Extended Modified Cooking of Southern Pine with Polysulphide — Effect on Elemental-Chlorine-Free Bleaching

J.E. JIANG and R.W. LOWE

The effect of polysulphide pulping on ODEoDD bleaching was investigated in the laboratory. No adverse effect was found on bleaching yield, chemical requirements, or brightness development. Polysulphide pulps prepared by extended modified cooking showed tear at tensile comparable to that of the control. Addition of polysulphide to extended modified cooking makes it possible to produce a fully bleached pulp from brownstock in the 15-18 kappa range with final yield and strength properties comparable to those from conventional kraft brownstock at about 30 kappa number.

RESULTS AND DISCUSSION

Effect on Bleaching Yields and Carbohydrates

Results in Table I show that the PS pulps gave overall bleaching yields (based on brownstock) comparable to those of the two control pulps, indicating that yield improvement in PS pulping can be retained during ODEoDD bleaching. Thus, addition of 2-3% PS in extended modified cooking to 15-18 kappa number can give the same final pulp yield as in conventional kraft cooking to 27-30 kappa number.

Compared to the two CK pulps, all EM pulps were found to give a total bleaching yield from 1-2.5% higher on a brownstock basis. The higher yields apparently resulted from a lower residual lignin content in the EM pulps than in the CK pulps (i.e., 15 vs. 27 kappa). Compared to the control pulps on a wood basis, the PS pulps gave a higher final bleached yield for a given brownstock yield (Fig. 2). The higher bleaching yields of EM PS pulps thus can partly compensate for a lower brownstock yield when cooking to a lower kappa number; this should be taken into consideration in process economic analysis for extended delignification.

Polysulphide was found to increase mainly the content of glucomannans for both the CK and EM pulps, as indicated by an increase in mannan and glucan contents (Table II). This is in agreement with the literature [5,6]. The contents of other hemicelluloses did not appear to be affected by PS pulping, and were found to decrease with increased delignification.

Bleaching did not change the carbohydrate compositions to any discernible extent for all pulps except one. The pulp with 3% PS addition, which had the highest content of mannan, gave a slightly higher bleaching yield loss in mannan and xylan.

Effect on Bleaching Response

Both the PS and the control pulps were found to give a similar response to oxygen delignification and pre-bleaching.
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Dr. Caulfield has written over 50 technical articles largely in the field of moisture interaction with cellulose and paper.

He is a member of the American Chemical Society (Cellulose, Paper and Textile Div. and Polymer Div. Inc.). For almost 25 years, he has been a member of TAPPI and its Paper Physics Committee. He is also a member of the Materials Research Society. Dr. Caulfield was elected a Fellow of the International Academy of Wood Science in 1984.

We look forward to Dr. Caulfield's contribution towards maintaining the high standards of review of the our Journal.

We are pleased to welcome Dr. Daniel F. Caulfield to the staff of JPPS as an Associate Scientific Editor.

Derek H. Page
Scientific Editor
It can be estimated from Table I that kappa numbers after both the oxygen and the oxidant extraction stages were approximately proportional to the brownstock kappa numbers. Figure 3 shows that the CK PS and the EM PS pulps resulted in a brightness increase comparable to their respective control pulps for a given chlorine dioxide charge, suggesting that PS pulping did not adversely affect pulp final brightening. This is in agreement with results reported in the literature [5-8].

Compared to the control, the EM PS pulp was about 5% higher in both burst (Fig. 5) and tensile (Fig. 6). The higher burst and tensile were probably due to the increased inter-fibre bonding from a higher hemicellulose content. In contrast to the EM PS pulp, little improvement in tensile was found for the CK PS pulp. This could be attributed to a possible ceiling for burst and tensile development.

Figure 7 shows that, because its higher tensile compensated for its lower tear, the EM PS pulp gave comparable tear at a given tensile. However, the CK PS pulp was about 10-15% lower in tear at a given tensile than the CK control. The difference in the effect of PS pulping on CK and EM pulps may be explained by the different ratios of hemicelluloses to cellulose in pulp. Results in Table II show that increased delignification results in a more severe loss in hemicelluloses than in cellulose. Therefore, PS pulping combined with extended delignification under proper conditions can compensate for the loss of hemicelluloses in extended delignification.

Figure 8 shows that PS pulping increased the ratio of hemicelluloses to glucan in the EM PS pulps from 0.15 to 0.17-0.19, a level comparable to that of the CK control pulp. It is interesting to note that both the EM PS pulps and the control CK pulp gave comparable strength properties (Figs. 4-6), suggesting a strong correlation between the ratio of hemicelluloses to cellulose and pulp strength properties. PS pulping increased the ratio of hemicelluloses to cellulose and pulp strength properties. PS pulping increased the ratio in the CK PS pulp from 0.18 to 0.22. It is probably this excessively high ratio of hemicelluloses to cellulose that is responsible for the severe tear loss in the CK PS pulp.

As expected, compared to their control pulps, the bleached PS pulps with a higher content of hemicelluloses showed a 15-20% decrease in refining energy requirement. This decrease is in the same order of magnitude as that found in unbleached PS pulps [4].

Effect on Physical Properties of Fully Bleached Pulps

Compared to the control pulps, the CK PS and the EM PS pulps were found to be about 10-15% lower in tear at a given freeness (Fig. 4). This is apparently in contrast to an earlier finding that no detrimental effect of PS pulping was found on tear at a given freeness for EM brownstocks at about 17 kappa [4]. The PS pulps somehow sustained a greater loss in tear than the control during bleaching.

This may be due to an interaction between the effect of bleaching on fibre flexibility as well as conformation and the effect of an increased amount of hemicelluloses on inter-fibre bonding. Since bleached pulps are more flexible and more conformable than brownstocks, the bleached PS pulps with a higher hemicellulose content probably tend to form more extensive inter-fibre bonding, thus resulting in a lower tear than the control. Results in Table III indicate that the PS pulps gave a lower bulk at a given freeness than their respective control pulp, which is consistent with this explanation.

Table I

<table>
<thead>
<tr>
<th>Cook ID</th>
<th>CK A2893</th>
<th>CK A2896</th>
<th>EM A2893</th>
<th>EM A2894</th>
<th>EM A2892</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyphenol charge, % on wood</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Brownstock kappa number</td>
<td>27.4</td>
<td>27.1</td>
<td>13.9</td>
<td>13.5</td>
<td>13.1</td>
</tr>
<tr>
<td>BS viscosity, mPa·s</td>
<td>31.7*</td>
<td>30.7*</td>
<td>31.1</td>
<td>34.1</td>
<td>42.1</td>
</tr>
<tr>
<td>BS screened yield, % on wood</td>
<td>46.1</td>
<td>48.8</td>
<td>42.8</td>
<td>44.5</td>
<td>45.1</td>
</tr>
</tbody>
</table>

* Chlorinated viscosity

Table II

<table>
<thead>
<tr>
<th>Cook ID</th>
<th>PS Pulping</th>
<th>Pulp type</th>
<th>Kappa number</th>
<th>Carbohydrate yield, % on wood</th>
<th>Glucose</th>
<th>Hemial / Glucan</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2893</td>
<td>0 BS</td>
<td>27.4</td>
<td>2.4</td>
<td>2.9</td>
<td>0.1</td>
<td>37.6 / 0.17</td>
</tr>
<tr>
<td>CK</td>
<td>2 BS</td>
<td>27.1</td>
<td>3.6</td>
<td>4.1</td>
<td>0.2</td>
<td>38.8 / 0.21</td>
</tr>
<tr>
<td>CK+PS</td>
<td>0 BS</td>
<td>27.4</td>
<td>2.4</td>
<td>2.9</td>
<td>0.1</td>
<td>36.9 / 0.18</td>
</tr>
<tr>
<td>A2896</td>
<td>2 BS</td>
<td>13.9</td>
<td>0.11</td>
<td>0.2</td>
<td>0.1</td>
<td>36.5 / 0.15</td>
</tr>
<tr>
<td>CK+PS</td>
<td>2 BS</td>
<td>12.5</td>
<td>0.1</td>
<td>2.4</td>
<td>0.1</td>
<td>35.7 / 0.15</td>
</tr>
<tr>
<td>EM</td>
<td>2 BS</td>
<td>2 BS</td>
<td>2.8</td>
<td>2.4</td>
<td>0.1</td>
<td>36.4 / 0.17</td>
</tr>
<tr>
<td>EM+PS</td>
<td>2 BS</td>
<td>15.1</td>
<td>0.1</td>
<td>2.8</td>
<td>0.2</td>
<td>37.2 / 0.18</td>
</tr>
<tr>
<td>EM+PS</td>
<td>3 BS</td>
<td>14.9</td>
<td>0.1</td>
<td>2.8</td>
<td>0.1</td>
<td>37.3 / 0.17</td>
</tr>
</tbody>
</table>

Glucose = 100-arabinose-xylose-mannotetraacetalulose-Klason lignin; BS = Brownstock; BP = Bleached stock.
Fig. 2. For a given brownstock yield, the PS pulps were found to give a slightly higher bleached yield, suggesting that PS pulps are more resistant to carbohydrate losses during ODE\textsubscript{2}DD bleaching.

Fig. 3. Effect of PS pulping on bleaching chemical demand. (Brownstock kappa numbers are given in parentheses in the legends.)

Fig. 4. Effect of PS pulping on bleached pulp tear strength. (Brownstock kappa numbers are given in parentheses in the legends.)

Fig. 5. Effect of PS pulping on bleached pulp burst strength. (Brownstock kappa numbers are given in parentheses in the legends.)

Fig. 6. Effect of PS pulping on bleached pulp tensile strength. (Brownstock kappa numbers are given in parentheses in the legends.)

Fig. 7. Effect of PS pulping on bleached pulp tear at tensile. (Brownstock kappa numbers are given in parentheses in the legends.)
SUMMARY AND CONCLUSIONS

The PS pulps showed comparable bleaching response, chemical requirements, and brightness development to the control pulps. Polysulphide pulping resulted in brownstocks with a slightly better bleaching yield. A higher retention of glucomannans was responsible for the yield increase in PS pulping. Bleaching did not change the carbohydrate compositions, and the brownstock yield improvement in PS pulping was retained during bleaching.

Compared to the control pulp, the bleached EM PS pulp was found to give 10–15% lower tear, and 5% higher burst and tensile at a given freeness. At a given tensile, the EM PS pulp showed a tear index comparable to that of the control. Compared to the control pulp, the CK PS pulp gave a 15% lower tear, at a given freeness or tensile, and a similar burst and tensile strength. The lower tear of the CK PS pulp is probably caused by an excessively high ratio of hemicelluloses to cellulose. As expected, the PS pulps were found to be 15–20% lower in refining energy requirements.

It can be concluded from this study that polysulphide pulping does not adversely affect ODEqDD bleaching. Combining PS pulping with extended modified cooking can preserve both pulp yield and pulp strength. A southern pine market pulp can be produced from a brownstock prepared by addition of PS to extended modified cooking to 15–18 kappa number, with final yield and strength properties comparable to those from a brownstock prepared by CK cooking to about 30 kappa number.

EXPERIMENTAL

Southern pine chips of commercial grade were screened in the laboratory. Fractions with a thickness between 3 and 8 mm and length less than 45 mm were collected for cooking. Laboratory cooking parameters and detailed procedures are given elsewhere [4].

Pulp bleaching was conducted according to the procedures described in an earlier paper [4]. There was a pH adjustment between the last two chlorine dioxide stages. After washing in the second last D stage, the pulp pH was raised to about 11 by addition of NaOH. After pH adjustment, the pulp was kept at 75°C for 5 min before being subjected to the final D stage bleaching without washing.

TAPPI methods were followed for all analytical tests. Technical Section, CUPA standard testing methods were used in the testing of pulp physical properties.


ABSTRACT: The effect of polysulphide pulping on ODEqDD bleaching was investigated in the laboratory. No adverse effect was found on bleaching yield, chemical requirements, or brightness development. Polysulphide pulps prepared by extended modified cooking showed tear at tensile comparable to that of the control. Addition of polysulphide to extended modified cooking makes it possible to produce a fully bleached pulp from brownstock in the 15–18 kappa range with final yield and strength properties comparable to those from conventional kraft brownstock at about 30 kappa number.

RÉSUMÉ: Nous avons étudié en laboratoire les effets de la fabrication de la pâte au polyphosphate sur le procédé de blanchiment ODEqDD. Nous n’avons observé aucun effet adverse sur le rendement du blanchiment, les besoins en produits chimiques, le développement du degré de blanchiment. Les pâtes au polyphosphate préparées au moyen d’une cuisson prolongée modifiée formaient un densité de déchirure au dynamomètre comparable aux pâtes sous observation. L’addition de polyphosphate à la pâte de cuisson prolongée modifiée autorise la production d’une pâte entièrement blanche à partir d’une pâte émergée dans la plage d’indices Kappa 15–18, dont le rendement final et les propriétés de résistance se comparant à celles de la pâte kraft émergée conventionnelle à un indice Kappa de 30.

KEYWORDS: CHLORINE FREE BLEACHING, POLYSULPHIDE PULPING.
REFERENCES


Electrical Conductivity of Pulp Suspensions Using the Donnan Equilibrium Theory

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An empirical equation is developed to predict the ionic conductivity of pulp slurries in aqueous electrolyte solutions. The equation incorporates the Donnan equilibrium constant and uses the concentration of bound acids as a property of pulp. The equation is valid for a range of pulp types, independent of the composition of the electrolyte solution, and gives the conductivity to ±5% for pulp consistencies from 1 to 10% with an electrolyte conductivity greater than 3.9 mS/cm.

INTRODUCTION

Continuous on-line measurement of pulp consistencies is desirable for many applications in the pulp and paper industry. Although consistency measurement by electrical means has been studied intermittently over many decades, neither electric conductivity nor capacitance has supplied a satisfactory way of determining consistency as their values are susceptible to changes in the properties of fibre and aqueous phases [1–4]. The objective of the work described below was to find a general correlation for the electric conductivity of pulp suspensions in aqueous electrolyte solutions and to shed some light on the transport of ions in pulp fibres.

Some conductivity data are available for pulp at very high consistencies. When absolutely dry, cellulosic materials may be considered as insulators with a specific conductivity as low as 10^{-18} S/cm [1]. At 10% moisture, the specific conductivity of wood pulp fibres is about 10^{-10} S/cm [1]. Regardless of the type of wood pulp, the conductivity continues to increase with an increase in moisture until it appears to reach a plateau value of 6 x 10^{-4} S/cm at about 30% moisture [1].

Scallan [1] recently studied the conductivity of fibres in dilute aqueous suspensions and found that the conductivity of a pulp suspension in 10^{-4} mol/L NaCl increased linearly with consistency up to 0.3%, suggesting that the wet pulp fibres are more conductive than the liquor. The conductivity of pulp fibres was attributed to the presence of mobile ions from dissociated bound acid groups of the fibre matrix.

Pulp fibres contain acidic groups, such as hydroxyl groups and carboxylic acids, which are bound within the fibre matrix. Some of these acids may be in the protonated form; others are in the salt form with free cations in close proximity to the bound anions. When the pulp fibre is placed in an electrolyte solution, an exchange of ions occurs between the external solution and the fibre wall which, at equilibrium, results in an uneven distribution of ions between the external solution and the fibre wall. The Donnan equilibria are a function of the dissociated bound acid concentration and the ionic strength of the external solution and are defined by the Donnan equilibrium constant, G:

\[
G = \frac{\gamma_{\text{I}}}{\gamma_{\text{E}}} \frac{[\text{H}^+]_{\text{I}}}{[\text{H}^+]_{\text{E}}} \frac{[\text{Na}^+]_{\text{I}}}{[\text{Na}^+]_{\text{E}}} = \left( \frac{\gamma_{\text{I}}}{\gamma_{\text{E}}} \frac{[\text{OH}^-]_{\text{I}}}{[\text{OH}^-]_{\text{E}}} \right) \left( \frac{[\text{CO}_2\text{H}]_{\text{I}}}{[\text{CO}_2\text{H}]_{\text{E}}} \right)^{1/2}
\]

where subscripts I and E refer respectively to concentrations of the internal and external solution, and X represents any ion with charge z. The ion activity coefficient is represented by γ.

Since G is always greater than one, the concentration of counter ions (i.e. cations such as H^+ and Na^+) in the internal solution