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Nonuniformity of Carbohydrate Degradation During Kraft Pulping—  
Measurement and Modeling Using a Modified G-Factor

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# **Nonuniformity of Carbohydrate Degradation during Kraft Pulping – Measurement and Modeling Using A Modified G-Factor**

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## **Abstract**

Nonuniform carbohydrate degradation during pulping can be more harmful to pulp strength than the same degree of degradation occurring uniformly. The non-uniformity is also not readily apparent because the measured viscosity is an indication of only the average degree of polymerization (DP) of cellulose. A modified G-factor model that incorporates the history of both temperature and [OH<sup>-</sup>] changes in wood chips during cooking is presented. By calculating G[OH<sup>-</sup>] for a given position within a wood chip, the viscosity at that position can be predicted and a pulp viscosity profile across the chip thickness can be obtained. This new method requires knowing the variation in [OH<sup>-</sup>] across the thickness of the wood chip and during the cook. These variations can be determined by solving a set of mass transfer equations with kinetic reaction terms, and is solved numerically by a computer program, which generates the values of the modified G-factor. These G-factor values are then converted to pulp viscosity. The model was experimentally validated by measuring the viscosity profiles over the thickness direction of hand-cut wood chips. The measured profile agreed well with the calculated profile. Both measured and calculated profiles showed that carbohydrate degradation of thick chips was very nonuniform with the viscosity of the cellulose at the chip center being 50 to 100% higher than that at the edge of the 10-mm thick chips. The difference in these viscosities for the 3-mm thick chip was much smaller and between 10 and 15%.

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## Introduction

Severe carbohydrate degradation in kraft pulping can reduce the pulp fiber strength, and can also potentially lead to higher carbohydrate dissolution, thus higher yield loss. The extent of the degradation is normally described in terms of the average cellulose chain length or the degree of polymerization (DP), which is determined from a measurement of viscosity of a cellulose solution.

The correlation of fiber strength with cellulose DP, however, is not a linear relationship. Figure 1 shows the zero-span breaking length as a function of cellulose DP for pulps produced by several processes (Gurnagul et al., 1992). For kraft pulps, zero-span breaking length fell only slightly with DP falls if the DP value remained above 1000. The lack of effect in pulps with DPs higher than 1000 has been explained as being a consequence of the cellulose degradation in kraft pulping being homogeneous, and inter chain H-bonding being adequate to maintain the strength of the cellulose fibrils. The decrease in zero-span breaking length at DPs lower than 1000 by this hypothesis is caused by the failure of H bonding to overcome the loss of structural integrity in the cellulose fibrils.. These DP values can be approximately related to TAPPI standard viscosity values (Clark, 1985): DP 1000 is about 12 mPa.s, and DP 1600 is close to 30 mPa.s. The typical value for an oxygen delignified kraft pulp is about 15 mPa.s, the value for a conventional kraft pulp at 30 kappa number is about 30 mPa.s. The strength behavior in the DP range of 1000-1600 for kraft pulp agrees with the fact that unbleached kraft pulp and oxygen-delignified pulp do not show any significant strength loss in the viscosity range of 15 to 30 mPa.s.

However, even if a kraft pulp, oxygen-delignified or not, has an average DP or viscosity value above the critical point, it does not ensure that the pulp will retain its full strength potential. This is because nonuniformity of the pulp viscosity can play a significant role in the overall pulp strength. Let us consider two pulps both having a viscosity value of 15 mPa.s. One is quite uniform, with a narrow viscosity distribution over fiber mass, e.g., from 13 to 17 mPa.s. The other one is very nonuniform, with a wide distribution e.g. from 5 to 25 mPa.s. The second pulp should have lower fiber strength because the fibers composed of cellulose chains with viscosities above 17 mPa.s and between 13 and 17 mPa.s will all have the same strength while the fibers composed of cellulose chains with viscosities less than 12 mPa.s will have lower strength. These observations agree well with industry observations.

The nonuniform viscosity distribution resulting from nonuniform carbohydrate degradation is more important for pulps that are oxygen delignified than for pulps that are not since the oxygen-delignified pulps have a viscosity close to the critical point. Narrow viscosity distribution or uniform carbohydrate degradation should be even more important for the process concept of extended oxygen delignification of high kappa number pulp, which could reduce the pulp viscosity up to 70%. Thus, understanding the effect of pulping conditions on cellulose DP distribution can assist us in choosing more suitable technologies to achieve other objectives, such as yield improvement or extended delignification, without impacting pulp strength.

It has been shown that the kinetics of carbohydrate degradation during kraft pulping are mainly influenced by temperature and hydroxide ion concentration, and not by sulfide concentration or addition of AQ. Since heat transfer is much faster than mass transfer at chip scale, the nonuniformity is not likely to be created by temperature non-uniformities but by [OH<sup>-</sup>] non-uniformities. Because of this, the classical G-factor method developed by Kubes et al. (1983), which only predicts the effect of temperature and time on carbohydrate degradation, cannot be

used directly to predict the effect of nonuniform  $[OH^-]$  inside wood chips on pulp viscosity uniformity.

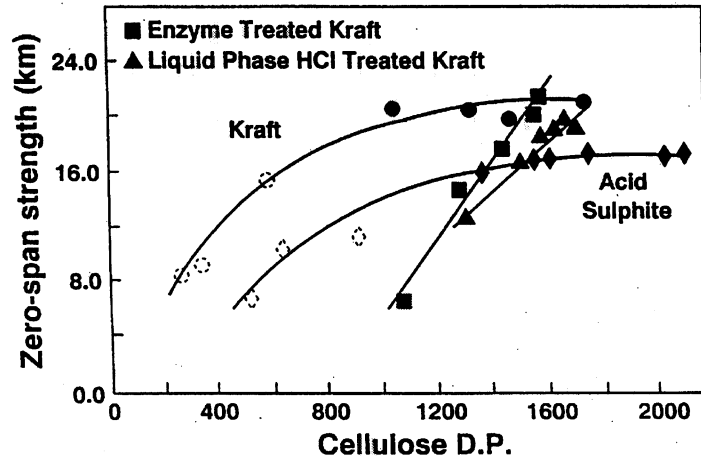


Figure 1. Zero-span strength of handsheets of black spruce pulps as a function of cellulose DP. The dotted symbols denote samples treated in vapor-phase HCl.

This report describes a new, modified G-factor method which incorporates the history of both temperature and  $[OH^-]$  changes during cooking and can be used to predict the pulp viscosity profile over the chip thickness. The predicted viscosity profile has been validated with experimentally measured profiles.

## Theory

### The Modified G-Factor Model

Based on the original kinetic expression proposed by Kubes et al. (1983), the rate of cleavage of glycosidic bonds is a function of the molar concentrations of glycosidic bonds,  $[Gly]$ , and hydroxide,  $[OH^-]$ :

$$\frac{d[C]}{dt} = k[Gly][OH^-] \quad (1)$$

where  $k$  is the reaction constant,  $[C]$  is the molar concentrations of carbohydrate. Unless DP is reduced well below 100,  $[Gly]$  stays almost constant, and so integration over the reaction time gives:

$$\frac{[C]}{[Gly]} - \frac{[C]_0}{[Gly]} = \int_0^t A e^{-\frac{E}{RT(t)}} [OH^-](x,t) dt \quad (2)$$

$$\text{Since } \frac{[C]}{[Gly]} = \frac{1}{DP_w}, \text{ and } DP_w^\alpha = 0.75\eta \quad (\alpha = 0.901, \approx 1) \quad (3)$$

the following equation was derived by Kubes *et al.* from Equation (2):

$$\frac{1}{\eta} - \frac{1}{\eta_0} = 0.75A \cdot [OH^-] \frac{1}{k_{373}} \int e^{\left[ \frac{E}{R} \left( \frac{1}{373} - \frac{1}{T(t)} \right) \right]} dt \quad (4)$$

where  $\eta_0$  is initial viscosity,  $\eta$  the viscosity at time  $t$ ,  $k_{373}$  the rate constant at 373°K,  $E$  the activation energy for cellulose degradation, 179 kJ/mol, and  $R$  the gas constant. Kubes *et al.* (1983) let

$$\int e^{\left[ \frac{E}{R} \left( \frac{1}{373} - \frac{1}{T(t)} \right) \right]} dt = G \quad (5)$$

The remaining terms in the right-hand side of the equation were considered constants and so Equation (4) became

$$\frac{1}{\eta} - \frac{1}{\eta_0} = a \cdot G \quad (6)$$

$G$  is a factor that can be calculated from the temperature history of the cook. However, because of mass transfer limitations, especially in the chip thickness direction,  $[OH^-]$  is not constant within the wood chips during cooking and therefore the term “ $a$ ” in Equation 6 is not constant either. If we have to include the effect of  $[OH^-]$ , Equation (2) becomes

$$\frac{1}{\eta} - \frac{1}{\eta_0} = a' \int [OH^-](t, x) \cdot e^{\left[ \frac{E}{R} \left( \frac{1}{373} - \frac{1}{T(t)} \right) \right]} dt = a' \cdot G([OH^-]) \quad (7)$$

When there is no concentration gradient within the chips, hydroxide or EA concentration during cooking becomes a function of cooking time and initial alkali charge, a set of conditions that were studied by Fleming and Kubes (1985). When there is a concentration gradient within the chips, this modified factor,  $G([OH^-])$ , has to be calculated numerically, and accumulated for progressive increments across the wood chips. When the time scale,  $\Delta t$ , is small enough,  $G_x([OH^-])$  can be calculated as

$$G_x([OH^-]) = \sum_0^t [OH^-]_{x,t} \cdot G_T \cdot \Delta t \quad (8)$$

where  $[OH^-]_{x,t}$  is hydroxide concentration for a given position at a given time,  $G_T$  the  $G$ -factor defined by Equation (5) at the digester temperature at a given time,  $\Delta t$  a small time interval during which temperature and  $[OH^-]$  can be treated as constant. Once  $G_x([OH^-])$  is obtained from the calculation, the viscosity of the pulp fiber at a given time and a given location inside the chips can be predicted from an experimentally measured calibration correlation. Two correlations based on published information will be shown later.

### ***Hydroxide Concentration Profile – Mass Transfer***

The most important and complex step in calculating this new G factor is to calculate the exact concentration of hydroxide at every location in the chips. This concentration profile can be obtained by solving a nonsteady state, one-dimensional mass transfer equation (assuming chip thickness is much smaller than width and height):

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left( D_i(x,t) \frac{\partial C_i}{\partial x} \right) + R_i(x,t) \quad (9)$$

where  $C_i$  is the concentration of the  $i$  species, e.g.,  $\text{OH}^-$  or  $\text{HS}^-$ ,  $D(x,t)$  is the diffusion coefficient, and  $R(x,t)$  is the chemical reaction kinetic rate. The initial and boundary conditions required to solve the equation include:

$$C_i = C_{i0} \quad (\text{at initial, or } t = 0) \quad (10)$$

$$\frac{\partial C_i}{\partial x} = 0 \quad (\text{at chip center, or } x = 0) \quad (11)$$

$$C_{i,\pm l} = C_{bulk} \quad (\text{at chip edge, or } x = \pm l) \quad (12)$$

The numerical procedure for this problem was well established by Gustafson et al. (1983). The kinetic equations were obtained from literature sources. These equations describe the rate of generation or consumption of various compounds, and are used to determine the  $R_i$  terms in the transport equations. The bulk concentration is calculated from mass balance. At the start of each iteration, the reaction rates of all species at each position in the chip were determined from the equations listed in the Appendix. The kinetic equations and procedure to calculate diffusion coefficients are given in the Appendix.

### **Experimental**

To validate the predicted viscosity profiles, we measured the viscosity profiles across the wood chip thickness after kraft cooking. Hand-cut southern pine chips with two thicknesses (3 and 10 mm) were cooked under conventional kraft conditions. Active alkali was 18% on wood, and sulfidity was 30% in AA. Liquor-to-wood ratio was 4:1 (L:kg) including moisture. Bomb digesters (0.5 L) were used for cooking, and were heated in a rotary oil bath. The time to heat the digester from room temperature to the final cooking temperature, 170°C, was 70 minutes. Cooking time at 170°C was controlled by H-factor.

After cooking, the cooked chips were washed, and then soaked in water overnight. The wet chips were then frozen to -20°C to prepare them for sectioning. The frozen cooked chips were sectioned with a hand-held planer. Chips of 3-mm thick were sectioned into 3 equal parts while chips of 10 mm were sectioned into 10 equal parts. Each fraction of sectioned chips were then disintegrated. The resulting pulps were well washed before they were bleached with sodium chlorite using CPPA Useful Method G.10U. Part of the pulps was made into handsheets for kappa number testing. Each fraction of the pulp was then tested for viscosity using TAPPI Standard Method T-230.

## Results and Discussion

### *Correlation of the New G-factor $G([OH])$ with Viscosity*

The relationship between  $G([OH])$  and viscosity can be experimentally evaluated under the conditions of very high liquor-to-wood ratio giving a high alkali charge on wood, long heating time to cooking temperature, and thin wood chips. If the total alkali charge is very high, e.g., over 100% on o.d. wood weight, the consumption of the alkali is small. The alkali concentration in the bulk liquor phase, thus, can be assumed to be constant during the cook. When a long heating time and thin wood chips are used, the mass transfer limitation or alkali concentration gradient over the chip thickness is eliminated. Under these conditions, the alkali concentration inside the wood chips can be assumed to be uniform and the same as that in bulk liquor. The conditions used by Kubes et al. (1983) in their study were used to develop this correlation. Under these conditions, Equation (7) becomes

$$\frac{1}{\eta} + \frac{1}{\eta_0} = a' \cdot G \cdot [OH^-]_0 = a' G([OH]) \quad (13)$$

where  $G$  is the original G-factor,  $[OH^-]_0$  the initial bulk effective alkali concentration, and  $a'$  and  $1/\eta_0$  are two constants. Figure 2 shows the reciprocal viscosity,  $1/\eta$ , as a function of  $G[OH]$  (hr.mol/L) for kraft and soda-AQ cooking. Regression of the data shows a relatively good linear relationship between  $1/\eta$  and  $G([OH])$ . Using these correlations, viscosity can be predicted once the value of  $G([OH])$  is calculated.

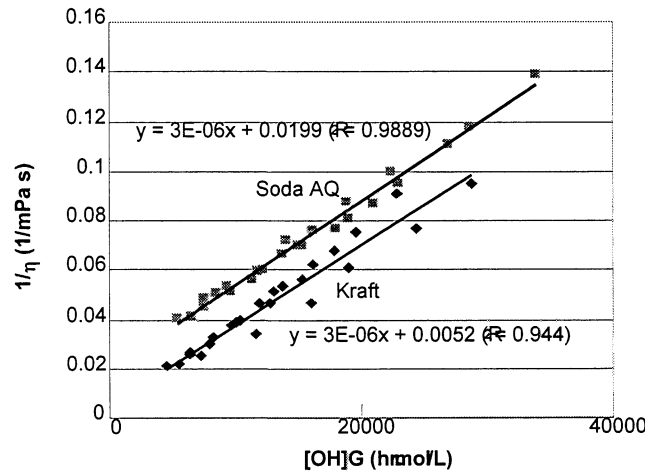


Figure 2. Relationship of viscosity and the new modified G-factor,  $G([OH])$ .

### *Effect of Mass Transfer on Alkali Profile*

Figure 3 shows the alkali profiles calculated based on Equation (9) with information shown in the Appendix for two wood chips with different thickness, 2 and 8 mm. The initial bulk alkali concentration was 1.68 mol/L. The time interval between each line was 20 minutes. The mass transfer rate to the center of 2-mm chips is very rapid. After only 40 minutes, alkali is already in the center of the chips. At this time, the temperature of the digester is still below 100°C, and



carbohydrate degradation and G-factor accumulation have not yet started. At 80 min, when cooking temperature is attained, the degradation reaction of the carbohydrate should be very uniform since the alkali concentration is very uniform across the chip thickness. In contrast, alkali has not yet reached the center of the 8-mm chips after 120 min, i.e., about half-hour already at cooking temperature 170°C. Alkali-induced cellulose degradation has not yet taken place at the center of the chips. The cellulose at the edge of the 8-mm chips has been exposed to a higher alkali concentration than that of the 2-mm chips because there has been little consumption of alkali which has kept the bulk concentration at a high level. G([OH]) factor accumulation at the chip center is zero, while at the chip edge the amount of accumulation is already high. Therefore, the G([OH]) profile for the 8-mm chips will indicate very nonuniform degradation of the carbohydrates while the original G-factor will show no difference in carbohydrate degradation across the chip thickness.

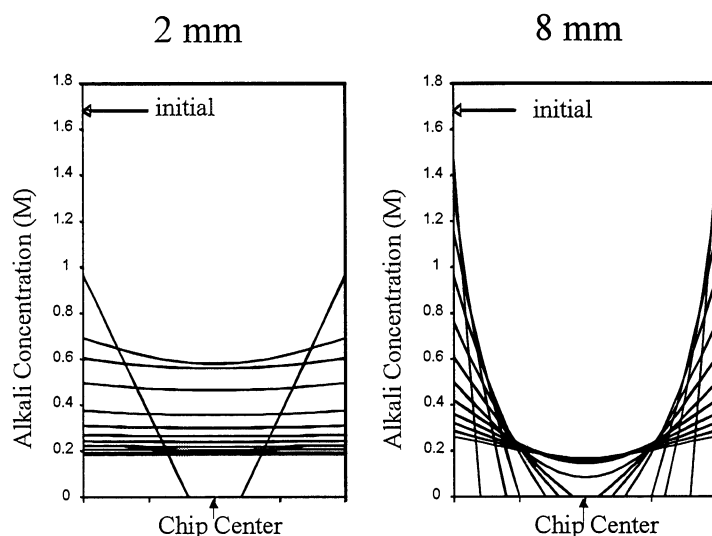


Figure 3. Alkali concentration profile for wood chips with two thicknesses, 2 and 8 mm. The time interval between each profile is 20 minutes.

#### *Comparison of the Predicted and Measured Nonuniformity of Viscosity*

Figure 4 shows the viscosity profiles for 3-mm thick chips after 1500 H-factor. The calculated data show the viscosity is quite uniform across the chip thickness. The difference between the center and the edge is less than three units. Although there were only two measured data points, one at the edge and one at the center, the measured data do confirm a uniform viscosity profile. However, there is 10-unit difference between the calculated and the measured viscosity across the chip. We do not know what the exact reason is for this difference though it could be a systematic error in the measurement or a constant error in the calculation.

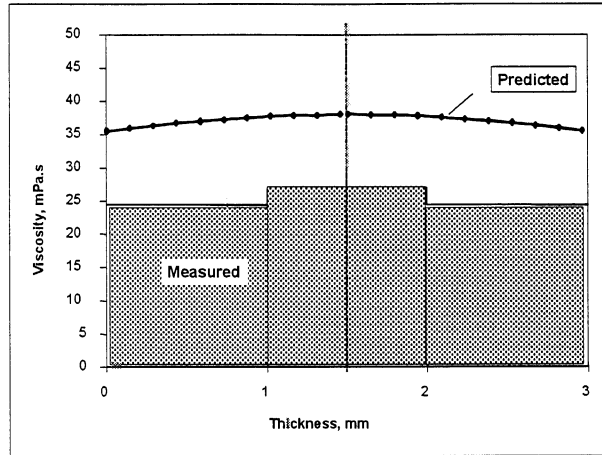


Figure 4. The measured and predicted viscosity profiles for 3-mm thick chips.

The agreement between the measured and the predicted values for 10-mm thick chips is much better in terms of the absolute values, confirming that the  $G([OH])$  model and the computational procedure are valid and can be used as a tool to evaluate the viscosity uniformity. The cellulose degradation is very nonuniform. The difference between the edge and the center, as measured, is more than 15 units, while as calculated it is up to 25 units. If this pulp was oxygen delignified and its average viscosity was decreased by 60%, about one-third of the pulp fibers could lose their fiber strength since their viscosity could have dropped below 12 mPa.s, the critical point shown in Figure 1. Even though, the average viscosity of the pulp would still be above 15 mPa.s. The measured profile shows a lower nonuniformity than that predicted. This is probably because the four chip surfaces in the two other directions were not blocked during cooking, which allows alkali to diffuse into the chips from these surfaces. The cellulose in the fibers nearest these surfaces would have lower viscosity.

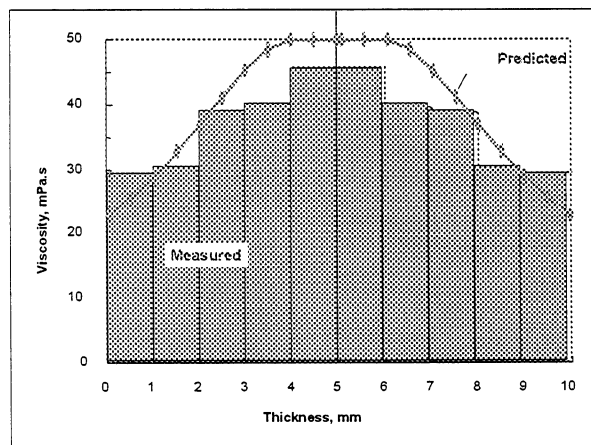


Figure 5. The measured and predicted viscosity profiles for 10-mm thick chips.

### *The Calculated Effect of Cooking Process Conditions on Viscosity Uniformity*

To show the ability of this model as a research tool to study the effect of the pulping process on viscosity uniformity, three different cooking processes were chosen: conventional cooking at 170°C, two-stage cooking at 160°C (Li et al., 1998), and Iso-Thermal Cooking (ITC) at 160°C (Andtbacka and Tibbling, 1994). The AA charge was 18%, and sulfidity was 30%. In two-stage cooking, half of the AA was charged at each stage, while the first-stage liquor contained a significant amount of residual AA from the recycled second-stage spent liquor. Detailed information on this process can be found in the reference (Li et al., 1998). The initial AA charge used in the ITC process was 65%, while 20% was charged to the back end of the first counter-current stage, and 15% is charged to the back end of second counter-current stage or the bottom of the digester. Figure 6 shows the average viscosity as a function of the average kappa number for 4-mm thick chips. Viscosity from both two-stage cooking and ITC was significantly higher, 15-20 units, than that of the conventional cooking. This higher selectivity from two-stage cooking and ITC was mostly the result of the lower cooking temperature. The viscosity of the two-stage pulp was slightly higher than that of the ITC pulp, which may be because of the differences in the alkali profiles.

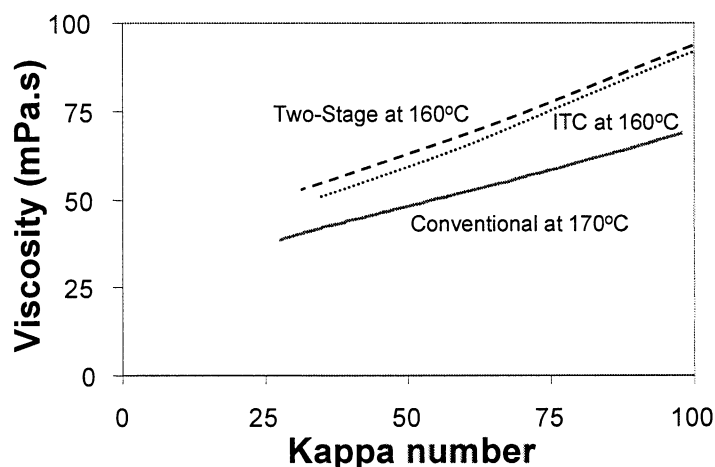


Figure 6. The calculated average viscosity as a function of kappa number for three different cooking processes using 4-mm thick chips.

The effect of the cooking process on uniformity is illustrated in Figure 7 by examining the viscosity profile across the wood chip thickness. The comparison is made at 55 kappa number. The viscosity for 2-mm chips is very uniform for all three types of cooking. Some nonuniformity begins to appear with 4-mm chips and becomes extreme with 8-mm chips. . The nonuniformity is the lowest for the ITC process, indicating that it is a very selective pulping process.

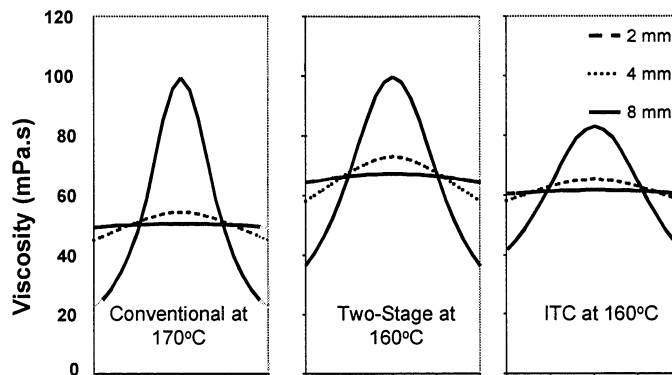


Figure 7. The viscosity profiles for three different cooking processes, and three different chip thicknesses. The average kappa number of all the pulps was 55.

## Conclusions

When the effect of hydroxide concentration is incorporated into the classical G-factor, a new parameter,  $G([\text{OH}])$  with a unit of  $\text{hr} \cdot \text{mol/L}$ , is required. If the numerical values of this parameter can be calculated for any given location in the wood chips, the cellulose viscosity at that location can be calculated. The linear relationship between  $G([\text{OH}])$  and reciprocal viscosity can be shown from published information, and this relationship can be used to convert the  $G([\text{OH}])$  value to a viscosity value. The calculation of the  $G([\text{OH}])$  value, however, requires a solution to the mass transfer equation for kraft cooking. The experimentally measured viscosity profile across the thickness of hand-cut wood chips agreed well with the calculated profile. Both indicated that carbohydrate degradation of thick chips was very nonuniform with the viscosity of the cellulose at the chip center being 50 to 100% higher than that at the edge of the 10-mm thick chips. The difference in these viscosities for the 3-mm thick chips was much smaller and between 10 and 15%.

## Acknowledgement

The theoretical background of the  $G([\text{OH}])$  and the numerical model used in this work were developed by Moeser and Li at the Pulp and Paper Research Institute of Canada (Paprican). The experimental evaluation and the writing of this report were performed by Rosen and Li at the Institute of Paper Science and Technology (IPST). The authors would like to thank Dr. Berry for reviewing the manuscript and providing many valuable comments. The authors would also like to thank Paprican and IPST for their support for completing this work, and the member companies of both institutes for their financial support.

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## Appendix

### **Lignin Reaction Kinetics:**

The delignification expressions used in the model came from the literature (Gustafson et al., 1983). Delignification was divided into three stages: initial, bulk, and residual. The expressions used were of the type:

Initial (lignin on wood > 22%):

$$\frac{dL}{dt} = 36.2T^{0.5} \exp\left(\frac{-4807.69}{T}\right)L \quad (a1)$$

Bulk (2% < lignin on wood < 22%):

$$\frac{dL}{dt} = \left[ \exp\left(35.19 - \frac{17200}{T}\right)[OH] + \exp\left(29.33 - \frac{14400}{T}\right)[OH]^{0.5}[S]^{0.4} \right] L \quad (a2)$$

Residual (lignin on wood < 2%):

$$\frac{dL}{dt} = \exp\left(19.64 - \frac{10804}{T}\right)[OH]^{0.7} L \quad (a3)$$

Where L = the mass % lignin on wood (%), [OH] = concentration of hydroxide (mol/L), and [S] = concentration of sulfide (mol/L). These equations are used to determine the rate of delignification and generation of dissolved lignin.

### **Carbohydrate Reaction Kinetics:**

Carbohydrates were divided into cellulose and hemicellulose. Expressions were taken from the literature (Pu et al., 1991):

Initial (cellulose on wood > 38.8%):

$$\frac{dC}{dt} = \exp\left(4.50 - \frac{4209.8}{T}\right)[OH]^{1.5}(C - 32)^{1.5} \quad (a4)$$

Bulk (cellulose on wood < 38.8%):

$$\frac{dC}{dt} = \exp\left(36.08 - \frac{18014.9}{T}\right)[OH](C - 32) \quad (a5)$$

Initial (hemicellulose on wood > 11.5%):

$$\frac{dH}{dt} = \exp\left(6.02 - \frac{4209.8}{T}\right)[OH]^{1.5}(H - 5)^{1.5} \quad (a6)$$

Bulk (hemicellulose on wood < 11.5%):

$$\frac{dH}{dt} = \exp\left(21.42 - \frac{11186.0}{T}\right)[OH](H - 5) \quad (a7)$$

Where C = the mass % cellulose on wood (%), H = the mass % hemicellulose on wood (%). These kinetic equations show that carbohydrate degradation is only a function of hydroxide concentration, and not affected by sulfide.

#### **Alkali Consumption Rate:**

The alkali consumption rates were derived from coefficients taken from literature sources. Alkali was considered to be consumed by lignin, cellulose, hemicellulose, and acidic groups. Consumption by acidic groups was considered to be instantaneous; that is, the alkali concentration at any position was zero until all of the moles of acidic groups at that position were neutralized. One mole of acidic groups neutralized one mole of alkali. Consumption of alkali by lignin, cellulose, and hemicellulose was determined by stoichiometric coefficients obtained from the literature. (Pu et al., 1991). Therefore:

$$\frac{d[OH^-]}{dt} = \left[ 0.0032 \frac{dL}{dt} + 0.0061 \left( \frac{dC}{dt} + \frac{dH}{dt} \right) \right] \frac{1}{V_i} \quad (a8)$$

Note that this equation is consumption by lignin, cellulose, and hemicellulose only, and that the wood species reaction rates need to be converted from %/s to g/s.

#### **Alkali and Sulfide Diffusion Coefficients:**

The diffusion coefficients were determined by the method proposed by Burazin, 1986:

$$D = D_{b,298} \frac{\mu_{w,298}}{\mu_{liquor}} \frac{T}{298} ECCSA_r \quad (a9)$$

$$\mu_{liquor} = \exp\left((10.63S^3 + 1.302S^2 + 1)\ln(\mu_w) + 27.31S^3 + 4.108S\right) \quad (a10)$$

$$\mu_w = \frac{100}{2.26 \left( (T - 285.5) + \left\{ (T - 285.5)^2 + 9854 \right\}^{0.5} \right) - 142.2} \quad (a11)$$

$$\text{for } 0.65 < Y < 1: \quad ECCSA_r = -0.6056Y + 0.7620 \quad (a12)$$

$$\text{for } Y < 0.65: \quad ECCSA_r = 0.5633Y^2 - 1.338Y + 1 \quad (a13)$$

Where  $D_{b,298}$  = diffusion coefficient at 298 K in bulk solution ( $\text{cm}^2/\text{s}$ ),  $\mu_{w,298}$  = viscosity of water at 298 K (cp),  $\mu_{liquor}$  = viscosity of the liquor (cp),  $ECCSA_r$  = effective capillary cross section in the radial direction,  $\mu_w$  = viscosity of water (cp),  $S$  = solids fraction, and  $Y$  = yield. The value of

the constants were taken from Burazin, 1986:  $\mu_{w,298} = 0.8937$  cp, alkali  $D_{b,298} = 2.12 \times 10^{-5}$  cm<sup>2</sup>/s, and sulfide  $D_{b,298} = 1.51 \times 10^{-5}$  cm<sup>2</sup>/s.

Note: The solids fraction term was calculated accurately for conventional cooks. For simulations in which the liquor was drained and replaced by new liquor, the solids fraction term was not corrected. This resulted in liquor viscosities having a small error. However the overall effect of this on the value of the diffusion coefficient was very small compared to effects of temperature and ECCSA.





