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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 feed stock 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).

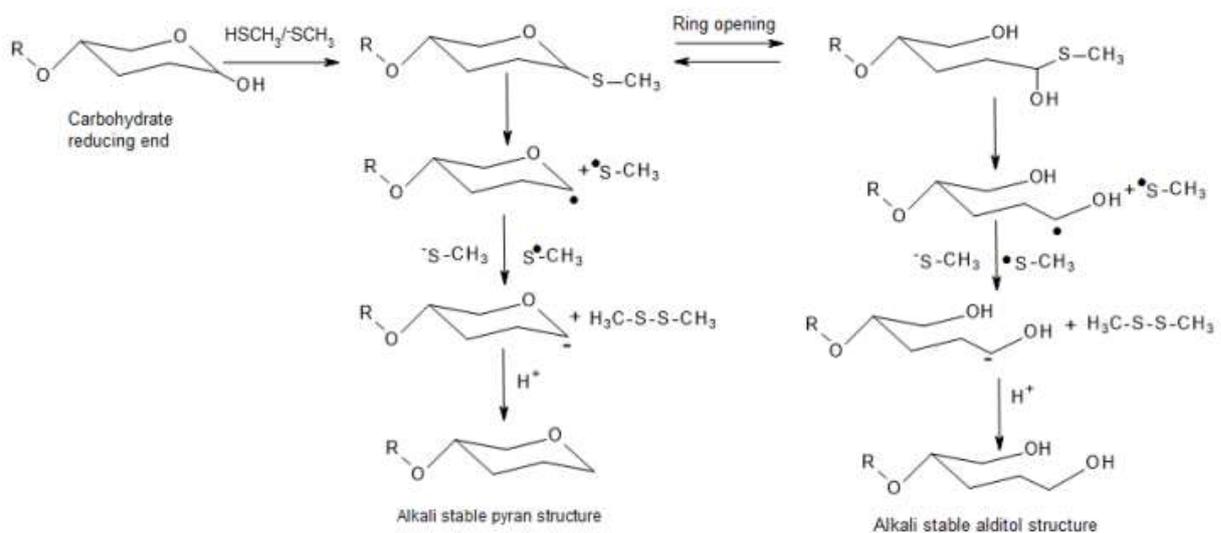
For softwoods, primary peeling leads to about 10% loss of cellulose (4% on O.D. wood basis) and 50% loss of galactoglucomannan (8% on O.D. wood basis) (Paananen 2009). Primary peeling of cellulose and galactoglucomannan occurs during the initial phase of kraft pulping at high alkalinity (pH ~ 14) and 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 Sarkanen 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 H<sub>2</sub>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 H<sub>2</sub>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

49 increase for linerboard pulp) and ammonium sulfide organosolv pulping (16% (on O.D. wood basis) for  
 50 bleachable western hemlock pulp, 12% for 15 kappa cottonwood pulp) lead to significantly higher kraft pulp  
 51 yield but require complicated recovery of the base and organic solvent. Sodium borohydride and polysulfide  
 52 processes result in the 8% and 6% (both on O.D. wood basis) increase in the softwood kraft pulp yield,  
 53 respectively (Sjostrom E. 1993). However, these technologies are not generally adopted in industry because  
 54 sodium borohydride is very expensive, and the use of polysulfide results in the formation of corrosive sulfur-  
 55 oxides.

56 The only technology that was very close to commercialization is the H<sub>2</sub>S pre-treatment. It was operated  
 57 on semi-commercial pilot scale with 13.5 tons per day capacity in a continuous two-vessel Kamyrd digester at the  
 58 Harmac mill in Canada for 4 to 5 weeks and about 267 tons of pulp was produced (Cox 1974). However, despite  
 59 a 15 to 25% rate of return on investment (ROI), this technology was not commercially implemented presumably  
 60 due to safety concerns regarding the high pressure H<sub>2</sub>S system.

61 Building on the H<sub>2</sub>S pre-treatment concept, pre-treatment of wood chips with sodium methyl  
 62 mercaptide/methyl mercaptan (SMM/MM) was investigated. Based on personal discussions with renowned  
 63 wood chemist Professor Thomas Rosenau at BOKU, Vienna, Austria, and using the similarity between SMM  
 64 and NaHS, a plausible mechanism for the stabilization of reducing end groups by SMM/MM was proposed as  
 65 shown in Figure 1. However, since CH<sub>3</sub>S<sup>-</sup> is a stronger nucleophile than HS<sup>-</sup>, the SMM pre-treatment  
 66 temperature can be significantly lower than 140 °C, the optimum temperature for the H<sub>2</sub>S pre-treatment. The  
 67 proposed mechanism for the stabilization of carbohydrate reducing end group stabilization by SMM is shown in  
 68 Figure 1. In this mechanism, the reducing end group reacts with SMM/MM to form mercaptide glucoside which  
 69 is in equilibrium with the open mercaptide glucoside structure. These then form relatively easily a radical by  
 70 homolytic cleavage of the mercaptide group. The glucoside radicals are quickly reduced by the mercaptide  
 71 radical in combination with a mercaptide ion to produce alkali stable pyran and alditol structures and dimethyl  
 72 disulfide. The pyran and alditol structures protect the sugars against end group peeling during kraft pulping.



73  
 74 **Fig. 1 Mechanism of wood pre-treatment by mercaptide ion**

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

## 87 Experimental Methods

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

93 All experiments were performed in quadruplet using four 235 mL cylindrical rocking digesters. About  
94 30 grams of wood chips (on O.D. basis) was used in each digester. In order to avoid the handling of MM gas, an  
95 aqueous solution of SMM (21% w/w) containing also a small amount of NaOH (0.4% w/w) with pH 12.9 was  
96 obtained from Arkema (King of Prussia, PA 19406). The SMM charge was 1.46 to 8.75 % w/w on wood (O.D.)  
97 basis. The liquor-to-wood ratio for SMM pre-treatment was 3 L/kg and the pre-treatment temperature was  
98 between 80 °C to 130 °C depending upon the experiment. The digesters were placed in an oil bath (Figure 2)  
99 with polyethylene glycol as the heat-transfer fluid. The digesters rotated back and forth by 180 degrees every 30  
100 seconds. The pre-treatment time was 60 minutes for most experiments.

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

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

116 In order to obtain statistically meaningful data on pulp yield, the mean yield was calculated using four  
117 data points. The data point with the highest deviation from the mean pulp yield was considered as an outlier and  
118 discarded. Then the pulp/black liquor of each of the remaining three experiments were analyzed.



119

120 **Fig. 2.a** - Multi-Digester Oil Bath System (MDOB) – Overall equipment setup



121

122 **Fig. 2.b** - MDOB – Clamps for holding the digesters and heat exchanger coil



123

124 **Fig. 2.c** - MDOB – Digester, lid, and brass cover



125

126 **Fig. 2.d** – MDOB - Dimensions of the digesters

127 Residual alkali was determined using a modified SCAN-N 2:88 method. Screened pulp was used for  
 128 the determination of kappa number (TAPPI Standard T-236), intrinsic viscosity (ASTM Standard, D1795-13),  
 129 and chemical composition. The National Renewable Energy Laboratory’s standard procedure called  
 130 Determination of Structural Carbohydrates and Lignin in Biomass (Sluiter et. al., 2012) was used to hydrolyze  
 131 pulp/wood samples and determine extractives (only for wood) and lignin content. The wood/pulp hydrolysate  
 132 was then analyzed using High-Performance Anion Exchange Chromatography with Pulsed Amperometric  
 133 Detection (HPAEC-PAD) to estimate the composition of monosugars in the hydrolysate/biomass. The  
 134 composition of carbohydrate polymers (Arabinan, Galactan, Glucan, Xylan, and Mannan) was calculated using  
 135 monosugar composition (van Heiningen et al. 2004). The uronic anhydride content was determined using the  
 136 chromophoric group analysis method developed by Scott (1979).

137 It should be noted that when estimating the total composition of biomass samples using the two-step  
 138 hydrolysis process, the sum of individual components does generally not exactly add up to 100% of the initial

139 mass. To account for this difference, the mass of carbohydrates measured using chromatographic analysis were  
 140 normalized using the normalization factor (Equation 1), which is defined as the ratio of the experimentally  
 141 measured mass of total carbohydrates (Equation 2) to the mass of total carbohydrates calculated by difference  
 142 between the pulp weight and total lignin weight (Equation 3). The measured masses of carbohydrates were then  
 143 divided by the normalization factor to estimate the normalized masses. Normalizing the carbohydrate  
 144 composition data using this method ensures that the sum of individual components adds up to 100% and implies  
 145 that all experimental and systematic errors associated with the biomass analysis are concentrated in the  
 146 carbohydrates composition data. This is reasonable because the analysis of total lignin content using the acid-  
 147 hydrolysis procedure is more accurate and is less subject to errors.  
 148

$$149 \quad N = \frac{TC_{\text{Measured}}(\text{gm})}{TC_{\text{By\_Difference}}(\text{gm})} \quad (1)$$

$$150 \quad TC_{\text{Measured}}(\text{gm}) = A + Ga + Gl + X + M + Ac + UA_{4-O-M} \quad (2)$$

$$151 \quad TC_{\text{By\_Difference}}(\text{gm}) = P(1 - L - A - E) \quad (3)$$

152

153 Where,

154 N: Normalization factor

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

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

157

158 A: Measured mass of Arabinan (gm)

159 Ga: Measured mass of Galactan (gm)

160 Gl: Measured mass of Glucan (gm)

161 X: Measured mass of Xylan (gm)

162 M: Measured mass of Mannan (gm)

163 Ac: Measured mass of Acetyl Groups (gm)

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

165

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

167 L: Mass fraction of total lignin in pulp sample

168 A: Mass fraction of ash in pulp sample

169 E: Mass fraction of extractives in pulp sample

170

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

176 In order to check the repeatability of the experimental data, two key experiments were redone using a  
 177 fresh batch of wood chips. Table 1 shows the results of the repeatability experiments. The error limits were  
 178 calculated using standard deviation with three data points. Although the yields for the control cooks were almost  
 179 the same, the yield for the cooks with SMM pre-treatment differed by 1% point. This difference is thought to be  
 180 due to the variation in the batch of wood chips.

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191 Table 1 Results for the repeatability studies

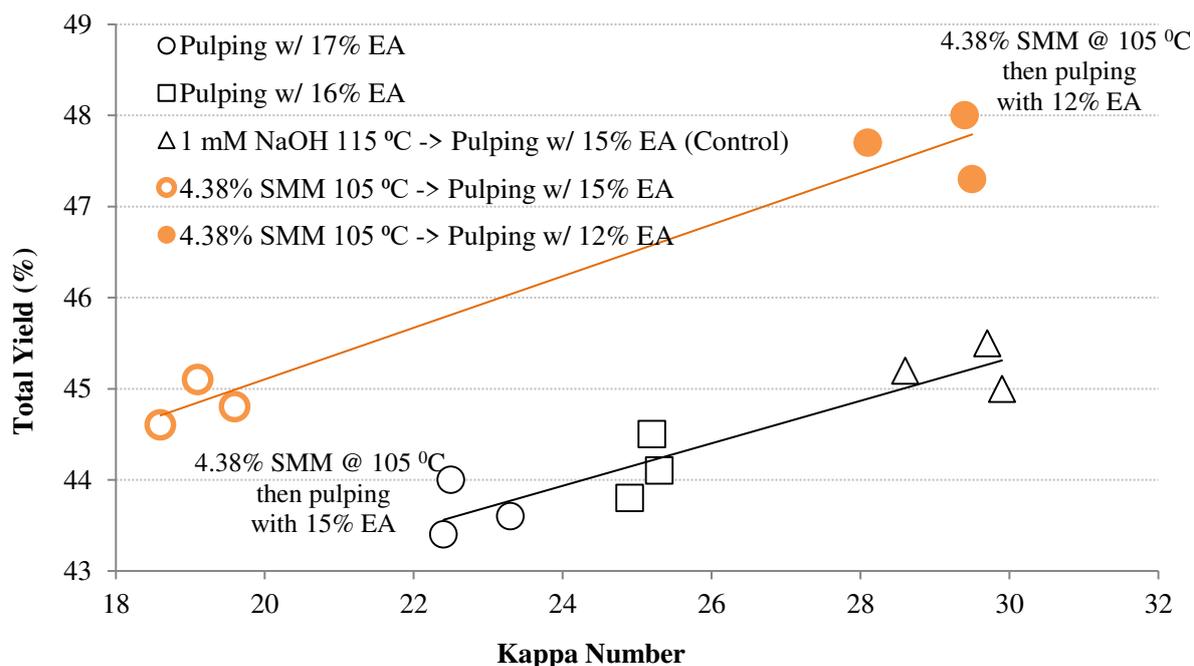
	Experimental Conditions	Kappa Number	Pulp Yield (%)	Rejects (%)	Residual effective alkali (g/L Na <sub>2</sub> O)
Experiments in the Year 2017	Control Pulping, 1 mM NaOH (at 115 °C) followed by pulping with 15% EA	29.4 ± 0.7	45.2 ± 0.3	0.04 ± 0.02	7.7 ± 0.2
	4.38% SMM (at 105 °C) followed by pulping 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

192

## 193 Results and Discussion

### 194 Pre-treatment with 4.38% SMM at 105 °C

195 The initial SMM pretreatment experiments were performed at a charge of 4.38% SMM on O.D. wood  
 196 basis at 105 °C for 60 minutes. The temperature of 105 °C was chosen assuming that at this temperature and a  
 197 low pH of about 12 of the pretreatment liquor, the kinetics of the primary peeling reactions of  
 198 galactoglucomannan and cellulose would be slow enough compared to the kinetics of the reducing end group  
 199 stabilization reactions of SMM.  
 200 Figure 3 shows the total pulp yield versus kappa results for the 15% EA control kraft cooks and those with pre-  
 201 treatment with 4.38% SMM followed by kraft cooking at 15% EA and 12% EA. Since the kappa number for the  
 202 cook with 4.38% SMM and 15 % EA was about 19, i.e. significantly below the target kappa number of about 25  
 203 - 30, a 12% EA cook was performed after pretreatment with 4.38% SMM. In all cases the amount of rejects was  
 204 negligible at 0.01 - 0.04% on O.D. wood. As expected, there is a linear relationship between total pulp yield and  
 205 kappa number for the control cooks. The results clearly show that the addition of SMM increased the retention  
 206 of wood carbohydrates with an increased pulp yield at the same kappa as the control of about 2.5%. It is also  
 207 important to notice that the 4.38% SMM pretreatment allowed decreasing the EA charge in kraft cooking from  
 208 15 to 12% while still achieving the same kappa number as the control kraft cook at 15% EA. The residual active  
 209 alkali (REA) at the end of the 12% kraft cook of 6.2 g Na<sub>2</sub>O/L is similar to that of the control cook of 7.7 g  
 210 Na<sub>2</sub>O/L.  
 211



212

213 **Fig. 3** Pre-treatment with 4.38% SMM at 105 °C

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

219

220 Table 2 Composition of Wood and Pulp Samples – Part 1

221

Sample Type	Composition of wood chips or pulps based on dry wood mass (%)				Pulp yield, based on dry wood mass (%)		Kappa Number
	Xylan	GGM <sup>1</sup>	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	----

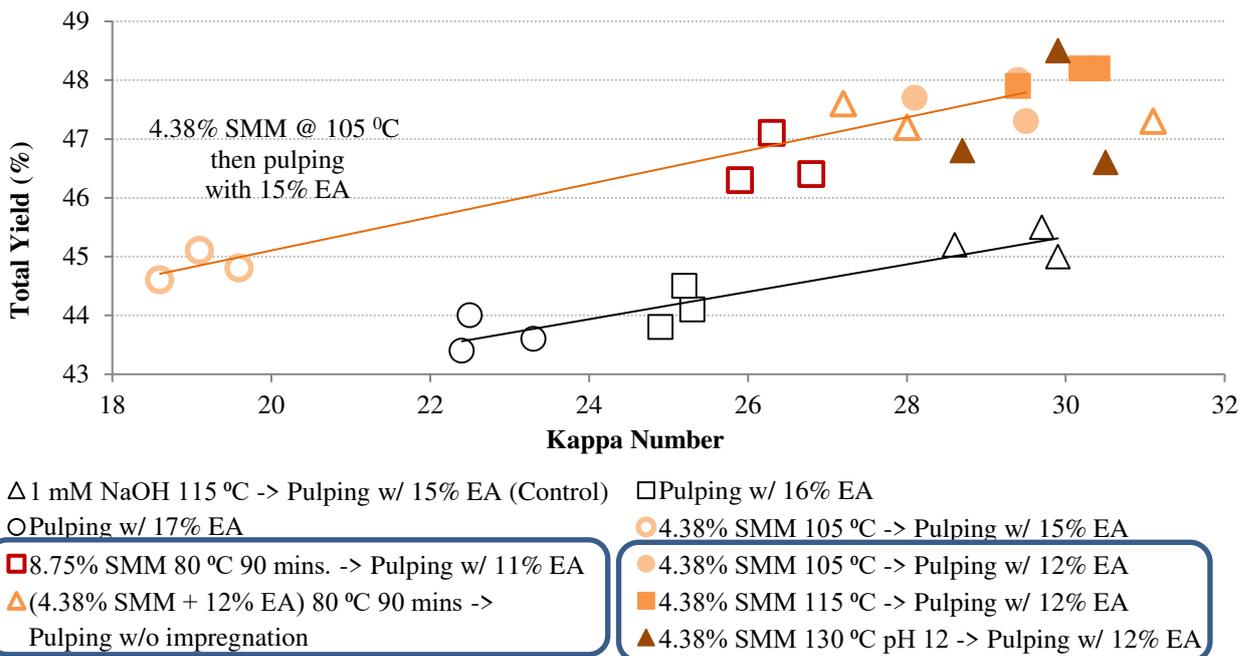
222 <sup>1</sup> = Galactoglucomannan

223

224 **Effect of various process variables on pulp yield**

225 *Effect of pre-treatment temperature*

226 As shown in Figure 4, the pretreatment temperature was varied between 80 °C to 130 °C. For the experiments  
 227 with pretreatment at 80 °C, the pretreatment time was increased to 90 minutes to compensate for the lower  
 228 pretreatment temperature. In addition, for the experiment involving co-addition of 4.38% SMM and 12% EA at  
 229 80°C, the usual white liquor impregnation (1 hour at 115 °C) was omitted. Since the data points for all the 4.38%  
 230 SMM and 12% EA experiments lie on the same line of total yield vs kappa plot, it can be concluded that the pre-  
 231 treatment temperature has no effect on the total pulp yield.



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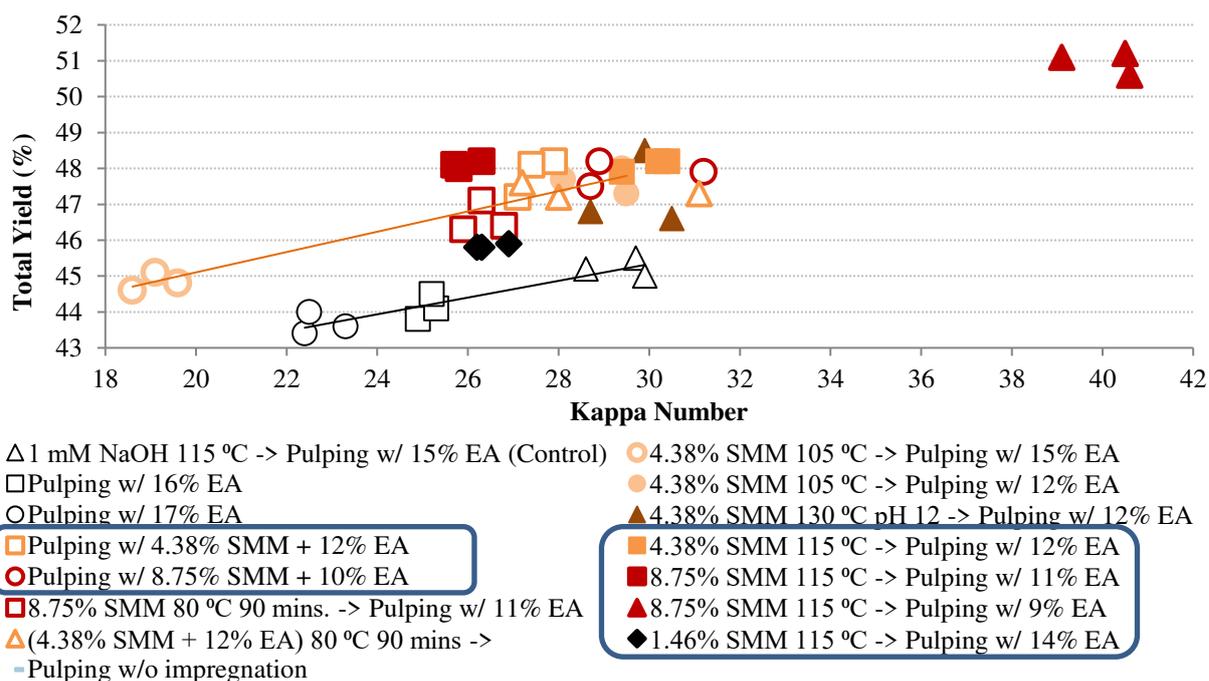
234 **Fig. 4** Effect pre-treatment temperature on pulp yield

235

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

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

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



255

256 **Fig. 5** Effect of SMM charge and Co-addition of SMM and White Liquor

257

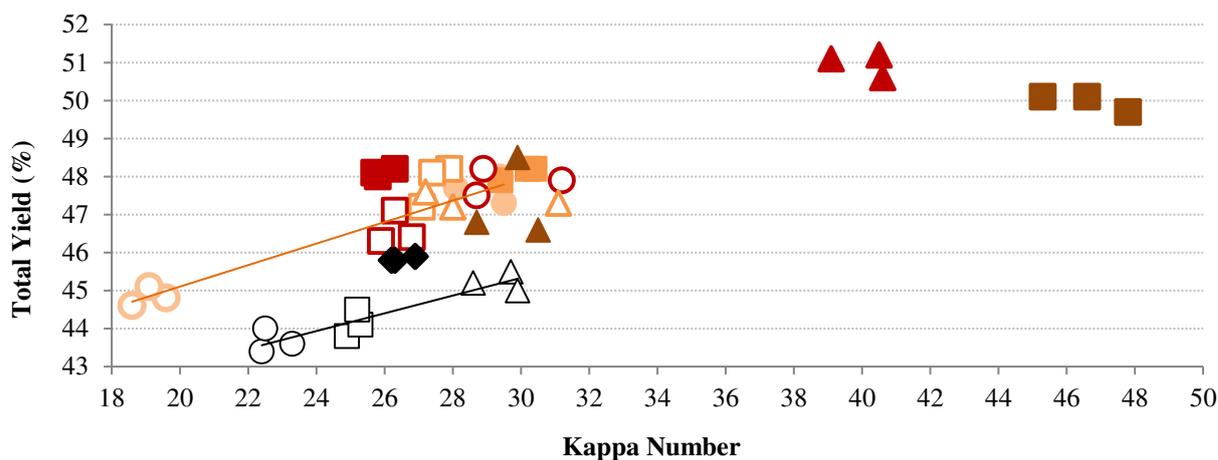
258 *Effect of pH of pre-treatment liquor*

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

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

267

268



- △ 1 mM NaOH 115 °C -> Pulping w/ 15% EA (Control)
- Pulping w/ 16% EA
- Pulping w/ 17% EA
- ▣ Pulping w/ 4.38% SMM + 12% EA
- Pulping w/ 8.75% SMM + 10% EA
- 8.75% SMM 80 °C 90 mins. -> Pulping w/ 11% EA
- ▲ (4.38% SMM + 12% EA) 80 °C 90 mins -> Pulping w/o impregnation
- 4.38% SMM 105 °C -> Pulping w/ 15% EA
- 4.38% SMM 105 °C -> Pulping w/ 12% EA
- ▣ 4.38% SMM 115 °C -> Pulping w/ 12% EA
- 4.38% SMM 130 °C pH 10 -> Pulping w/ 12% EA
- ▲ 4.38% SMM 130 °C pH 12 -> Pulping w/ 12% EA
- 8.75% SMM 115 °C -> Pulping w/ 9% EA
- 8.75% SMM 115 °C -> Pulping w/ 11% EA
- ◆ 1.46% SMM 115 °C -> Pulping w/ 14% EA

269

270 **Fig. 6** Effect of pH of pre-treatment liquor

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

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

278 As forced by the normalization, it can be seen that there is complete agreement between the calculated and  
 279 experimentally measured pulp yield increase for all experiments. For the experiments with 4.38% SMM, pre-  
 280 treatment at too high (130 °C) temperature resulted in the loss of cellulose, probably due to peeling reactions.  
 281 Pre-treatment at 115 °C resulted in the retention of more cellulose as compared with that of 80 °C, which might  
 282 mean that the stabilization reaction of cellulose by SMM at 80 °C is too slow to retain additional cellulose. The  
 283 amount of xylan retention was mostly related to alkali charge because more xylan is dissolved at higher alkaline  
 284 concentration. The experiments with pre-treatment at 130 °C resulted in a higher retention of xylan presumably  
 285 because more alkali was consumed by cellulose peeling which in turn lowered the solubility of xylan in the  
 286 cooking liquor. The amount of galactoglucomannan retained was very small even for the experiments with  
 287 pretreatment at 80 °C. Since primary peeling of galactoglucomannan starts at about 80 °C (Montagna 2013),  
 288 while primary peeling of cellulose is only significant at 130 °C (Paananen 2010 and Nieminen 2014) it may be  
 289 that SMM stabilizes some cellulose before peeling but that the glucomannan stabilization by SMM is too slow  
 290 compared to primary peeling of glucomannan. The residual alkali was generally within the acceptable ranges of  
 291 4-10 g/L. Similarly, the amount of rejects was less than 0.1% except for two experiments, pre-treatment with  
 292 8.75% SMM liquor followed by pulping with 9 % EA (0.33% rejects) and pre-treatment with 4.38 % SMM (pH  
 293 10) liquor followed by pulping with 12% EA (0.23% rejects), most likely due to insufficient alkali during  
 294 cooking as indicated by the low REAs of 4.3 and 3.3 g Na<sub>2</sub>O/L respectively.

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

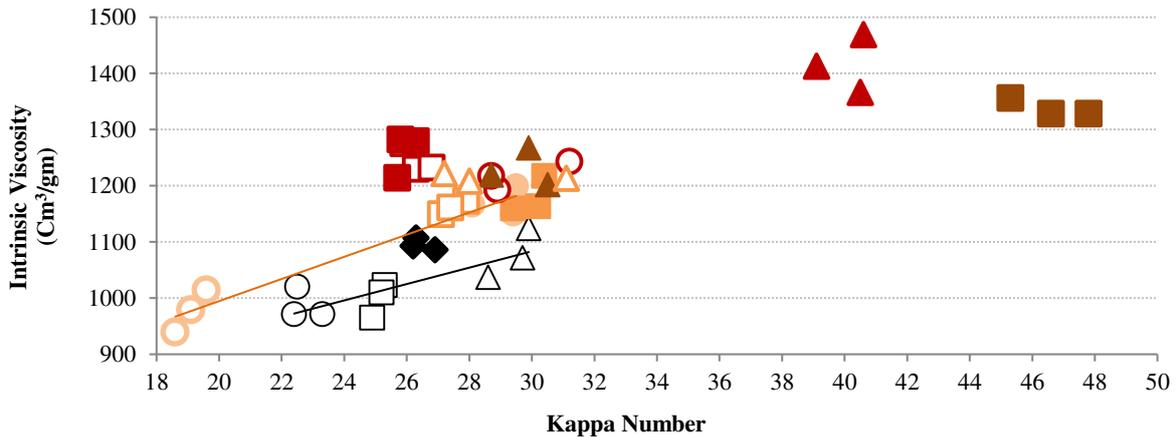
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302 **Intrinsic Viscosity of MM Kraft pulps**

303 Figure 7 shows the intrinsic viscosities of MM kraft pulps and the control kraft pulp. The viscosities of MM  
 304 pulps are about 150 mL/gm higher than that of control pulp for kappa numbers of about 30. The higher viscosity  
 305 of MM pulps shows that the addition of MM leads to less degradation of cellulose as compared with kraft  
 306 pulping.  
 307



- △ 1 mM NaOH 115 °C -> Pulping w/ 15% EA (Control)
- Pulping w/ 16% EA
- Pulping w/ 17% EA
- ◻ Pulping w/ 4.38% SMM + 12% EA
- ◐ Pulping w/ 8.75% SMM + 10% EA
- ◑ 8.75% SMM 80 °C 90 mins. -> Pulping w/ 11% EA
- ◒ (4.38% SMM + 12% EA) 80 °C 90 mins -> Pulping w/o impregnation
- 4.38% SMM 105 °C -> Pulping w/ 15% EA
- ◐ 4.38% SMM 105 °C -> Pulping w/ 12% EA
- ◑ 4.38% SMM 115 °C -> Pulping w/ 12% EA
- ◒ 4.38% SMM 130 °C pH 10 -> Pulping w/ 12% EA
- ◓ 4.38% SMM 130 °C pH 12 -> Pulping w/ 12% EA
- ◔ 8.75% SMM 115 °C -> Pulping w/ 9% EA
- ◕ 8.75% SMM 115 °C -> Pulping w/ 11% EA
- ◖ 1.46% SMM 115 °C -> Pulping w/ 14% EA

308

309 **Fig. 7** Intrinsic viscosities of MM kraft pulps and control kraft pulps

310

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

315 
$$\frac{1}{Y_T G} = \frac{1}{Y_C} = \frac{1}{Y_{CW}} + \frac{(\Delta DP)_S}{Y_{CW}} \frac{1}{DP} \tag{4}$$

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

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

330

331 
$$\frac{1}{Y_{C1}} - \frac{1}{Y_{C2}} = 929 \left( \frac{1}{DP_1} - \frac{1}{DP_2} \right)$$
 (5)

332  
 333 The Degree of Polymerization of cellulose, DP, in the final kraft pulp is calculated as (da Silva Perez and van  
 334 Heiningen 2015):  
 335

336 
$$DP = \left( \frac{1.65[\eta] - 116H}{G} \right)^{1.111}$$
 (6)

337  
 338 where  $[\eta]$  is the intrinsic viscosity of the pulp, H is the hemicellulose mass fraction of the pulp, and G is the  
 339 cellulose mass fraction of the pulp. The values for  $[\eta]$ , H, G and DP for the three cooks are listed in Table 4.  
 340

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

342

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

343  
 344 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  
 345 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  
 346 for the pulp pretreated with 4.38% SMM at 115°C followed by pulping at 12% EA. This compares to the measured  
 347 cellulose fraction of this pulp of 0.3694, i.e. a cellulose yield increase of 0.37 % (on O.D. wood basis) is  
 348 predicted versus 1.85 % measured (Table 5). Similarly, if equation (5) is applied for the pulp obtained by co-  
 349 addition of 4.38% SMM and 12% EA, then a cellulose fraction,  $Y_{C2}$ , and cellulose yield increase of 0.3538 and  
 350 0.29% respectively are calculated. These compare to the measured cellulose fraction and pulp yield increase for  
 351 this pulp of 0.3669 and 1.6% respectively. Thus it can be concluded that the increased retention of cellulose of  
 352 about 0.3-0.4% (on O.D. wood basis) for the two 4.4% SMM and 12% EA pulps due to reduced secondary  
 353 peeling is only a fraction (about 20%) of that due to suppression of primary peeling of cellulose by stabilization  
 354 of the reducing ends of cellulose in fresh wood chips.  
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372 Table 5. Comparison of measured and calculated cellulose yield (as fraction) and as % yield increase for  
 373 selected pulps

Experimental Conditions	Y <sub>C</sub> , Measured Cellulose Yield (fraction of O.D. wood mass)	Y <sub>C</sub> , 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

374  
 375 In summary, the present results show that addition of 4.38% SMM leads to an increase in the pulp yield of up to  
 376 2.5% mostly due to increased retention of cellulose and xylan. There was no significant increase in the retention  
 377 of glucomannan. The intrinsic viscosities of pulps of SMM cooks are about 150-200 ml/g higher than those of  
 378 the control cook and account for about 0.3-0.4% cellulose yield increase (on O.D. wood basis) due to reduced  
 379 alkaline hydrolysis and subsequent secondary peeling.

## 380 Conclusions

381 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.  
 382 wood basis) and allowed a decrease in the EA charge by 3%. The addition at too high (130 °C) or too low (80  
 383 °C) temperature resulted in less retention of cellulose; and hence, 115 °C seems to be the optimum temperature  
 384 for the SMM addition. Addition of 8.75% SMM produced diminishing returns and the use of 1.46% SMM  
 385 didn't lead to a significant increase in the yield. The use of SMM liquor with pH 10 led to significant decrease  
 386 in the yield and increase in rejects. The increase in the pulp yield was mostly due to increased retention of  
 387 cellulose and xylan. There was no significant increase in the retention of glucomannan, presumably because the  
 388 rate of stabilization of galactoglucomannan reducing end groups was slower than the rate of primary peeling.  
 389 The increase in cellulose yield is mostly due to less primary peeling of cellulose because of conversion of the  
 390 reducing end groups of cellulose into alkali-stable pyran and/or alditol structures. About 20% of the cellulose  
 391 yield increase is due to less secondary peeling because alkaline hydrolysis during kraft cooking is reduced by  
 392 the lower effective alkali charge when SMM is used.

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489

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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 Na <sub>2</sub> O)
					Calculated from pulp analysis data	Measured from pulp yield data			
	Xylan	GGM <sup>1</sup>	Cellulose	Lignin					
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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