Increasing Softwood Pulp Yield by Minimizing Primary Peeling of Wood Carbohydrates Using Sodium Methyl Mercaptide Before and During Kraft Pulping

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Research Article

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Increasing Softwood Pulp Yield by Minimizing Primary Peeling of Wood Carbohydrates using Sodium Methyl Mercaptide before and during Kraft Pulping

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Abstract

The objective of this work was to determine the effect of sodium methyl mercaptide (SMM) on the minimization of peeling reactions of southern pine chips in the kraft pulping process. Two methods were evaluated for SMM addition to the pulping process: 1) pre-treatment before pulping or 2) co-addition with white liquor. The effect of SMM charge, pre-treatment temperature and time, and pH of pre-treatment liquor was studied.

The experimental results showed about 1.5 to 2.5 % (on O.D. (oven dry) wood basis) increase in the pulp yield after pre-treatment with or co-addition of 4.38% SMM (on O.D. wood basis). The use of 4.38% SMM allowed a decrease of the white liquor effective alkali charge (EA, on O.D. wood basis) by 3%. 4.38% SMM charge seemed to be optimum for the pre-treatment. Pre-treatment at lower pH resulted in a significant decrease in yield and an increase in rejects. The increase in pulp yield was mostly due to the increased retention of cellulose and xylan. The retention of galactoglucomannan was negligible. About 80% of the cellulose yield increase is due to the suppression of primary peeling. The remainder (0.3-0.4% of the yield increase (on O.D. wood basis) is due to reduced alkaline hydrolysis and subsequent secondary peeling.

Keywords: Softwood Kraft Pulping, High-Yield Pulping, Sodium Methyl Mercaptide, Methyl Mercaptan, Carbohydrate Peeling Reactions, and Southern Pine

Introduction

Kraft pulping is the most widely used pulping technology due to flexibility in the choice of woody feedstock species, highest fiber strength, and a highly efficient recovery system for the recovery of the pulping chemicals and energy. However, kraft pulping leads to significant degradation of hemicelluloses as compared to cellulose. Therefore, the pulp yield is usually less than 50% as opposed to a theoretical maximum of about 70 to 75% when both cellulose and hemicelluloses are not degraded. Since the cost of wood used for kraft pulping process accounts for over 50% of the production cost of softwood kraft pulp, followed by about 25% for the capital cost, it is clear that the most effective approach to decrease the production cost of softwood kraft pulp is to increase the pulp yield (Kangas et al., 2014).

For softwoods, primary peeling leads to about 10% loss of cellulose (4% on O.D. wood basis) and 50% loss of galactoglucomannan (8% on O.D. wood basis) (Paananen 2009). Primary peeling of cellulose and galactoglucomannan occurs during the initial phase of kraft pulping at high alkalinity (pH ~ 14) and at temperatures higher than about 80 °C (Montagna et al., 2013). Softwood xylan is more stable against peeling because the easy cleavage of the arabinose side chain leads to an alkali stable metasaccharinic acid end group. However, a small amount of xylan is still lost during impregnation due to limited solubility of xylan in caustic.

Peeling reactions can be minimized by conversion of the carbohydrate reducing (aldehyde) end groups into alkali stable structures. These reactions involve either the oxidation of an aldehyde group into a carboxylic acid or its reduction into an alcohol. The reductive pre-treatments involve the use of hydrogen sulfide (Brage et al. 2013; Hartler and Olson 1972 and 1973; Proctor 1976; Proctor et al. 1970; Vaaler 2008; Vinje and Worster 1970; Vinje et al. 1973), sodium borohydride (Aurell and Hartler 1963), and ammonium sulfide (Stone et al. 1973; Chiang and Sarkansen 1983). Oxidative pre-treatments are carried out using polysulfide (Kibrick et al. 1960), anthraquinone (Holton et al. 1977), hydrogen peroxide, and peracetic acid (Shimada et al. 1968). The \( \text{H}_2\text{S} \) pre-treatment followed by kraft pulping of softwood chips leads to an increase of about 6 % (on O.D. wood basis) in the yield of bleachable grade pulp. When \( \text{H}_2\text{S} \) pre-treatment is applied for linerboard production, it results in 9% (on O.D. wood basis) pulp yield increase. Aqueous ammonium sulfide pulping (12% pulp yield
increase for linerboard pulp) and ammonium sulfide organosolv pulping (16% (on O.D. wood basis) for bleachable western hemlock pulp, 12% for 15 kappa cottonwood pulp) lead to significantly higher kraft pulp yield but require complicated recovery of the base and organic solvent. Sodium borohydride and polysulfide processes result in the 8% and 6% (both on O.D. wood basis) increase in the softwood kraft pulp yield, respectively (Sjostrom E. 1993). However, these technologies are not generally adopted in industry because sodium borohydride is very expensive, and the use of polysulfide results in the formation of corrosive sulfur-oxides.

The only technology that was very close to commercialization is the H$_2$S pre-treatment. It was operated on semi-commercial pilot scale with 13.5 tons per day capacity in a continuous two-vessel Kamyr digester at the Harmac mill in Canada for 4 to 5 weeks and about 267 tons of pulp was produced (Cox 1974). However, despite a 15 to 25% rate of return on investment (ROI), this technology was not commercially implemented presumably due to safety concerns regarding the high pressure H$_2$S system.

Building on the H$_2$S pre-treatment concept, pre-treatment of wood chips with sodium methyl mercaptide/methyl mercaptan (SMM/MM) was investigated. Based on personal discussions with renowned wood chemist Professor Thomas Rosenau at BOKU, Vienna, Austria, and using the similarity between SMM and NaHS, a plausible mechanism for the stabilization of reducing end groups by SMM/MM was proposed as shown in Figure 1. However, since CH$_3$S$^-$ is a stronger nucleophile than HS$^-$, the SMM pre-treatment temperature can be significantly lower than 140 °C, the optimum temperature for the H$_2$S pre-treatment. The proposed mechanism for the stabilization of carbohydrate reducing end group stabilization by SMM is shown in Figure 1. In this mechanism, the reducing end group reacts with SMM/MM to form mercaptide glucoside which is in equilibrium with the open mercaptide glucoside structure. These then form relatively easily a radical by homolytic cleavage of the mercaptide group. The glucoside radicals are quickly reduced by the mercaptide radical in combination with a mercaptide ion to produce alkali stable pyran and alditol structures and dimethyl disulfide. The pyran and alditol structures protect the sugars against end group peeling during kraft pulping.

![Fig. 1 Mechanism of wood pre-treatment by mercaptide ion](image)

There are two references in the literature on the use of SMM/MM as an additive in the kraft pulping process. In the first case, MM was used as an additive in polysulfide kraft pulp to increase the overall sulfidity and accelerate the rate of delignification. When MM was added to the polysulfide-kraft process, the pulp yield increased by 1% and the kappa number was reduced from 27.9 to 21.7. Since there is about 0.15% (on O.D. wood basis) change in the pulp yield for each kappa unit (Sixta 2006), it shows that MM addition led to about 2% increase in the yield for polysulfide-kraft cooking (Vaelttilae 2007). In the second reference, the volatile sulfur gases released during kraft cooking were recycled back to the digester and it led to 2.0 to 2.5% increase in pulp yield (Tirado et.al., 1969). In the first reference, MM was added along with polysulfide (Vaelttilae 2007); whereas, in the second reference, it was charged with hydrogen sulfide, dimethyl sulfide, and dimethyl disulfide (Tirado et.al., 1969). Since the yield improvement was mostly due to the reactive species such as SMM/MM and H$_2$S, and the mercaptide ion is more reactive than H$_2$S; it is important to understand the separate contribution of SMM/MM on the pulp yield increase.
Experimental Methods

Pulping experiments were performed using southern pine chips obtained from International Paper and WestRock US mills. The chips were screened using a chip classifying system and the fraction with thickness and width ranging from 3 to 5 mm and 3/8 to 9/8 inch, respectively, was collected. Screened chips were then air-dried to about 90 to 95% consistency using a fan at room temperature. The air-dried wood chips were mixed and stored in plastic bags.

All experiments were performed in quadruplet using four 235 mL cylindrical rocking digesters. About 30 grams of wood chips (on O.D. basis) was used in each digester. In order to avoid the handling of MM gas, an aqueous solution of SMM (21% w/w) containing also a small amount of NaOH (0.4% w/w) with pH 12.9 was obtained from Arkema (King of Prussia, PA 19406). The SMM charge was 1.46 to 8.75 % w/w on wood (O.D.) basis. The liquor-to-wood ratio for SMM pre-treatment was 3 L/kg and the pre-treatment temperature was between 80°C to 130°C depending upon the experiment. The digesters were placed in an oil bath (Figure 2) with polyethylene glycol as the heat-transfer fluid. The digesters rotated back and forth by 180 degrees every 30 seconds. The pre-treatment time was 60 minutes for most experiments.

At the end of pre-treatment, the digesters were cooled to room temperature (using a water bath) while make-up white liquor was being prepared. The final pH of the pre-treatment liquor was between 9.5 to 10.5. The total liquor-to-wood ratio after adding make-up white liquor was 4.5 L/kg. It should be noted that for some experiments, the SMM solution was charged together with the make-up white liquor to simulate more practical pulp mill conditions. After adding the make-up white liquor (Sulfidity: 30%, Causticization Efficiency: 80%), the digesters were placed in the oil bath for an hour at 115°C to achieve impregnation of white liquor into chips. At the end of impregnation, the digesters were removed from the oil bath and cooled to room temperature while the oil bath was being heated to the cooking temperature of 170°C. The digesters were then immersed in the bath and cooked to target H-factor of about 1960 hrs.

After cooking, the digesters were cooled in a water bath and their weights were recorded to check for leakage. The digesters were stored in a refrigerator until the pulp was washed. After separating black liquor from the macerated wood chips, the pulp was disintegrated and washed using a pulp disintegrator and a 75-mesh nylon bag, respectively. The resulting pulp suspension was filtered using a buchner funnel to make a pulp pad which was then air dried to determine the total pulp yield. The pulp was screened using a Somerville-type screen with 0.15 mm width slots.

In order to obtain statistically meaningful data on pulp yield, the mean yield was calculated using four data points. The data point with the highest deviation from the mean pulp yield was considered as an outlier and discarded. Then the pulp/black liquor of each of the remaining three experiments were analyzed.
Residual alkali was determined using a modified SCAN-N 2:88 method. Screened pulp was used for the determination of kappa number (TAPPI Standard T-236), intrinsic viscosity (ASTM Standard, D1795-13), and chemical composition. The National Renewable Energy Laboratory’s standard procedure called Determination of Structural Carbohydrates and Lignin in Biomass (Sluiter et. al., 2012) was used to hydrolyze pulp/wood samples and determine extractives (only for wood) and lignin content. The wood/pulp hydrolysate was then analyzed using High-Performance Anion Exchange Chromatography with Pulsed Amperometric Detection (HPAEC-PAD) to estimate the composition of monosugars in the hydrolysate/biomass. The composition of carbohydrate polymers (Arabinan, Galactan, Glucan, Xylan, and Mannan) was calculated using monosugar composition (van Heiningen et al. 2004). The uronic anhydride content was determined using the chromophoric group analysis method developed by Scott (1979).

It should be noted that when estimating the total composition of biomass samples using the two-step hydrolysis process, the sum of individual components does generally not exactly add up to 100% of the initial
mass. To account for this difference, the mass of carbohydrates measured using chromatographic analysis were normalized using the normalization factor (Equation 1), which is defined as the ratio of the experimentally measured mass of total carbohydrates (Equation 2) to the mass of total carbohydrates calculated by difference between the pulp weight and total lignin weight (Equation 3). The measured masses of carbohydrates were then divided by the normalization factor to estimate the normalized masses. Normalizing the carbohydrate composition data using this method ensures that the sum of individual components adds up to 100% and implies that all experimental and systematic errors associated with the biomass analysis are concentrated in the carbohydrates composition data. This is reasonable because the analysis of total lignin content using the acid-hydrolysis procedure is more accurate and is less subject to errors.

\[
N = \frac{TC_{\text{Measured}}(\text{gm})}{TC_{\text{By Difference}}(\text{gm})} \tag{1}
\]

\[
TC_{\text{Measured}}(\text{gm}) = A + Ga + Gl + X + M + Ac + UA_{4-O-M} \tag{2}
\]

\[
TC_{\text{By Difference}}(\text{gm}) = P(1 - L - A - E) \tag{3}
\]

Where,

N: Normalization factor

TC_{\text{Measured}} (gm): Total measured mass of all carbohydrates

TC_{\text{By Difference}} (gm): Total mass of all carbohydrates estimated by difference

A: Measured mass of Arabinan (gm)

Ga: Measured mass of Galactan (gm)

Gl: Measured mass of Glucan (gm)

X: Measured mass of Xylan (gm)

M: Measured mass of Mannan (gm)

Ac: Measured mass of Acetyl Groups (gm)

UA_{4-O-M}: Measured mass of 4-O-methylglucuronic anhydride (gm)

P: Mass of pulp sample (gm, oven dry basis)

L: Mass fraction of total lignin in pulp sample

A: Mass fraction of ash in pulp sample

E: Mass fraction of extractives in pulp sample

The empirical equations were used to estimate the composition of macropolymers (cellulose, galactoglucomannan, and xylan) in pulp samples (van Heiningen et al. 2004). The wood-based composition was obtained by multiplying the normalized pulp composition data with the experimentally measured values of pulp yield. The calculated pulp yield was determined by adding up the wood-based compositions of various components (cellulose, hemicellulose, and lignin) of pulp.

In order to check the repeatability of the experimental data, two key experiments were redone using a fresh batch of wood chips. Table 1 shows the results of the repeatability experiments. The error limits were calculated using standard deviation with three data points. Although the yields for the control cooks were almost the same, the yield for the cooks with SMM pre-treatment differed by 1% point. This difference is thought to be due to the variation in the batch of wood chips.
| Experimental Conditions | Kappa Number | Pulp Yield (%) | Rejects (%) | Residual effective alkali (g/L Na₂O) |
|-------------------------|--------------|---------------|-------------|-------------------------------------|
| Experiments in the Year 2017 | | | | |
| Control Pulping, 1 mM NaOH (at 115 °C) followed by pulping with 15% EA | 29.4 ± 0.7 | 45.2 ± 0.3 | 0.04 ± 0.02 | 7.7 ± 0.2 |
| 4.38% SMM (at 105 °C) followed by pulping with 12% EA, at 170 °C | 29.0 ± 0.8 | 47.7 ± 0.4 | 0.01 ± 0.01 | 6.3 ± 0.1 |
| Experiments in the Year 2019 | | | | |
| Control Pulping, 15% EA, at 170 °C | 26.3 ± 0.4 | 45.4 ± 0.1 | 0.08 ± 0.01 | 8.0 ± 0.3 |
| 4.38% SMM (at 105 °C) followed by pulping with 12% EA, at 170 °C | 28.5 ± 0.3 | 46.9 ± 0.1 | 0.13 ± 0.01 | 6.2 ± 0.3 |

Results and Discussion

Pre-treatment with 4.38% SMM at 105 °C

The initial SMM pretreatment experiments were performed at a charge of 4.38% SMM on O.D. wood basis at 105 °C for 60 minutes. The temperature of 105 °C was chosen assuming that at this temperature and a low pH of about 12 of the pretreatment liquor, the kinetics of the primary peeling reactions of galactoglucomannan and cellulose would be slow enough compared to the kinetics of the reducing end group stabilization reactions of SMM.

Figure 3 shows the total pulp yield versus kappa results for the 15% EA control kraft cooks and those with pretreatment with 4.38% SMM followed by kraft cooking at 15% EA and 12% EA. Since the kappa number for the cook with 4.38% SMM and 15% EA was about 19, i.e. significantly below the target kappa number of about 25 - 30, a 12% EA cook was performed after pretreatment with 4.38% SMM. In all cases the amount of rejects was negligible at 0.01 - 0.04% on O.D. wood. As expected, there is a linear relationship between total pulp yield and kappa number for the control cooks. The results clearly show that the addition of SMM increased the retention of wood carbohydrates with an increased pulp yield at the same kappa as the control of about 2.5%. It is also important to notice that the 4.38% SMM pretreatment allowed decreasing the EA charge in kraft cooking from 15 to 12% while still achieving the same kappa number as the control kraft cook at 15% EA. The residual active alkali (REA) at the end of the 12% kraft cook of 6.2 g Na₂O/L is similar to that of the control cook of 7.7 g Na₂O/L.
Fig. 3 Pre-treatment with 4.38% SMM at 105 °C

The compositions of the softwood feedstock, 15% EA control kraft pulp, and the 4.38% SMM pretreated followed by 12% EA kraft cook are listed in Table 2, all reported based on original dry wood mass. The increased yield of the different components (xylan, GGM, cellulose and total lignin) in the 4.38% SMM pretreated 12% EA kraft pulp compared to the 15% EA control kraft pulp is given at the bottom of the table. It shows that the increase in the pulp yield is mostly due to the increased retention of cellulose and xylan.

Table 2 Composition of Wood and Pulp Samples – Part 1

| Sample Type | Composition of wood chips or pulps based on dry wood mass (%) | Pulp yield, based on dry wood mass (%) | Kappa Number |
|-------------|-------------------------------------------------------------|----------------------------------------|--------------|
|             | Xylan | GGM¹ | Cellulose | Lignin | Calculated from pulp analysis data | Measured |
| Southern Pine chips | 11.76 | 15.61 | 41.73 | 28.88 | ---- | 100 | ---- |
| Control Pulp, 1 mM NaOH @ 115 °C → Pulping with 15% EA | 4.61 | 3.64 | 35.09 | 1.86 | 45.20 | 45.20 | 29.4 ± 0.7 |
| 4.38% SMM @ 105 °C → Pulping with 12% EA | 5.56 | 3.87 | 36.16 | 2.10 | 47.70 | 47.70 | 29.0 ± 0.8 |
| Increased yield with SMM (based on dry wood mass) | 0.96 | 0.23 | 1.07 | 0.24 | 2.50 | 2.50 | ---- |

¹ = Galactoglucomannan
Effect of various process variables on pulp yield

Effect of pre-treatment temperature

As shown in Figure 4, the pretreatment temperature was varied between 80 °C to 130 °C. For the experiments with pretreatment at 80 °C, the pretreatment time was increased to 90 minutes to compensate for the lower pretreatment temperature. In addition, for the experiment involving co-addition of 4.38% SMM and 12% EA at 80°C, the usual white liquor impregnation (1 hour at 115 °C) was omitted. Since the data points for all the 4.38% SMM and 12% EA experiments lie on the same line of total yield vs kappa plot, it can be concluded that the pre-treatment temperature has no effect on the total pulp yield.

Fig. 4 Effect pre-treatment temperature on pulp yield

Effect of SMM Charge and Co-addition of SMM and White Liquor

The effect of SMM charge was studied by varying SMM charge from 1.46 to 8.75 % on O.D. wood basis (Figure 5). As expected, the pre-treatment with 1.46% SMM led to a slightly lower increase in the pulp yield compared with 4.38% SMM. For the pre-treatment with 8.75% SMM, there was a less than proportional increase in the pulp yield as compared with that of the 4.38% SMM. Pre-treatment with 8.75% SMM allowed only a 4% decrease in the EA charge as opposed to the expected value of about 6%. Hence, 4.38% MM seemed to be the optimum charge for the pre-treatment.

In industrial settings, pre-treatment of wood chips with SMM prior to pulping would require an additional digester and/or additional piping, which may have a negative impact on the economic feasibility of the process. Therefore, it was investigated whether SMM and white liquor could be charged together. Figure 5 shows the results for the experiments involving co-addition of SMM and white liquor. For the experiment with 4.38% SMM; the co-addition lead to same pulp yield as the SMM pretreatment-kraft cook, while the kappa number was 3 units lower than that of the pulp obtained after pre-treatment. The co-addition of 8.75% MM led to a bit higher kappa number as compared with the pretreatment experiment, but this may be due to the 1% difference in the white liquor charge. The initial pH of the liquor used in the co-addition type experiments was higher, due to white liquor, than those of the pretreatment experiments and thus made the wood chips more susceptible to primary peeling reactions. However, both type of experiments still proceeded about the same increase in pulp yield.
Effect of pH of pre-treatment liquor

Since the peeling reactions usually occur at high pH and the initial pH of the liquor used in the pre-treatment type experiments was about 12, lowering the pH of the pretreatment liquor, using sodium bicarbonate, was considered as another way to minimize peeling reactions.

Figure 6 shows the effect of pH of pre-treatment liquor on the pulp yield. The pulp yield and residual alkali for the experiment with pH 10 liquor were significantly lower than those of the pH 12 liquor. The lower yield was thought to be due to the loss of alkali in neutralizing sodium bicarbonate present in the pretreatment liquor. In addition, some SMM could have lost as a vapor while preparing the pretreatment liquor which involved addition of 21% SMM solution to a sodium bicarbonate solution.
Fig. 6 Effect of pH of pre-treatment liquor

Table 3 (located at the end of the manuscript) lists the percentage increase in the retention of xylan, galactoglucomannan (GGM), cellulose and lignin relative to the control kraft pulp at 15% EA, all expressed on original dry wood mass. Based on these percentages, the increase in pulp yield (relative to the yield of the kraft control) is calculated. This calculated pulp yield increase is also listed in Table 3 together with the measured pulp yield increase. Finally, the Table includes the kappa number and percentage of rejects and residual alkali content of the final black liquor.

As forced by the normalization, it can be seen that there is complete agreement between the calculated and experimentally measured pulp yield increase for all experiments. For the experiments with 4.38% SMM, pre-treatment at too high (130 °C) temperature resulted in the loss of cellulose, probably due to peeling reactions. Pre-treatment at 115 °C resulted in the retention of more cellulose as compared with that of 80 °C, which might mean that the stabilization reaction of cellulose by SMM at 80 °C is too slow to retain additional cellulose. The amount of xylan retention was mostly related to alkali charge because more xylan is dissolved at higher alkaline concentration. The experiments with pre-treatment at 130 °C resulted in a higher retention of xylan presumably because more alkali was consumed by cellulose peeling which in turn lowered the solubility of xylan in the cooking liquor. The amount of galactoglucomannan retained was very small even for the experiments with pretreatment at 80 °C. Since primary peeling of galactoglucomannan starts at about 80 °C (Montagna 2013), while primary peeling of cellulose is only significant at 130 °C (Paananen 2010 and Nieminen 2014) it may be that SMM stabilizes some cellulose before peeling but that the glucomannan stabilization by SMM is too slow compared to primary peeling of glucomannan. The residual alkali was generally within the acceptable ranges of 4-10 g/L. Similarly, the amount of rejects was less than 0.1% except for two experiments, pre-treatment with 8.75% SMM liquor followed by pulping with 9% EA (0.33% rejects) and pre-treatment with 4.38% SMM (pH 10) liquor followed by pulping with 12% EA (0.23% rejects), most likely due to insufficient alkali during cooking as indicated by the low REAs of 4.3 and 3.3 g Na₂O/L respectively.

When looking at the absolute pulp yield increases and reduction in the effective alkali charge during pulping, the addition of 4.38% SMM at 115 °C with 12% EA during pulping results in the optimum increase in pulp yield for both SMM pre-treatment and SMM-white liquor co-addition experiments. Therefore, co-addition of SMM and white liquor would be more practical in industrial settings.

Composition of wood and pulp, residual effective alkali, and rejects

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Table 3 (located at the end of the manuscript) lists the percentage increase in the retention of xylan, galactoglucomannan (GGM), cellulose and lignin relative to the control kraft pulp at 15% EA, all expressed on original dry wood mass. Based on these percentages, the increase in pulp yield (relative to the yield of the kraft control) is calculated. This calculated pulp yield increase is also listed in Table 3 together with the measured pulp yield increase. Finally, the Table includes the kappa number and percentage of rejects and residual alkali content of the final black liquor.

As forced by the normalization, it can be seen that there is complete agreement between the calculated and experimentally measured pulp yield increase for all experiments. For the experiments with 4.38% SMM, pre-treatment at too high (130 °C) temperature resulted in the loss of cellulose, probably due to peeling reactions. Pre-treatment at 115 °C resulted in the retention of more cellulose as compared with that of 80 °C, which might mean that the stabilization reaction of cellulose by SMM at 80 °C is too slow to retain additional cellulose. The amount of xylan retention was mostly related to alkali charge because more xylan is dissolved at higher alkaline concentration. The experiments with pre-treatment at 130 °C resulted in a higher retention of xylan presumably because more alkali was consumed by cellulose peeling which in turn lowered the solubility of xylan in the cooking liquor. The amount of galactoglucomannan retained was very small even for the experiments with pretreatment at 80 °C. Since primary peeling of galactoglucomannan starts at about 80 °C (Montagna 2013), while primary peeling of cellulose is only significant at 130 °C (Paananen 2010 and Nieminen 2014) it may be that SMM stabilizes some cellulose before peeling but that the glucomannan stabilization by SMM is too slow compared to primary peeling of glucomannan. The residual alkali was generally within the acceptable ranges of 4-10 g/L. Similarly, the amount of rejects was less than 0.1% except for two experiments, pre-treatment with 8.75% SMM liquor followed by pulping with 9% EA (0.33% rejects) and pre-treatment with 4.38% SMM (pH 10) liquor followed by pulping with 12% EA (0.23% rejects), most likely due to insufficient alkali during cooking as indicated by the low REAs of 4.3 and 3.3 g Na₂O/L respectively.

When looking at the absolute pulp yield increases and reduction in the effective alkali charge during pulping, the addition of 4.38% SMM at 115 °C with 12% EA during pulping results in the optimum increase in pulp yield for both SMM pre-treatment and SMM-white liquor co-addition experiments. Therefore, co-addition of SMM and white liquor would be more practical in industrial settings.
**Intrinsic Viscosity of MM Kraft pulps**

Figure 7 shows the intrinsic viscosities of MM kraft pulps and the control kraft pulp. The viscosities of MM pulps are about 150 mL/gm higher than that of control pulp for kappa numbers of about 30. The higher viscosity of MM pulps shows that the addition of MM leads to less degradation of cellulose as compared with kraft pulping.

The University of Maine (UM) Pulp Yield equation can be used to calculate pulp yield as a function of intrinsic viscosity (van Heiningen et al. 2004). This is an indirect method and it is based on a fundamental relationship between alkaline pulping yield and the mass fraction and degree of polymerization (DP) of cellulose in pulp. The UM equation is:

\[
\frac{1}{Y_T G} = \frac{1}{Y_C} + \frac{(\Delta D_P)_S}{Y_{CW} DP} + \frac{1}{Y_{CW} DP}
\]

where \(Y_T\) is lignin-free pulp yield (as a mass fraction) based on O.D. wood, \(G\) is lignin-free cellulose mass fraction in pulp, \(Y_c\) is the cellulose mass fraction of pulp based on O.D. wood, \(Y_{CW}\) is the cellulose mass fraction at the start of kraft pulping, i.e. after impregnation, \((\Delta D_P)_S\) is the number of glucose units lost by secondary peeling after a cellulose chain is cleaved by alkaline hydrolysis during kraft cooking, and DP is the Degree of Polymerization of cellulose in the final kraft pulp. Each wood species has a unique set of values for \((\Delta D_P)_S\) and \(Y_{CW}\). These two constants are not dependent on sulfidity, H-factor, EA charge and temperature of the kraft or kraft-polysulfide cook. The constants for southern pine are: \((\Delta D_P)_S = 340\) and \(Y_{CW} = 0.366\).

If it is now assumed that SMM does not stabilize cellulose during pretreatment or impregnation, i.e. \(Y_{CW}\) is the same irrespective of whether SMM was added, and that the increase in cellulose retention due to SMM treatment is solely due to less secondary peeling. Application of equation (4) to two 4.38% SMM pulps (pretreatment with 4.38% SMM at 115°C followed by pulping at 12% EA and the other pulp obtained by co-addition of 4.38% SMM and 12% EA) and the kraft control (1 mM NaOH @115°C -> 15% EA), and subtraction of these two equations where the subscripts 1 and 2 represent the kraft cook and 2 the 4.38% SMM kraft pulp cooks, respectively, results in:
\[ \frac{1}{Y_{C1}} - \frac{1}{Y_{C2}} = 929 \left( \frac{1}{DP_1} - \frac{1}{DP_2} \right) \]  
\[ (5) \]

The Degree of Polymerization of cellulose, DP, in the final kraft pulp is calculated as (da Silva Perez and van Heiningen 2015):

\[ DP = \left( \frac{1.65[\eta] - 116H}{G} \right)^{1.111} \]  
\[ (6) \]

where \([\eta]\) is the intrinsic viscosity of the pulp, \(H\) is the hemicellulose mass fraction of the pulp, and \(G\) is the cellulose mass fraction of the pulp. The values for \([\eta]\), \(H\), \(G\) and DP for the three cooks are listed in Table 4.

Table 4. Values of DP, \([\eta]\), H and G for selected softwood cooks

| Experimental Conditions | Intrinsic Viscosity \([\eta], \text{cm}^3/\text{gm}\) | Mass Fraction of Hemicelluloses in Pulp (H) | Mass Fraction of Celluloses in Pulp (G) | Degree of Polymerization (DP) |
|-------------------------|---------------------------------|----------------------------------------|-------------------------------------|-----------------------------|
| 1 mM NaOH @115 °C -> Pulping w/ 15% EA (Control Pulp) | 1050 | 0.182 | 0.776 | 5180 |
| 4.38% SMM @115 °C -> Pulping w/ 12% EA | 1217 | 0.192 | 0.768 | 6185 |
| Pulping w/ 4.38% SMM & 12% EA together | 1173 | 0.191 | 0.768 | 5939 |

Based on the DP values in Table 4 and \(Y_{C1}\) being 0.3509 and \(DP_1\) equal to 5180 for the control kraft cook (see Table 3 and 4 resp.), it can be calculated using equation (5) and \(DP_2\) from Table 4 that \(Y_{C2}\) is equal to 0.3546 for the pulp pretreated with 4.38% SMM at 115°C followed by pulping at 12% EA. This compares to the measured cellulose fraction of this pulp of 0.3694, i.e. a cellulose yield increase of 0.37 % (on O.D. wood basis) is predicted versus 1.85 % measured (Table 5). Similarly, if equation (5) is applied for the pulp obtained by co-addition of 4.38% SMM and 12% EA, then a cellulose fraction, \(Y_{C2}\), and cellulose yield increase of 0.3538 and 0.29% respectively are calculated. These compare to the measured cellulose fraction and pulp yield increase for this pulp of 0.3669 and 1.6% respectively. Thus it can be concluded that the increased retention of cellulose of about 0.3-0.4% (on O.D. wood basis) for the two 4.4% SMM and 12% EA pulps due to reduced secondary peeling is only a fraction (about 20%) of that due to suppression of primary peeling of cellulose by stabilization of the reducing ends of cellulose in fresh wood chips.
**Table 5. Comparison of measured and calculated cellulose yield (as fraction) and as % yield increase for selected pulps**

| Experimental Conditions | $Y_C$, Measured Cellulose Yield (fraction of O.D. wood mass) | $Y_C$, Calculated Cellulose Yield (fraction of O.D. wood mass) | Measured increase in cellulose yield (% on O.D. wood mass) | Cellulose yield increase due to less alkaline hydrolysis and secondary peeling (% on O.D. wood mass) |
|-------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| 1 mM NaOH @115 °C -> Pulping w/ 15% EA (Control Pulp) | 0.3509 | - | - | - |
| 4.38% SMM @115 °C -> Pulping w/ 12% EA | 0.3694 | 0.3546 | 1.85 | 0.37 |
| Pulping w/ 4.38% SMM & 12% EA together | 0.3669 | 0.3538 | 1.60 | 0.29 |

In summary, the present results show that addition of 4.38% SMM leads to an increase in the pulp yield of up to 2.5% mostly due to increased retention of cellulose and xylan. There was no significant increase in the retention of glucomannan. The intrinsic viscosities of pulps of SMM cooks are about 150-200 ml/g higher than those of the control cook and account for about 0.3-0.4% cellulose yield increase (on O.D. wood basis) due to reduced alkaline hydrolysis and subsequent secondary peeling.

**Conclusions**

The addition of 4.38% SMM (on O.D. wood basis) resulted in 1.5 to 2.5% increase in the pulp yield (on O.D. wood basis) and allowed a decrease in the EA charge by 3%. The addition at too high (130 °C) or too low (80 °C) temperature resulted in less retention of cellulose; and hence, 115 °C seems to be the optimum temperature for the SMM addition. Addition of 8.75% SMM produced diminishing returns and the use of 1.46% SMM didn’t lead to a significant increase in the yield. The use of SMM liquor with pH 10 led to significant decrease in the yield and increase in rejects. The increase in the pulp yield was mostly due to increased retention of cellulose and xylan. There was no significant increase in the retention of glucomannan, presumably because the rate of stabilization of galactoglucomannan reducing end groups was slower than the rate of primary peeling. The increase in cellulose yield is mostly due to less primary peeling of cellulose because of conversion of the reducing end groups of cellulose into alkali-stable pyran and/or alditol structures. About 20% of the cellulose yield increase is due to less secondary peeling because alkaline hydrolysis during kraft cooking is reduced by the lower effective alkali charge when SMM is used.

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Consent to participate: Not applicable

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Table 3 Composition of pulp samples, rejects, and residual alkali

| Sample Type                                                                 | Actual composition (for 15% EA control pulp) OR increase in the composition (for the remaining samples) relative to control pulp, based on dry wood mass (%) | Increase in the pulp yield, based on dry wood mass (%) | Kappa Number | Rejects (%) | Residual effective alkali (g/L Na₂O) |
|------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------|--------------|-------------|-------------------------------------|
|                                                                              | Xylan | GGM | Cellulose | Lignin | Calculated from pulp analysis data | Measured from pulp yield data |                                          |                          |                           |                                    |
| 1 mM NaOH @115 °C -> Pulping w/ 15% EA (Control Pulp)                       | 4.61  | 3.64| 35.09     | 1.86   | ----                             | ------                    | 29.4 ± 0.7                     | 0.04 ± 0.02               | 7.7 ± 0.15                   |
| Pulping w/ 16 % EA                                                          | 0.21  | -0.04| -0.91     | -0.36  | -1.10                            | -1.10                     | 25.1 ± 0.2                     | 0.05 ± 0.00               | 9.3 ± 0.20                   |
| Pulping w/ 17 % EA                                                          | -0.10 | -0.11| -0.74     | -0.55  | -1.50                            | -1.50                     | 22.7 ± 0.5                     | 0.06 ± 0.05               | 10.6 ± 0.20                  |
| 4.38% SMM @105 °C -> Pulping w/ 15% EA                                      | 0.20  | 0.29 | -0.50     | -0.39  | -0.40                            | -0.40                     | 19.1 ± 0.5                     | 0.03 ± 0.02               | 9.5 ± 0.68                   |
| 4.38% SMM @105 °C -> Pulping w/ 12% EA                                      | 0.96  | 0.23 | 1.07      | 0.24   | 2.49                             | 2.50                      | 29.0 ± 0.8                     | 0.01 ± 0.01               | 6.2 ± 0.04                   |
| 4.38% SMM @115 °C -> Pulping w/ 12% EA                                      | 0.87  | 0.12 | 1.85      | 0.06   | 2.90                             | 2.90                      | 30.0 ± 0.5                     | 0.04 ± 0.00               | 5.6 ± 0.06                   |
| 4.38% SMM, pH 12, 130 °C -> Pulping w/ 12% EA                              | 1.31  | 0.11 | 0.31      | 0.38   | 2.10                             | 2.10                      | 29.7 ± 0.9                     | 0.01 ± 0.01               | 5.8 ± 0.08                   |
| 4.38% SMM + 12% EA (@ 80 °C, 90 mins.) pulping w/o impregnation             | 0.61  | 0.56 | 0.80      | 0.23   | 2.20                             | 2.20                      | 28.8 ± 2.1                     | 0.05 ± 0.01               | 6.0 ± 0.10                   |
| 8.75% SMM @ 80 °C, 90 mins. -> Pulping w/ 11% EA                           | 1.07  | 0.13 | 0.04      | 0.16   | 1.40                             | 1.40                      | 26.3 ± 0.5                     | 0.04 ± 0.03               | 6.4 ± 0.15                   |
| 4.38% SMM, pH 10, @ 130 °C -> Pulping w/ 12% EA                            | 1.57  | 0.36 | 1.04      | 1.83   | 4.80                             | 4.80                      | 46.6 ± 1.3                     | 0.23 ± 0.04               | 3.3 ± 0.23                   |
| 1.46% SMM @115 °C -> Pulping w/ 14% EA                                      | 0.44  | 0.04 | 0.09      | 0.03   | 0.60                             | 0.60                      | 26.5 ± 0.4                     | 0.00 ± 0.00               | 7.0 ± 0.13                   |
| 8.75% SMM @ 115 °C -> Pulping w/ 9% EA                                      | 1.74  | 0.48 | 2.25      | 1.34   | 5.80                             | 5.80                      | 40.1 ± 0.8                     | 0.33 ± 0.05               | 4.3 ± 0.01                   |
| 8.75% SMM @115 °C -> Pulping w/ 11% EA                                      | 1.16  | 0.12 | 1.83      | -0.21  | 2.90                             | 2.90                      | 25.9 ± 0.3                     | 0.02 ± 0.00               | 6.5 ± 0.15                   |
| Pulping w/ 4.38% SMM & 12% EA together                                     | 0.64  | 0.26 | 1.60      | 0.10   | 2.60                             | 2.60                      | 27.5 ± 0.4                     | 0.03 ± 0.02               | 6.2 ± 0.22                   |
| Pulping w/ 8.75% SMM & 10% EA together                                      | 1.27  | -0.04| 1.26      | 0.22   | 2.70                             | 2.70                      | 29.6 ± 1.4                     | 0.12 ± 0.17               | 5.6 ± 0.22                   |

1 = Galactoglucomannan
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