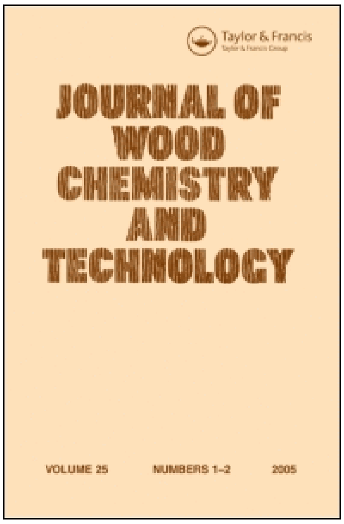

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THE VISCOSITIES OF UNBLEACHED ALKALINE PULPS
IV. THE EFFECT OF ALKALI

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ABSTRACT

An equation has been developed to relate the viscosity of unbleached pulp to the residual alkali in the spent liquor, and the time-temperature profile of the cook (expressed as the G-factor). The equation is applicable to kraft, kraft-AQ and soda-AQ pulping and to a variety of wood species.

INTRODUCTION

When wood pulp was cooked with a large excess of effective alkali (so that the alkali concentration did not change appreciably during cooking), the rate of viscosity loss was found to be first order with respect to hydroxide ion concentration [1]. Theoretical considerations to support the experimental observations led to equations 1 and 2, where $[\eta]_o$ and $[\eta]_t$ are the

$$\frac{1}{[\eta]_t} - \frac{1}{[\eta]_o} = \int_o^t k_{vis}(t)\cdot dt \qquad (1)$$

$$k_{vis} = 0.75\ k'\ [OH^-] \qquad (2)$$

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intrinsic viscosities of the pulp before cooking, and after cooking for time t; k_{vis} is the rate constant for viscosity loss at constant hydroxide ion concentration; and k' is the bimolecular rate constant for chain cleavage. By substituting for k_{vis} in equation 1, we obtain equation 3 which describes the effect of alkali on pulp viscosity, $[\eta]_t$. For certain special experimental cooks in which the alkali charge is set high enough so that the alkali concentration remains constant during pulping, equation 3 can be simplified to equation 4.

$$\frac{1}{[\eta]_t} - \frac{1}{[\eta]_o} = 0.75 \int_0^t k'(t) \cdot [OH^-](t) \cdot dt \qquad (3)$$

$$\frac{1}{[\eta]_t} - \frac{1}{[\eta]_o} = 0.75\ [OH^-] \int_o^t k'(t) \cdot dt \qquad (4)$$

In these equations, $k'_{(t)}$ indicates that the rate constant k' (which is temperature dependent) is varying as a function of time as the digester temperature changes. The value of the integral $\int_o^t k'(t) \cdot dt$ is proportional to the "G-factor", which can be calculated as described earlier [1]. Thus, equation 4 predicts that a plot of $1/[\eta]$ vs. G x $[OH^-]$ will be linear, provided that $[OH^-]$ does not vary during the cook.

RESULTS AND DISCUSSION

Constant Hydroxide Ion Concentration

An attempt was made to confirm the prediction of Equation 4 by using data taken from illustrations in an article by Basta and Samuelson [2]. They used a liquor-to-wood ratio of 130:1 to cook spruce woodmeal, and as a result, the alkali concentration was almost unchanged after the cook. When the product of the

G-factor and the initial hydroxide concentration was plotted against the reciprocal viscosity of the pulp, a straight line graph was obtained ($R^2 = 0.95$). This result, illustrated in Figure 1, supports the validity of Equation 4. The intercept on the ordinate (0.74×10^{-3}) corresponds to an intrinsic viscosity of 1350 dm^3/kg which in turn corresponds to a $\overline{DP}_w$ of 2140 [3a]. This value corresponds to the viscosity of the cellulose in uncooked spruce woodmeal. It is within the range quoted for nitrated wood cellulose [3b], although much lower than values obtained by Timell et al. [4,5].

Basta and Samuelson have used "intrinsic viscosity" values which are symbolized by "$[\eta]$", and are measured by SCAN C-15:62. Because a linear relationship exists [1] between $[\eta]^{-1}$ and η^{-1} (where η refers to the TAPPI T-230 cuene viscosity), Equation 4 will apply to both kinds of viscosity measurement.

Decreasing Hydroxide Ion Concentration

The data plotted in Figure 1 show that viscosity prediction using the G-factor is possible provided that the alkali concentration is well defined. In industrial alkaline pulping, however, the hydroxide ion concentration varies as a function of time in a complex way. Since the integral $\int_o^t [OH^-]\cdot dt$ for an industrial cook seems to be inaccessible, the problem is to find some alkali term which will give a linear correlation with the integral.

In an attempt to find such a term we have examined the commonly measured parameters: initial effective alkali (EA_i), and residual effective alkali in the liquor at the end of the cook (EA_r). The residual alkali term seemed from the outset to be more promising: Basta and Samuelson provided residual alkali

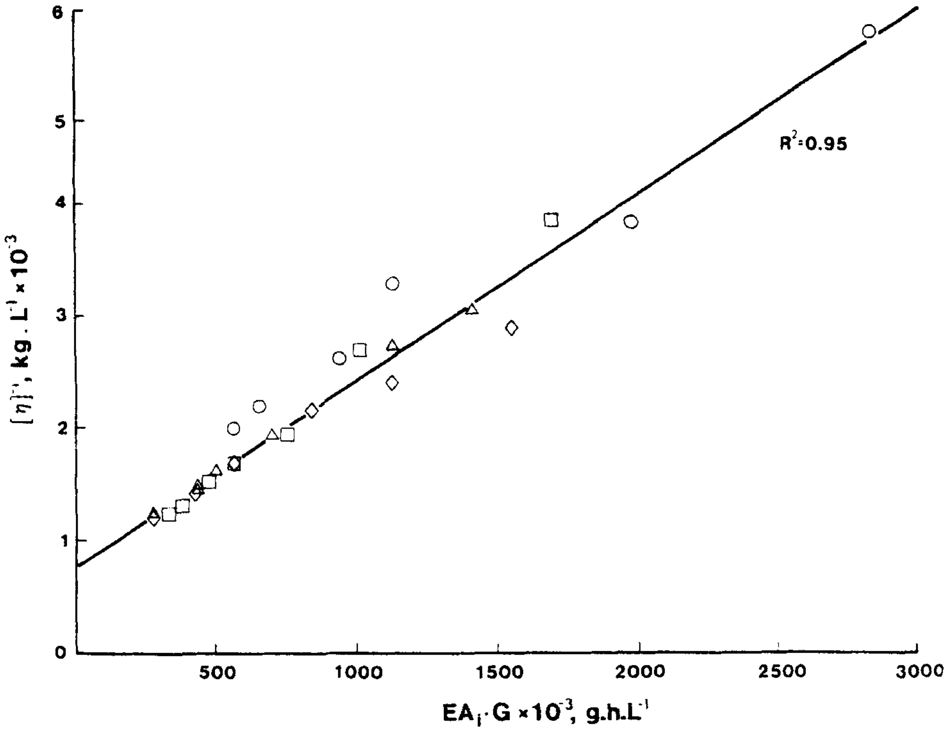

FIGURE 1. Soda pulping of spruce woodmeal at a liquor-to-wood ratio of 130:1. Data from Ref. 2 spanning a range of alkali charges and cooking times produce a straight-line graph when reciprocal viscosity is plotted against G x initial hydroxide concentration. ◇ indicates cooks with an initial alkali concentration of 7.75 g/L, △ indicates 15.5 g/L, ☐ indicates 31 g/L and O indicates 62 g/L as Na_2O.

data which correspond to the initial alkali values used in Figure 1. The residual alkali values differed only slightly from the initial values, but the fit of the data to a plot of $[\eta]^{-1}$ versus $EA_r \cdot G$ was improved ($R^2 = 0.97$).

When our own data for normal kraft cooks done at constant cooking time were examined by plotting the reciprocal of the cuene viscosity against the alkali terms, neither graph was perfectly straight (Figure 2). However, a straight line does give a rather close fit to the data over the region of industrial significance (i.e., EA_i = 40-65 g/L, EA_r = 5-25 g/L). It therefore seems likely either EA_i or EA_r would be adequate alkali terms for the purpose of viscosity prediction under well controlled pulping conditions.

Figure 3 shows a plot of $[EA_i \times G]$ against reciprocal viscosity for cooks done under normal kraft pulping conditions. Some scatter is evident, especially at lower viscosity levels, but the majority of the points fall close to the line which curves slightly in the high viscosity region. Both hardwood and softwood data points seem to fit roughly the same curve. A straight-line plot was also considered for these data, but when $[EA_i \times G]$ is zero, a straight-line plot indicates a negative reciprocal viscosity which has no physical meaning.

Figure 4 shows plots of $[EA_r \times G]$ versus reciprocal viscosity for the same cooks as those on which Figure 3 is based. In this case we obtained straight-line plots with different slopes for hardwoods and softwoods. The relationship illustrated in Figure 4 is expressed by equation 5 where the values of C and

$$\frac{1}{\eta} = k\ [EA_r]G + C \qquad (5)$$

k were 5.6×10^{-3} and 2.5×10^{-7} for hardwoods, or 7.2×10^{-3} and 1.6×10^{-7} for softwoods.

The predictive value of equation 5 and of Figure 3 was tested with a number of cooks in which species, alkali charge, cooking process, time and temperature were varied over a wide range. In Table 1 the predicted viscosity values are compared with the

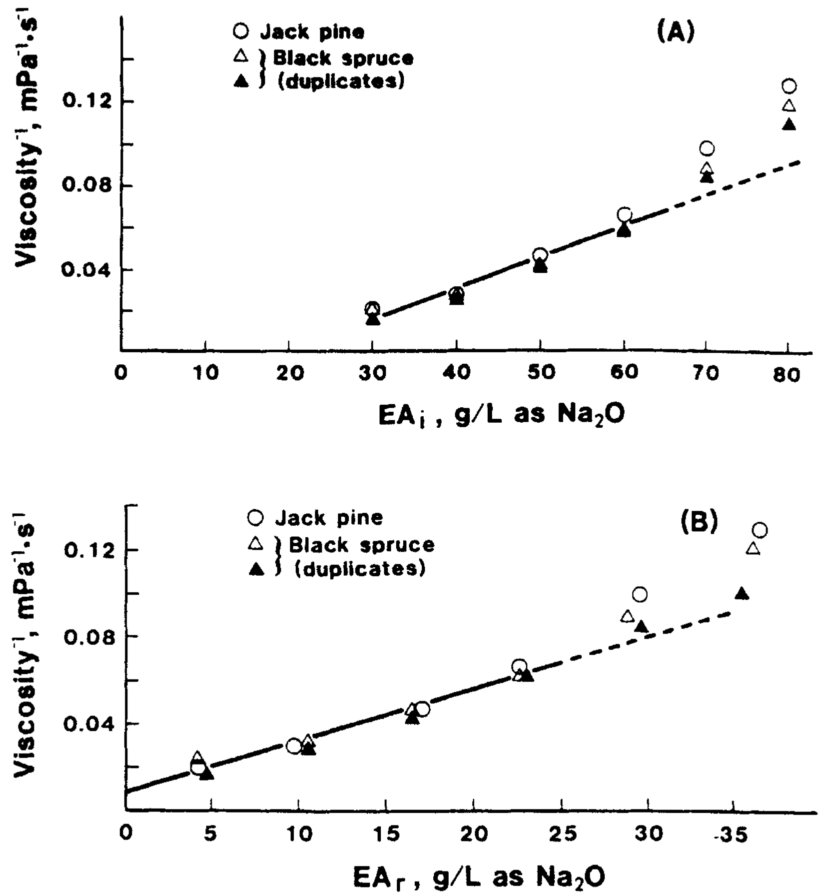

FIGURE 2. Constant G-factor pulping: reciprocal viscosity is plotted against (A) the initial effective-alkali concentration and (B) corresponding residual alkali concentrations for normal kraft cooks terminated at a constant G-factor of 14,060 (equivalent to 1400 H at 170°C).

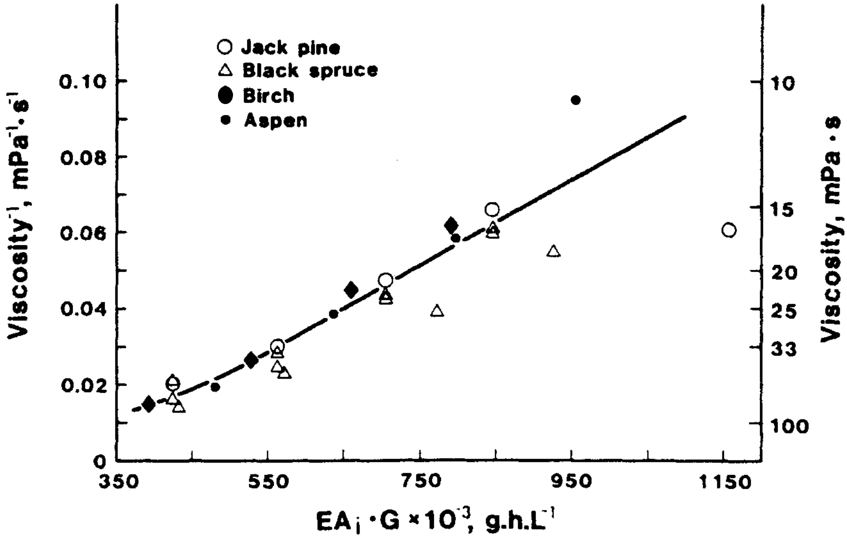

FIGURE 3. Pulping at different G-factors with the alkali charge limited to the industrial range. Reciprocal viscosity is plotted against EA_i x G, with EA_i values of 30-65 g/L (as Na_2O) and G values ranging from 13,150 to 25,700; sulfidity, 30%.

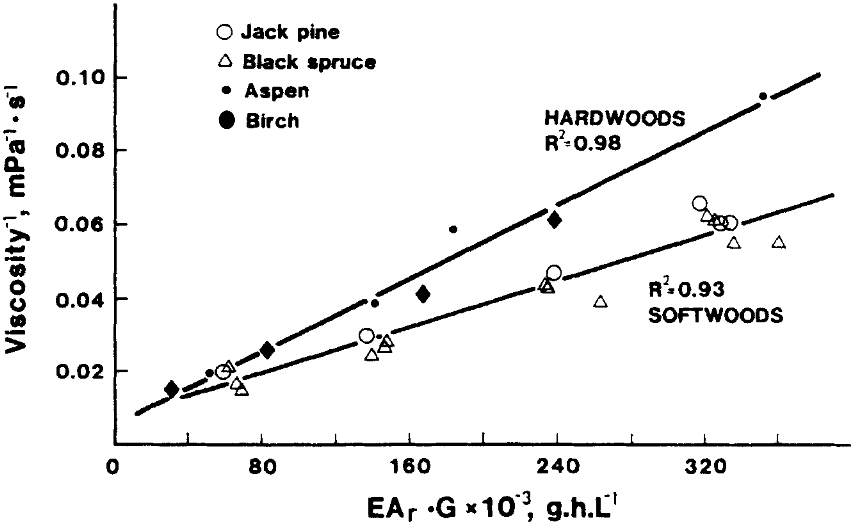

FIGURE 4. Reciprocal viscosity is plotted against EA_r x G for kraft pulping of hardwoods, and softwoods at 30% sulfidity. The EA_i values and G-factor ranges were the same as in Figure 3.

TABLE 1. Prediction of Pulp Viscosity

Wood Species	Type of Cook a)	Temp., °C	Time at Temp., h	G	EA_l b,c) g/L as Na_2O	EA_r c) g/L as Na_2O	Viscosity Predicted from Fig. 3, mPa•s	Viscosity Predicted from Eq. 5, mPa•s	Actual Viscosity Found, mPa•s	Kappa Number	Total Yield, %
Jack Pine	Bleachable-grade kraft	167	2	14,300	42.5	11.9	28.2	29.0	26.5 ± 0.5	26.3	44.0
Western Hemlock	Kraft, excessive alkali	170	1.5	15,000	60.0	23.2	14.7	15.9	17.0 ± 0.5	16.7	41.8
Black Spruce	Kraft, "high temperature"	177	1	22,126	45.0	12.8	12.8	19.1	21.7 ± 0.5	19.0	46.2
Douglas Fir	Sack kraft	172	1	12,900	35.0	6.50	47.8	48.5	48.0 ± 1.4	52.8	48.6
E. Hardwood mixture	Bleachable-grade kraft	172	1	12,900	36.5	6.30	45.2	38.5	36.6 ± 1.1	20.2	47.5
Aspen	Bleachable-grade soda-AQ (0.05%)	170	1.75	17,250	32.5	4.38	33.0	40.8	38.2 ± 0.3	18.2	58.5
Red Cedar	Bleachable-grade kraft	170	1.5	15,000	40.0	10.70	30.0	30.3	26.8 ± 0.9	33.0	46.0
Aspen	High-viscosity kraft-AQ (0.05%)	160	3	8,880	30.0	2.99	~100	81.7	66.1	11.0	58.7

a) Constant conditions: liquor to wood ratio; 4 L/kg (excluding wood moisture). Chips presteamed to about 53% moisture, 30% sulfidity, time to temperature = 90 minutes. Each type of cook was done in duplicate; the data reported here are the mean values obtained, and the range of the observed viscosity values is indicated.

b) EA_l refers to the concentration of alkali in the cooking liquor before dilution with wood moisture.

c) 16 g/L = 1 lb/cu. ft.

measured cuene viscosities. All the cooks and measurements were done in duplicate. The viscosity predictions from EA_r values and Equation 5 were more accurate than those made by using EA_i values and the curve shown in Figure 3. This can be clearly seen for the aspen soda-AQ cook, and for the kraft cooks of black spruce, and for the hardwood mixture; in the other cases, both prediction methods came close to the observed values. The last cook in Table 1 represents an attempt to see how well Equation 5 performs when extended to a region well outside the normal commercial range.

The EA_i values used in this work correspond to the alkali concentration of the added cooking liquor, and a constant dilution with wood moisture is assumed. It is not surprising that residual alkali values were found to correlate better with viscosity because they compensate, at least in part, for excessive wood moisture, rotten wood, and different wood acidities, all of which decrease the concentration of the cooking alkali.

EXPERIMENTAL

Wood chips (250 g, o.d.) were cooked with 1 litre of liquor in 2L stainless steel bombs which were rotated in an oil bath. The constants k and C were evaluated for the H-factor range 1100-2500. The residual alkali concentration was determined by titrating to a final pH of 10.5 using 1.0 M hydrochloric acid. The pulp viscosities were measured by TAPPI Standard Method T-230 os-76 after first delignifying the pulp in the following way:

Unbleached pulp (15 g, o.d.) at 20% consistency was shredded and mixed with 150 mL of aqueous sodium chlorite (100 g/L). 100 mL of buffer solution (pH 4.0) containing sodium acetate (5 g) and acetic acid (10 g) was added and the pulp mass was well mixed once again. The pulp was allowed to react in a sealed container for 18 h at room temperature and the delignified pulp was then diluted and washed.

CONCLUSIONS

Our earlier work showed that cooks done at different temperatures but at a constant G-value would produce pulps of similar viscosity. Thus the G-factor can be used like the H-factor; for a particular wood furnish, alkali charge, and liquor-to-wood ratio, there is a correlation between G-factor and viscosity — just as there is a correlation between H-factor and kappa number. The work has now been extended so that pulp viscosities can be calculated with reasonable precision even when the wood furnish and alkali charge are varied. Although differences in liquor-to-wood ratio or in methods of residual alkali measurement would call for some adjustment of the constants k and C, it is anticipated that the relationship expressed by Equation 5 will be applicable to a spectrum of alkaline pulping processes, provided that no oxidants are present.

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APPENDIX

DATA USED IN FIGURES 2, 3 AND 4

COOK NUMBER	SPECIES	TEMP., °C	TIME AT TEMP., MIN.	G-FACTOR	EA_I g/L Na_2O	EA_r g/L Na_2O	EA_rxG	VISCOSITY (η), mPa.s	η^{-1}
21802	Birch	170	78	13,150	60	18.0	236,700	16.1	0.0621
21805	Birch	170	78	13,150	50	12.6	165,690	24.1	0.0415
21808	Birch	170	78	13,150	40	6.3	82,850	38.1	0.0262
21816	Birch	170	78	13,150	30	2.3	30,250	66.8	0.0150
22213	Aspen	170	90	15,884	30	3.3	52,410	51.7	0.0193
22215	Aspen	170	90	15,884	40	8.8	139,780	26.0	0.0385
22217	Aspen	170	90	15,884	50	11.5	182,670	17.1	0.0585
22219	Aspen	170	90	15,884	60	22.0	349,500	10.5	0.0952
21787	J. Pine	170	84	14,064	60	22.5	316,440	15.1	0.0662
21790	J. Pine	170	84	14,064	50	16.9	237,680	21.3	0.0470
21793	J. Pine	170	84	14,064	40	9.7	136,420	33.8	0.0296
21796	J. Pine	170	84	14,064	30	4.2	59,070	49.0	0.0204
22195	J. Pine	175	90	25,700	45	12.6	323,820	16.5	0.0606
22197	J. Pine	175	90	25,700	45	12.7	326,390	16.4	0.0610
21697	B. Spruce	170	84	14,060	60	22.8	320,570	16.1	0.0621
21700	B. Spruce	170	84	14,060	50	16.6	233,400	22.9	0.0437
21739	B. Spruce	170	84	14,060	40	10.5	147,760	35.4	0.0282
21742	B. Spruce	170	84	14,060	30	4.3	60,460	47.0	0.0213
21581	B. Spruce	170	84	14,060	60	23.1	324,790	16.3	0.0613
21582	B. Spruce	170	84	14,060	50	16.6	233,400	23.2	0.0431
21583	B. Spruce	170	84	14,060	40	10.4	146,220	37.5	0.0266
21584	B. Spruce	170	84	14,060	30	4.7	66,080	59.0	0.0170
22173	B. Spruce	170	94	15,400	60	23.4	360,360	18.2	0.0550
22175	B. Spruce	170	94	15,400	50	17.1	263,340	25.6	0.0391
22185	B. Spruce	170	85	14,216	40	9.8	139,320	40.2	0.0249
22187	B. Spruce	170	85	14,216	30	4.9	69,660	66.9	0.0149
22199	B. Spruce	175	105	29,600	45	11.3	334,480	18.1	0.0553