

# RELATIONSHIP BETWEEN ALKALINE PULP YIELD AND THE MASS FRACTION AND DEGREE OF POLYMERIZATION OF CELLULOSE IN PULP

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## ABSTRACT

Pulp yield has a major impact on the competitiveness of a mill. Unfortunately a “real-time” pulp yield measurement method is not available at the present time. This paper presents a yield measurement method based on a theoretical relationship between alkaline pulping yield and the mass fraction and degree of polymerization (DP) of cellulose in pulp. The relationship is derived from the cellulose mass balance and kinetics of the alkaline hydrolysis, peeling and stopping reactions of cellulose. It is validated for soda, soda-AQ, kraft, kraft-AQ, polysulfide and polysulfide-AQ pulping of Rock Maple, Yellow Birch, Poplar and Black Spruce.

## INTRODUCTION

Wood is the dominant cost factor for a pulp mill. Therefore an increase in pulp yield has a major impact on its competitiveness. In order to optimize pulp yield, for example by changing operating conditions, a mill must be able to monitor the yield accurately. Traditionally, pulp yield is estimated based on wood usage and pulp sales data covering a period of 3-6 months to eliminate the dynamics of the mill operation. However, this approach can not be used to monitor yield changes occurring for brief periods, e.g., during evaluation of process modifications (Easty and Malcolm, 1982).

There are two general approaches available to measure mill pulp yield: the direct and indirect methods. In the direct pulp measurement method the yield is determined from the wood and pulp mass or mass flow rates. The indirect pulp yield measurement methods rely on measurement of pulp or spent pulping liquor properties to determine the yield using pre-established “calibration curves”. Direct measurement of industrial pulp yield is difficult. For the batch cooking process, one can use so-called “hanging baskets” whereby the yield is measured of wood chips contained in a basket suspended inside the digester (MacLeod and Pelletier, 1987). This procedure requires well trained operators and scientists, and auxiliary equipment must be installed. In the case of continuous digesters, the yield can be determined from the solids content and flow rates of the chips and pulp streams entering and leaving respectively the digester vessel. However, the imprecision of these measurements invalidates the establishment of an accurate mass flow rate balance for pulp yield purposes.

Several indirect pulp yield measurements methods have been reported in literature. The yield-kappa relationship method is based on a constant cellulose/hemicellulose/lignin relationship irrespective of cooking conditions (Easty and Malcolm, 1982). However, it is well known that these relationships are affected by the

choice of species and pulping conditions (McDonough, 1998). In another method, Luthe et al. (2002) uses the mannan content of softwood pulps to evaluate the yield of polysulfide and anthraquinone pulping trials. However, this technique does not apply to hardwoods. The  $Y_{\text{cell}}$  method by Easty and Malcolm (1982) is based on the assumption that the cellulose content remains constant during cooking. The pulp yield is then calculated as the ratio of the cellulose mass fraction of a particular wood species (the so-called  $Y_{\text{cell}}$  value) and that of the derived pulp. A weakness of this method is that it ignores cellulose loss during cooking by secondary peeling. Another indirect method is the determination of pulp yield from fiber coarseness. Since there is a linear relation between coarseness and yield (Maccoccia et al., 1998), this method is promising. Unfortunately it is not precise due to limited accuracy of coarseness measurements. Pulp yield can also be estimated from black liquor properties. Genco et al. (1990) confirmed that total organic carbon (TOC) values of black liquor correlate well with batch digester pulp yields. However, the pulps must have the same kappa number. Finally, Maccoccia et al. (1998) proposed an empirical linear relationship between the lignin free yield and a combined parameter containing the Tappi viscosity and cellulose content of the pulp.

Cellulose is a homopolymer subject to well known degradation kinetics during alkaline pulping. Therefore, the development of the cellulose mass fraction based on wood may be predicted theoretically. The pulp yield is then calculated as the ratio of this predicted mass fraction and the measured cellulose mass fraction of pulp. In the present paper this theoretical relationship between pulp yield and the cellulose mass fraction based on wood and the cellulose mass fraction of pulp is derived, and then tested for several wood species and different alkaline pulping processes.

## THEORY

### Pulp Yield Prediction Equation

The average degree of polymerization of cellulose chains in wood,  $DP_0$ , decreases during pulping to a lower value,  $DP$ , due to alkaline hydrolysis and primary and secondary peeling. The cellulose mass fraction of pulp based on wood,  $Y_c$ , (expressed as g cellulose/g o.d. wood) is related to the cellulose mass fraction of the original wood,  $Y_{c,w}$ , as

$$Y_c = \frac{n \cdot (DP)}{n_0 \cdot (DP_0)} Y_{c,w} \quad (1)$$

where  $n_0$  is the number of cellulose chains in the original wood, and  $n$  is the number of cellulose chains in the pulp derived by cooking from this wood.

When it is assumed that the loss of degree of polymerization due to primary peeling,  $(\Delta DP)_p$ , occurs for each cellulose chain, and that the loss of degree of polymerization due to secondary peeling,  $(\Delta DP)_s$ , is the same after each chain scission by alkaline hydrolysis, the following mass balance can be made:

$$n_0(DP_0) - n(DP) = n_0(\Delta DP)_p + (n - n_0)(\Delta DP)_s \quad (2)$$

Rearrangement of equation (2) gives:

$$\frac{n}{n_0} = \frac{DP_0 + (\Delta DP)_s - (\Delta DP)_p}{DP + (\Delta DP)_s} \quad (3)$$

Insertion of (3) in (1) gives:

$$Y_C = \frac{K_1}{1 + \frac{(\Delta DP)_s}{DP}} \quad (4)$$

where

$$K_1 = \frac{[DP_0 + (\Delta DP)_s - (\Delta DP)_p]}{DP_0} Y_{C,w} \quad (5)$$

Equation (4) can be rearranged as:

$$K_1 = Y_C + Y_C \frac{(\Delta DP)_s}{DP} \quad (6)$$

After dividing equation (6) by  $K_1 Y_C$  one obtains:

$$\frac{1}{Y_C} = \frac{1}{K_1} + \frac{1}{K_1} \frac{(\Delta DP)_s}{DP} \quad (7)$$

It should be noted that because  $DP_0$  is more than one order of magnitude larger than  $(\Delta DP)_s$  or  $(\Delta DP)_p$ , and because  $(\Delta DP)_s$  and  $(\Delta DP)_p$  are of the same order of magnitude and have an opposite sign in equation (5), one may replace  $K_1$  in equation (7) by  $Y_{C,w}$ .

From a mass balance it follows that  $Y_C$  is equal to the product of the lignin-free pulp yield (as mass fraction) based on o.d. wood,  $Y_T$ , and the lignin-free cellulose mass fraction in pulp,  $G$ , or that :

$$Y_C = Y_T \cdot G \quad (8)$$

By combining equations (7) and (8), and replacing  $K_1$  by  $Y_{C,w}$  the pulp yield prediction equation is obtained:

$$\frac{1}{Y_T \cdot G} = \frac{1}{Y_{C,w}} + \frac{(\Delta DP)_s}{Y_{C,w}} \cdot \frac{1}{DP} \quad (9)$$

Equation (9) will be called the UoM (University of Maine) equation. It can be used to calculate the lignin free pulp yield,  $Y_T$ , of a pulp sample when  $G$  and  $DP$  of the pulp are determined by sugar analysis and viscometry respectively, and the values of  $Y_{C,w}$  and  $(\Delta DP)_s$  are determined by laboratory cooks or are known for this furnish.

The last term on the right hand side of equation (9) represents the cellulose loss due to secondary peeling which follows each chain scission by alkaline hydrolysis. If this term is neglected, equation (9) reduces to the Ycell method of Easty and Malcolm(1982), whereby  $Y_{C,w}$  is now equal to  $Y_{cell}$ , the cellulose yield based on wood. Thus the present method may be considered an improvement of the Ycell method because it also takes into account the cellulose loss due to the peeling during cooking. Another important fundamental aspect of the present analysis is that the value of  $(\Delta DP)_s$  can be obtained by plotting  $1/(Y_T \cdot G)$  versus  $1/DP$ . If a straight line is obtained, then the average chain length removed by the peeling until terminated by the stopping reaction,  $(\Delta DP)_s$ , may be calculated from the slope,  $(\Delta DP)_s/Y_{C,w}$  and the y-axis intercept,  $1/Y_{C,w}$ , the inverse of the cellulose mass fraction of the original wood.

It should be noted that equation (9) differs from the yield equation presented earlier by our group (Van Heiningen et al, 2002). Although the equations are of the same form, the second term on the right hand side in the earlier paper erroneously was multiplied by  $1/K_1$ . This leads to an underestimation of  $(\Delta DP)_s$  by a factor of  $1/K_1$ .

### Calculation of the DP of Cellulose from the Intrinsic Viscosity of Pulp

The DP of cellulose is calculated using the relationship of Da Silva Perez and Van Heiningen (2002):

$$DP = \left( \frac{(1.65[\eta] - 116H)}{G} \right)^{1.111} \quad (10)$$

where  $[\eta]$  is intrinsic viscosity of the pulp in  $cm^3/g$ , and  $G$  and  $H$  are the mass fractions of cellulose and hemicelluloses in the (lignin containing!) pulp respectively. This formula considers the actual weight of cellulose rather than the pulp weight being responsible for the viscosity, and makes a correction for the small contribution of the hemicelluloses to the pulp intrinsic viscosity. The values of  $G$  and  $H$  are obtained from the mono-sugar analysis of the hydrolysate of the pulp obtained following double hydrolysis by sulphuric acid (Davis, 1998), and making the appropriate mass corrections for the presence of glucose in glucomannan and xylan, and the presence of lignin and hexeneuronic acids (Genco et al, 1990). The correction for the hemicelluloses (i.e. the term 116H) is based on a DP of hemicelluloses of 140. Since this term is much smaller than  $1.65[\eta]$ , the accuracy of equation (10) is mostly determined by the accuracy of the cellulose content of the pulp,  $G$ , and the intrinsic viscosity  $[\eta]$ .

### Calculation of Cellulose and Hemicelluloses Content of Pulp

The cellulose and hemicelluloses content of pulp were calculated following the procedure described by Genco et al. (1990), and is summarized in Table 1.

The lignin-free mass fractions of cellulose, glucomannan and xylan in pulp, respectively  $G$ ,  $M$  and  $X$  are obtained by multiplication of respectively  $G$ ,  $M$  and  $X$  by  $1/(1-L)$ . For example for the lignin-free cellulose content of pulp,  $G = G/(1-L)$ . The mass fraction of cellulose in pulp **based on the original weight of wood**, or  $Y_C$  is then simply  $G \cdot Y_T$ , where  $Y_T$  is the lignin-free pulp yield (see equation (8)). Similarly  $Y_M$  and  $Y_X$  are obtained as  $M \cdot Y_T$  and  $X \cdot Y_T$ , respectively, the mass fractions of glucomannan and xylan in pulp **based on the original weight of wood**. Finally, the lignin-free total yield,  $Y_T$ , is obtained from the total yield,  $Y_T$ , (see Experimental) as  $Y_T = Y_T/(1-Y)$ .

## EXPERIMENTAL

### Cooking

Cooks were performed for three hard woods (Rock Maple, Poplar and Yellow Birch) and one soft wood (Black Spruce). Wood logs were debarked, and knots removed from the wood manually. The debarked logs were chipped, air-dried and screened. The fraction passing through 9/8 inch holes but retained on the screen with 5/8 inch holes was used. The air-dried and screened chips were stored in double plastic bags in the cold room. Before cooking the moisture content of the wood chips was carefully determined using a representative sample. A known weight of chips (1.5-2.0 kg o.d.) was cooked in a 12 liter rocking batch digester at a liquid to wood ratio of 4.0 l/kg. The cooks were degassed around 95-100 °C, kept at 120 °C for 50-55 minutes, and the time at cooking temperature of 170°C was adjusted depending on the H-factor. The H-factor for Rock Maple, Poplar, Yellow Birch and Black Spruce were 800, 600, 800 and 1100 hours respectively.

Alkaline cooks were performed at four sulfidities, 0, 7.5, 15 and 30%, and an effective alkali (EA) charge for the hard woods of 21% (as  $Na_2O$  on o.d. wood) and 23% for Black Spruce.

TABLE 1. CALCULATION OF CELLULOSE AND HEMICELLOSES CONTENT OF PULP	
Eq. #	Description
11	Lignin (L) (pulp mass fraction). Determined as sum of Klason and UV lignin, or $0.147 \cdot \text{Kappa}$
12	Extractives (E) (pulp mass fraction)
13	Ash (A) (pulp mass fraction)
14	4-O-methylglucuronic anhydride (U) (pulp mass fraction). Determined by method of Scott (1979)
15	Arabinan polymer (AR) (mg) = arabinose (mg) * (132/150)
16	Galactan polymer (GA) (mg) = galactose (mg) * (162/180)
17	Glucan polymer (GL) (mg) = glucose (mg) * (162/180)
18	Mannan polymer (MA) (mg) = mannose (mg) * (162/180)
19	Xylan polymer (XY) (mg) = xylose (mg) * (132/150) + $U \cdot 0.6 \cdot \text{pulp weight (mg)} \cdot (132/176)$
20	Total Carbohydrate (mg) = AR+GA+GL+MA+XY
21	Total Sugar (mg) = pulp weight (in mg) $\{1 - [L + E + A + U \cdot (190/176)]\}$
22	Recovery (R) = Total carbohydrate / Total sugar
23	Normalized Glucan (mg) = Glucan (mg)/R
24	Normalized Xylan (mg) = Xylan (mg)/R
25	Normalized Mannan (mg) = Mannan (mg)/R
26	Cellulose (G) (mass fraction) = [Normalized Glucan - (Normalized Mannan)/ b]/(pulp weight) For hardwood: b = 1.6 (For Birch kraft pulp, based on Janson (1974)) For softwood: b = 4.15 (Average value for Pine Spruce kraft pulp, based on Janson (1974))
27	Hemicellulose (H) (mass fraction) = Total Sugar/(pulp weight) - G
28	Glucmannan (M) (mass fraction) = [Norm. Mannan * (1+1/b) + Norm. Galactan]/(pulp weight)
29	Xylan (X) (mass fraction) = H - M

Four different polysulfide cooks at elemental sulfur additions of 0, 1, 2 and 4% (based on o.d wood) to 30% sulfidity liquors were performed on all four wood species at the same H-factor and EA charges as that of the alkaline cooks. The polysulfide liquor was prepared by dissolving elemental sulfur and  $\text{Na}_2\text{S}$  in de-aired water of 60 °C while stirring for 20 minutes. Then NaOH was added. All the above cooks were also repeated with a charge of 0.1% anthraquinone based on o.d. wood.

#### Total Pulp Yield Determination

The cooked chips were disintegrated, washed and then screened; with the rejects retained on a slotted 0.006 inch screen and the fibers retained on a 60 mesh screen. The (o.d.) weight of the rejects was determined. The wet pulp weight was measured after increasing the dryness of the pulp to about 25-30% by centrifugation and subsequent homogenization of the entire sample in a Hobart mixer. The total yield,  $Y_T$ , was calculated based on the average dryness of 4 pulp samples from the bag, the total wet pulp weight, the dry weight of the rejects and the dry weight of the chips added to the cook.

#### Pulp Analyses

The intrinsic viscosity was measured according to ASTM standard D 1795-62. The uronic anhydride content of pulp was determined using the chromophoric group analysis method developed by Scott (1979). The extractive content was determined gravimetrically following soxhlet extraction with 1-2 dichloromethane. The ash content of pulp was determined according to TAPPI standard method T211 om-85. The mono sugar content of the pulps was determined by HPAEC-PAD analysis on the hydrolysate produced by double hydrolysis with sulfuric acid (Pronto, 1998 and

Davis, 1998). The cellulose content of pulp was determined from the mono sugar content (see Table 1.)

## RESULTS AND DISCUSSION

### Rock Maple

#### Kraft and Kraft-AQ Cooking

Figure 1 shows the effect of sulfidity on total pulp yield,  $Y_T$ , with or without AQ addition. The total pulp yield decreases with increasing sulfidity for both kraft and kraft-AQ cooking. The main reason for the decrease is that more lignin is removed with increasing sulfidity due to the increased rate of delignification. It is also clear that addition of 0.1% AQ increases the total pulp yield by about 1.5% at the same sulfidity.

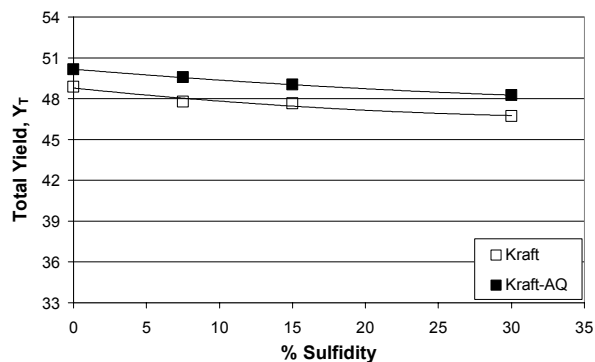


Figure 1. Total Yield,  $Y_T$ , versus Sulfidity for Rock Maple

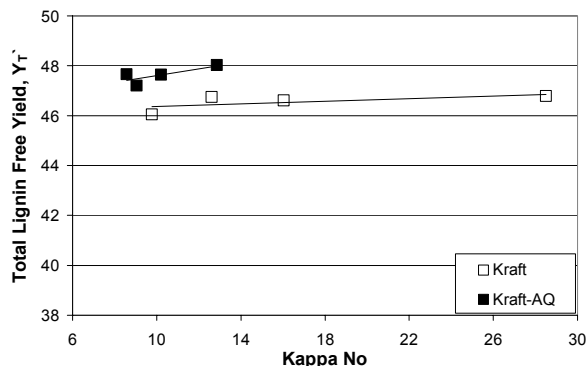


Figure 2. Lignin-free Total Yield for Kraft (-AQ) Cooking of Rock Maple

The lignin-free total pulp yield,  $Y_T'$  is plotted against kappa number in Figure 2. It shows that the addition of AQ leads to a higher carbohydrate retention of about 1.5 % (based on wood) at kappa 13 compared to about 1 % at kappa 8. The increased carbohydrate retention with AQ addition is caused by stabilization of carbohydrate reducing ends by oxidation with AQ. In order to identify the cause of the small increase in lignin free yield with increasing kappa number, the cellulose mass fraction in pulp (based on o.d. wood),  $Y_C$ , is plotted against kappa number in Figure 3. It can be seen that  $Y_C$  increases slightly with increasing kappa for kraft cooking, while the range of kappa numbers is too small to notice a significant change for kraft-AQ. The glucomannan and xylan mass fractions in pulp (based on o.d. wood),  $Y_M$  and  $Y_X$ , do not change significantly for either of the two types of hemicelluloses. Therefore the small yield improvement with increasing kappa number for kraft-AQ cooking is mostly the result of improved cellulose retention

The yield data are plotted in Figure 4 according to the UoM yield equation. It shows that two separate linear relationships are obtained for the kraft and kraft-AQ cooks. As expected based on the UoM equation (9),  $1/Y_T'G'$  increases with  $1/DP$ . Figure 4 also shows that  $1/Y_T'G'$  decreases from about 2.60 to 2.55 with the addition of 0.1% AQ, i.e. the cellulose mass fraction based on wood increases from 0.385 to 0.392 % due to oxidation of the reducing ends by anthraquinone.

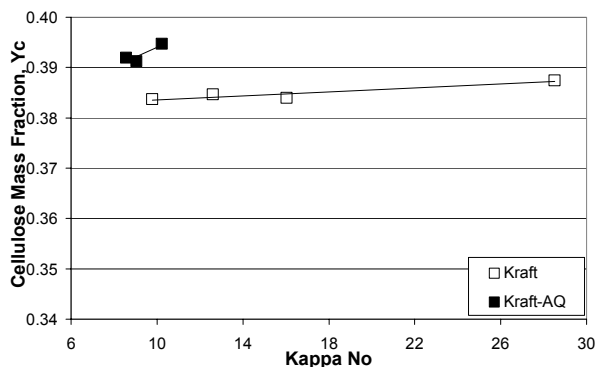


Figure 3. Cellulose Yield for Kraft (-AQ) Cooking of Rock Maple

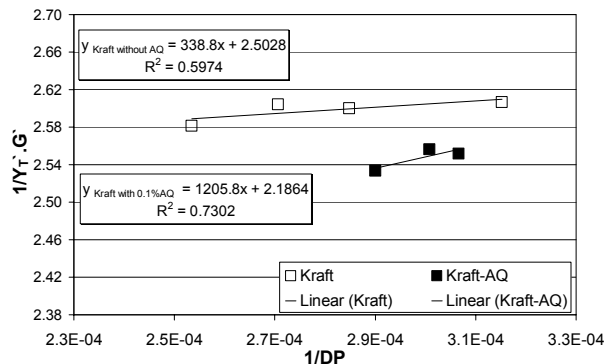


Figure 4. UoM Equation for Rock Maple Kraft (-AQ) cooking

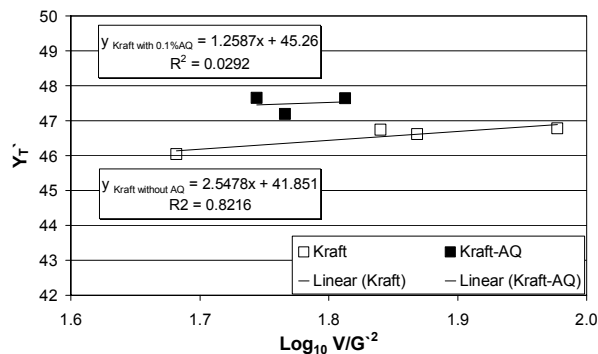


Figure 5. Marcocchia Equation for Rock Maple Kraft (-AQ) cooking

The cooking results for Rock Maple are also plotted in Figure 5 according to the yield prediction equation proposed by Marcocchia et al (1998). They show a linear increase in  $Y_T'$  with increasing values of  $(\log V) / (G^2)$  as expected, and also that two different equations are needed to describe kraft and kraft-AQ cooking.

#### Polysulfide and Polysulfide-AQ Cooking

Figure 6 shows that the total yield increases about 1% with each 1% increase elemental S addition for PS and PSAQ cooking of Rock Maple. The increase in yield is due to oxidation of the reducing end groups of the carbohydrates by polysulfide, and the decrease in alkali concentration of the polysulfide liquor with increasing charge of elemental sulfur. The lower concentration is caused by consumption of hydroxide when sulfur reacts with  $Na_2S$  to form polysulfide, and by formation of thiosulfate at high temperatures (Dorris, 1994).

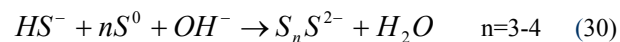


Figure 6 also shows that the difference in total yield of PS and PSAQ cooks is very small at 1% S addition or higher.

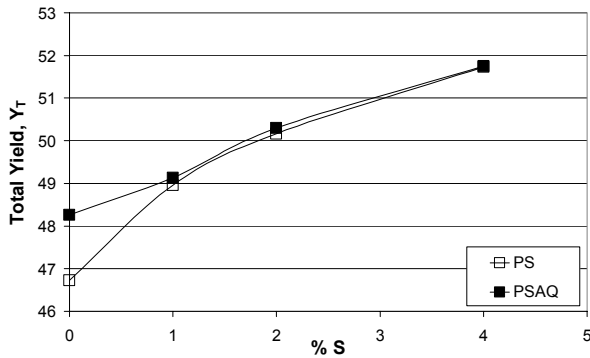


Figure 6. Total Yield, Y<sub>T</sub>, versus % S Charge for Rock Maple

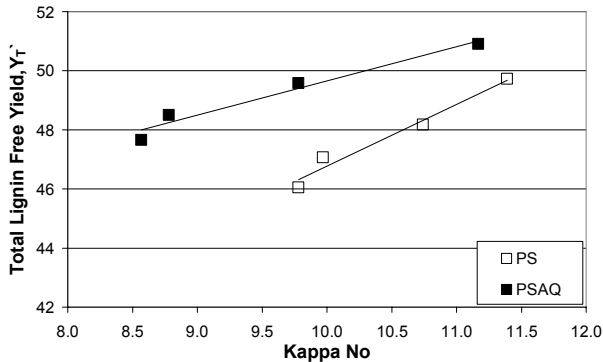


Figure 7. Lignin-free Total Yield for PS (-AQ) Cooking of Rock Maple

It was found that the kappa number increases with increasing polysulfide charge for both PS and PSAQ cooking. Ahlgren and Teder(1967) reported that the delignification rate was not significantly affected by changes in the polysulfide concentration. Therefore the increase in kappa number in the present experiments most likely is caused by the decrease in alkali concentration with increasing elemental sulfur charge. Figure 7 shows that the lignin-free total yield increases with increasing kappa number and thus increasing elemental sulfur charge. It is also seen that the effect of AQ on the yield decreases with increasing kappa number. Therefore the results in Figure 7 show that the positive affect of AQ on both yield and delignification diminishes with increasing elemental sulfur charge.

In order to explain this behavior, the cellulose mass fraction (on wood) of the PS and PSAQ pulps are plotted against kappa number in Figure 8. It is apparent that the cellulose mass fraction increases less with increasing kappa number for PSAQ than PS pulps. Figure 9 shows a significant increase in xylan mass fraction (on wood) with kappa number (or increasing polysulfide charge). Since McDonough (1998) reports that dissolution, not peeling is the main mechanism for xylan removal, the increase in xylan mass fraction might be caused by the lower residual alkali concentration with increasing percentage of elemental sulfur in polysulfide cooking liquor. The same reason may explain the additional increase in xylan retention due to AQ in the PSAQ cooks. The glucomannan mass fraction (on wood) also increases with increasing kappa number (see Figure 10). It is known that mannan is removed by peeling during high temperature cooking, but that most of the removal occurs by physical dissolution during the heat-up period relatively unaffected by alkali concentration

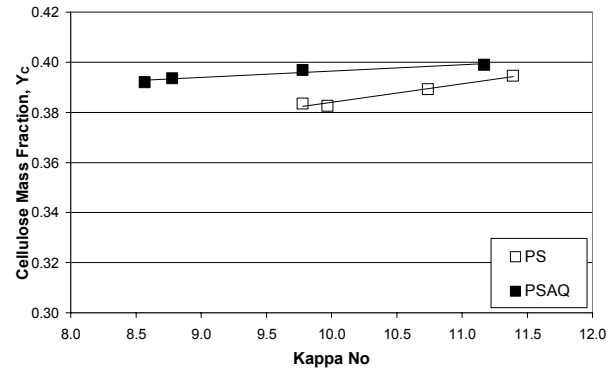


Figure 8. Cellulose Yield for PS(-AQ) Cooking of Rock Maple

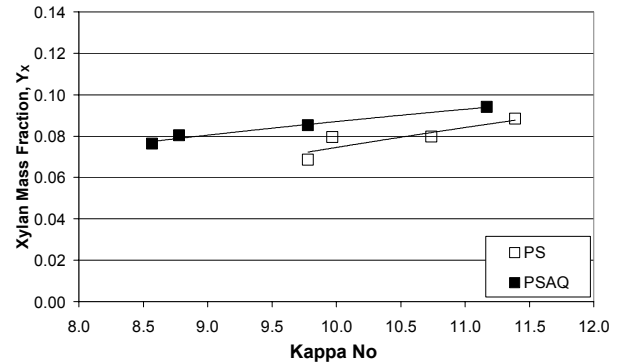


Figure 9. Xylan Yield for PS (-AQ) Cooking of Rock Maple

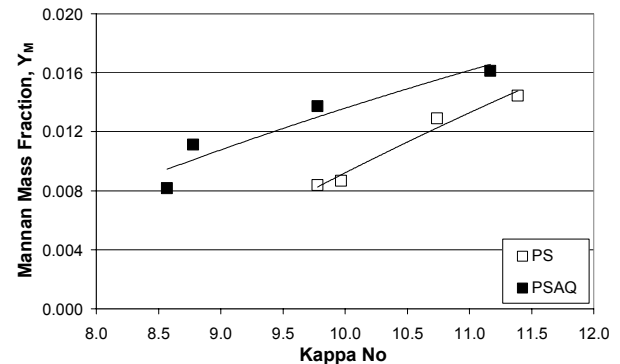


Figure 10. Mannan Yield for PS (-AQ) Cooking of Rock Maple

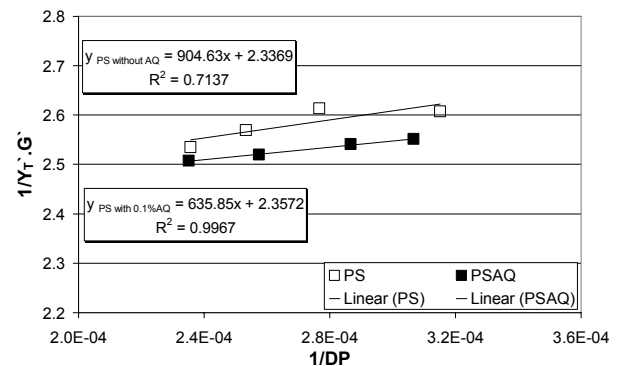


Figure 11. UoM Equation for PS (-AQ) Cooking of Rock Maple

(McDonough, 1998). Therefore, the likely reason for the increase in mannan retention is oxidation of the reducing

ends of glucomannan by polysulfide. The addition of AQ further increases the mannan mass fraction at the same kappa number. The PS and PSAQ yield results plotted according to the UoM equation are shown in Figure 11. Two different linear correlations are obtained for PS and PSAQ cooking. The explanation is that the addition of AQ leads to less peeling and thus more cellulose retention. The UoM plots of Figures 4 and 11 for kraft, kraft-AQ, PS and PSAQ cooking of Rock Maple are combined in Figure 12. It is apparent that the results of Kraft and PS pulps can be represented by the same correlation, while another single linear relation is adequate for Kraft-AQ and PSAQ pulps. Therefore, the UoM pulp yield prediction is not affected by changes in sulfidity or polysulfide, but the parameters must be adjusted when AQ is added to the cooks. The significance of this finding is that polysulfide does not lead to a change in retention of cellulose, while AQ does. On the other hand the addition of AQ does not lead to a significant increase in xylan or glucomannan retention, while polysulfide does. This suggests that AQ and polysulfide, which increase pulp yield by respectively improved cellulose and hemicellulose retention, operate by a different mechanism.

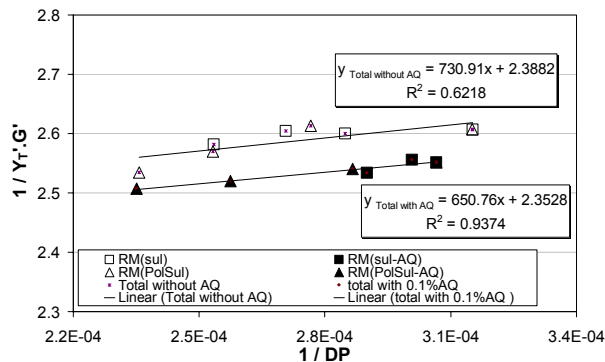


Figure 12. UoM Equation for All Cooks of Rock Maple

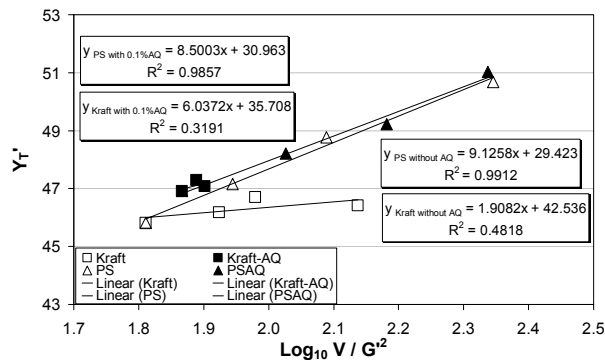


Figure 13. Marcoccia Equation All Cooks of Rock

The Kraft, Kraft-AQ, PS and PSAQ cooking results are also plotted in Figure 13 according to the Marcoccia equation. It is apparent that a different linear relationship is obtained for each of the four cooking processes. Therefore the Marcoccia approach cannot be used to predict the yield of polysulfide cooks using a “calibration curve” which has been obtained from kraft cooks of the same wood furnish.

### Yellow Birch

Figure 14 shows all the yield results of Yellow Birch according to the UoM yield equation. Like the

cooking results for Rock Maple, the yield data of Yellow Birch for the AQ and non-AQ cooking processes are each described by a separate correlation. When the cooking data are plotted according to the Marcoccia equation, again a different correlation is obtained for each of the four cooking processes.

### Poplar

The UoM equation plot for all the Poplar cooks are shown in Figure 15. The same behaviour is seen as for Yellow Birch and Rock Maple.

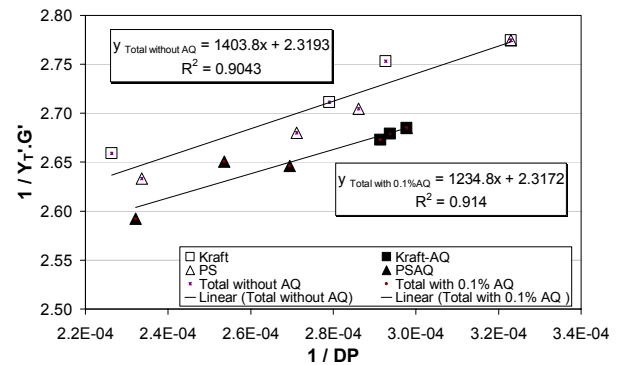


Figure 14. UoM Equation for All Cooks of Yellow Birch

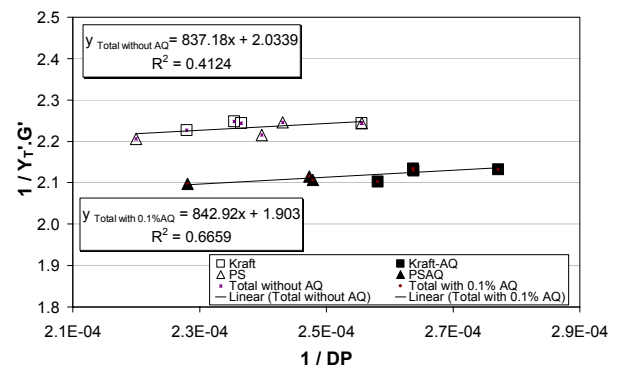


Figure 15. UoM Equation for All Cooks of Poplar Black Spruce

The kraft, kraft-AQ, PS and PS-AQ cooking results of Black Spruce are shown in Figure 16. It can be seen that the non-AQ and AQ cooks are again described by two separate correlations. It should be noticed that the range of 1/DP for Black Spruce extends up to  $5.4 \times 10^{-4}$ , almost 50% higher than the maximum of about  $3 \times 10^{-4}$  for the three hardwoods. The latter number already corresponds to very low values for the intrinsic viscosity and Tappi viscosity of about  $700 \text{ cm}^3/\text{g}$  and  $13 \text{ cP}$  respectively. Therefore the cellulose of Black Spruce pulps with a 1/DP value larger than  $3 \times 10^{-4}$  are strongly degraded as is obvious from the low viscosities of about  $7 \text{ cP}$  obtained for all kraft and kraft-AQ cooks of Black Spruce. Further research is under way to obtain pulps with more practical intrinsic viscosity values.

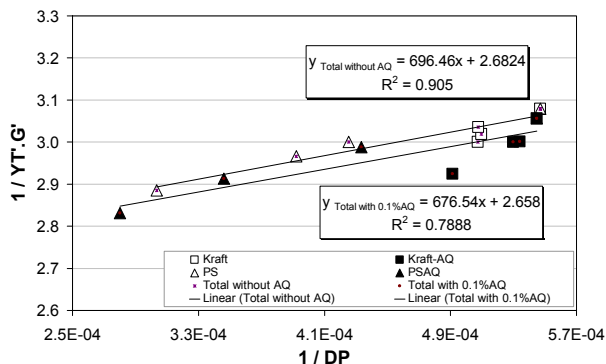


Figure 16. UoM Equation for All Cooks of Spruce

### Values of $Y_{C,W}$ and $(\Delta DP)_S$

The values of  $Y_{C,W}$  and  $(\Delta DP)_S$ , for non-AQ and AQ cooking of all species are summarized in Table 2.

Species	Rock Maple		Yellow Birch		Poplar		Black Spruce	
	$Y_{C,W}$	$(\Delta DP)_S$	$Y_{C,W}$	$(\Delta DP)_S$	$Y_{C,W}$	$(\Delta DP)_S$	$Y_{C,W}$	$(\Delta DP)_S$
Kraft and PS	0.412	306	0.431	605	0.492	412	0.372	260
Kraft-AQ and PSAQ	0.425	277	0.431	533	0.525	442	0.376	254
Wood Cellulose Mass Fraction (literature)	0.402		0.426		0.510		0.411	

The values for  $(\Delta DP)_S$  are significantly larger than the values reported for cotton of 65 at 170 °C (Franzon and Samuelson, 1957) and 68 over the entire temperature range of 60 to 190 °C (Lai and Sarkanen, 1967). However, both reference studies rely on nitrated cellulose as their reference material for the DP determination. Evans and Wallis (1989) have since shown that cellulose degradation by nitration leads to an under prediction of the DP of cotton by a factor of about 2.3. This raises the literature values of  $(\Delta DP)_S$  to 150-160 for cotton, close to the  $(\Delta DP)_S$  of 182 found in our previous study ( Van Heiningen et al, 2002) when applying the present technique to alkaline cooks of cotton. However, these values of  $(\Delta DP)_S$  for cotton are still a factor 2-4 lower than the present results for wood. A possible explanation for the difference may be that the degradable chain length,  $(\Delta DP)_S$  is determined by the size of the amorphous regions, i.e. the peeling reaction is mostly terminated by physical inaccessibility of the crystalline regions rather than the stopping reaction (Haas et al. 1967). This implies that the average size of the amorphous regions in wood is larger than that in cotton. This is not unreasonable since the crystallinity of wood cellulose is smaller than that of cotton ( Fengel and Wegener, 1984).

The values of  $Y_{C,W}$  of the four wood species and the cellulose mass fraction reported in the literature (Timell, 1969; Cote et al., 1966) for these four species are also listed in Table 2. It can be seen that the differences between  $Y_{C,W}$  and the literature values of the cellulose mass fraction of the three hardwood species are small, providing further confidence in the present yield measurement method. The value of  $Y_{C,W}$  for Black Spruce is significantly lower than the literature value, 0.372 versus 0.411.

Generally the value of  $(\Delta DP)_S$  is somewhat lower and the value of  $Y_{C,W}$  higher for the AQ cooks compared to the non-AQ cooks (see Table 2). This implies that cellulose

is stabilized by AQ both during heat-up and during the cooking process. The values of  $Y_{C,W}$  for non-AQ and AQ cooks are quite different for Poplar. This might be due to a systematic error which is presently under investigation.

### USE OF UoM EQUATION FOR DETERMINATION OF PULP MILL YIELD

The pulp yield of a mill is determined as follows. Mill personnel select duplicate samples of chips and washed brown stock pulp that are representative of the collected chips. The cooking conditions of the mill operation are recorded. Duplicate cooks are performed in the laboratory to determine  $Y_{C,W}$  using equation (9) and measured values of the yield, composition and viscosity of the laboratory pulps. The mill pulp samples are also analyzed for their content of cellulose, hemicellulose and lignin content, and intrinsic viscosity. The yield of the mill pulp samples is then calculated using the UoM equation with a value of  $(\Delta DP)_S$  taken from Table 2. Alternatively,  $(\Delta DP)_S$  may be determined experimentally by performing a few cooks which produce widely different pulp viscosities. This procedure is a significant improvement over the  $Y_{cell}$  method because it corrects for yield loss due to secondary peeling, and provides a value for  $Y_{C,W}$  which is theoretically related to the pulp yield.

### CONCLUSION

A fundamental relationship between alkaline pulping yield and the mass fraction and degree of polymerization (DP) of cellulose in pulp has been derived. The equation is validated for kraft, kraft-AQ, PS and PSAQ cooking of three hardwoods, Rock Maple, Yellow Birch and Poplar, and one softwood, Black Spruce. This so-called UoM equation contains two parameters,  $(\Delta DP)_S$  and  $Y_{C,W}$ , respectively the number of glucose units removed by secondary peeling and the cellulose mass fraction in pulp based on wood. These two parameters are a function of the species used and whether or not AQ is added to the cooks. However they are not a function of all other cooking parameters such as sulfidity, alkalinity, temperature, H-factor and polysulfide addition. The cooking results show that the addition of AQ leads to an increased retention of cellulose, while polysulfide produces a significant increase in xylan and glucomannan retention. This suggests that AQ and polysulfide operate by a different mechanism. A method is described how the UoM equation may be used to determine pulp mill yield.

### ACKNOWLEDGEMENTS

The financial support of Andritz, Domtar and Pioneer Chemicals is gratefully acknowledged. Special thanks also to Bertil Stromberg, Bruno Marcoccia, Michelle Pronto, Marco Solinas, Azim Shariff, and Chris Kanter.

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