at constant G-factor (equation 4) produced pulps of equal viscosity. Once a G-factor versus viscosity plot has been established for a given effective alkali charge and concentration, pulp viscosities can be predicted for a variety of times and temperatures. Because viscosity loss

has a higher activation energy than delignification, higher pulping temperatures will always lead to lower pulp viscosities at any given lignin content.

If the value of  $[\eta_0]$  in equation 14 is roughly constant for most wood furnishes, we can predict that the final pulp viscosity should be independent of wood species. Our preliminary results show this to be so, and these will be the subject of a future report.

### EXPERIMENTAL

Black spruce mill chips were cooked in 2L stainless steel bombs rotating in an oil bath. High liquor:wood ratios were used so that the hydroxide ion concentration was approximately constant throughout the cook. The AQ charge in the soda-AQ cooks was 0.25% on o.d. wood and the sulfidity of the kraft liquor was 30% in every case. Before the viscosities were determined (Tappi Standard Method T-230), the unbleached pulps were delignified by acid chlorite bleaching<sup>18</sup>.

The relative rates of viscosity loss ( $k'_{vis}$ ) given in Table III were calculated by combining the definition of  $k_{vis}$  (equation 18) with the Arrhenius equation (eq. 2), yielding equation 19. Inserting the constants,  $E_{a,vis} = 179,000$  and  $R = 8.315$ , leads to equation 20, which was used to generate Table III.

$$k'_{vis} = \frac{k_{vis}(T)}{k_{vis}(373)} \quad (18)$$

$$k'_{vis} = \ln^{-1} \left\{ \frac{E_{a,vis}}{R} \left( \frac{1}{373} - \frac{1}{T} \right) \right\} \quad (19)$$

$$k'_{vis} = \ln^{-1} \left( 57.71 - \frac{21,527}{T} \right) \quad (20)$$

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