Polysulphide pulping of western softwoods: Yield benefits and effects on pulp properties

By C. Luthe and R. Berry

Abstract: The yield benefits provided by PS and PSAQ and their effects on pulp properties were evaluated for four Western softwoods. A 1.0 to 1.4% yield increase resulted for every 1% PS on wood charged. Yield increases of 2.8 to 4.1% were observed for PSAQ pulping, with coarser fibre wood species responding less well to both additives. Decreases in tear at a constant freeness ranged from 7% for SPF to 17% for cedar. Initial and maximum tensile were increased by using PS by as much as 17% and 8%, respectively. PS pulps also beat faster than their kraft counterparts.

Polysulphide (PS) is recognized as an effective additive for increasing yield in kraft pulp mills [1-8]. Its wider application may be encouraged by the invention of Paprican’s Paprilox® process [9], which produces polysulphide liquor in the recausticizing plant [10]. Paprilox® allows for the production of polysulphide liquor with less capital investment than the competing MOXY™ [11] and Chiyoda [12] processes. There have been several successful pilot-plant and full-scale batch trials involving the generation of polysulphide by the Paprilox® process at Canadian mills [13-15] and Paprilox® has undergone successful long-term trials in the hardwood fibreline of a Canadian kraft mill [16,17].

The success of the first mill installation of Paprilox® has prompted several other mills to express interest in this process. Before committing to implementation, however, these mills want to know both the likely yield benefit from their furnish. Although refinability and tensile strength can improve, tear losses ranging from 0 to 15% have been reported for Northern spruce and pine polysulphide brownstocks relative to the kraft pulps [3,7,8-21] and a tear deficit of 13% has been reported for fully-bleached polysulphide pulp from Southern pine [22]. Although the importance of out-of-plane tear loss has been questioned [23], many pulp customers have an out-of-plane tear specification that currently needs to be met.

To begin to assess the effects of polysulphide implementation, the yield benefits provided by PS and PSAQ were measured for four western Canadian wood species and the properties of the unbleached pulps were examined. The findings of these studies are presented in this paper.

Experimental

Mill chips were air-dried (>90% solids content) and classified (2-8 mm) using a Domtar Classifier. The active alkali (AA) charges used were 20% for Douglas fir, Western hemlock and spruce-pine-fir (SPF), and 22% for Western red cedar (expressed as Na₂O on o.d. wood). The sulphidity (AA basis) was maintained at 34% on the kraft and KAQ cooks. For the PS cooks, it was 17%. The PS charge on o.d. wood ranged from 1.75 to 1.95% depending on the AA charge. Anthraquinone, when used, was charged at the 0.05% level (o.d. wood basis). A liquor-to-wood ratio of 3.5:1 (including the moisture in the chips) was used, unless otherwise specified.

For cooking (200-g (o.d basis), 2-L cooking vessel), the temperature was raised to 170°C in 90 minutes and held at 170°C for the time needed to attain the target H-factor. When the predetermined H-factor was reached, the cooking vessels were removed from the oil bath and cooled to room temperature in cold water. Brownstocks for physical testing were produced in a 56-L digester, under otherwise comparable conditions as described above. Calcium pulps were made by washing the pulp extensively with tap water. The calcium pulp was converted to its sodium form as described in [24]. Carbohydrates in chlorite-delignified pulp were measured using high performance anion-exchange chromatography coupled with amperometric detection [25].

Results, Discussion

Delignification of Western Softwoods: The relative rates of delignification for kraft, KAQ, PS and PSAQ cooking of western softwoods, at 20% AA, were evaluated over a range of H-factors between 600 and 1,400. In accordance with mill practice, a higher AA charge—22%—was used for Western red cedar. The H-factor requirements for a 30 kappa number target are shown in Table I. Comparing the delignification data for the three wood species pulped at 20% AA, SPF delignified the fastest, hemlock the slowest. As expected, for all four species delignification was accelerated by AQ (by 10 to 17%) in both the kraft and PS processes [26,27].

Pulp Yields of Western Softwoods: The yields for the four Western wood species under kraft, KAQ, PS, and PSAQ process conditions were determined from their respective cooking experiments. As indicated by the regression data given in Table II, good linearity was generally associated with the yield versus kappa relationships. The

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unusually low slopes for some of the relationships are because screened yields were used in the data analysis and rejects levels were highest (up to 0.7%, o.d. wood basis) at the high kappa numbers.

The yields at 30 kappa number - calculated from the corresponding yield vs. kappa linear regression equations - and the yield gains provided by the various additives relative to the kraft process are shown in Figs 1 and 2. Figure 1 clearly shows that the absolute yield associated with any one set of process conditions is dependent on the wood species being pulped. This is most apparent for Western red cedar, which, because of its relatively high lignin and extractives content [28], has the lowest overall yield for all four pulping processes. It should be noted that the PS charge for the cedar cooks (1.93%) was higher than for the other furnish (1.75%) because of the higher AA charge of 22% used in pulping. For comparative purposes, the PS yield gains for cedar were also calculated for pulping with a 20% AA charge. This calculation was possible because we had experimental yield data for cedar pulping with an 18% AA charge and the yield gains provided by a 1% charge of PS were identical at 18 and 22% AA. For a PS charge of 1.75% (i.e., at 20% AA), the PS and PSAQ yield gains relative to kraft were calculated to be 2.5 and 3.6%, respectively.

The data in Fig. 2 also indicate a dependency of additive performance on wood species. For example, a 0.05% charge of AQ on wood provided a 0.8% yield benefit for Western hemlock, but only a 0.2% yield gain for Douglas fir. Since process chemistry conditions (20% AA, 34% sulphidity) were held constant for both species, the well-known effects of sulphidity and AA on AQ performance [29-31] could be ruled out. As shown in Table III, residual EAs for cooks done at 20% AA were comparable, ranging between 12.3 and 16.5 g/L, depending on the pulping process. Furthermore, while it has been reported that the yield gain provided by AQ is primarily a consequence of faster delignification [26], the pulping rate during kraft cooking was actually accelerated to a slightly greater extent by AQ with Douglas fir than with hemlock - by 14% versus 10%, at the 30 kappa number target. The muted response of Douglas fir to AQ has also been observed during some western mill applications of the additive under kraft

![FIG. 1. Screened pulp yields at 30 kappa number and when using a 20% AA charge on pulp for selected Western wood species. The cedar values are from pulping at 22% AA.](image1)

![FIG. 2. Pulp yield increases at 30 kappa number, relative to kraft, for selected Western wood species. The PS charge was 1.75% (o.d. wood basis), except for cedar where it was 1.93%. The yield gains are shown above the bars.](image2)

### TABLE I. H-factor requirements to reach a 30 kappa target.

<table>
<thead>
<tr>
<th>Species</th>
<th>Kraft</th>
<th>KAQ</th>
<th>PS</th>
<th>PSAQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cedar</td>
<td>900</td>
<td>750 (17)</td>
<td>800</td>
<td>700 (13)</td>
</tr>
<tr>
<td>Hemlock</td>
<td>1225</td>
<td>1100 (10)</td>
<td>1225</td>
<td>1025 (16)</td>
</tr>
<tr>
<td>Douglas Fir</td>
<td>1100</td>
<td>950 (14)</td>
<td>1100</td>
<td>950 (14)</td>
</tr>
<tr>
<td>SPF</td>
<td>1020</td>
<td>900 (12)</td>
<td>960</td>
<td>800 (17)</td>
</tr>
</tbody>
</table>

Value in brackets is the % decrease in H-factor requirement for a 30 kappa target provided by AQ.

### TABLE II. Linear regression equations and regression coefficients for yield versus kappa relationships.

<table>
<thead>
<tr>
<th>Species</th>
<th>Kraft</th>
<th>KAQ</th>
<th>PS</th>
<th>PSAQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Cedar</td>
<td>$y = 0.14x + 36.30$</td>
<td>0.90</td>
<td>$y = 0.13x + 37.35$</td>
<td>0.90</td>
</tr>
<tr>
<td>Hemlock</td>
<td>$y = 0.08x + 41.81$</td>
<td>0.75</td>
<td>$y = 0.17x + 39.93$</td>
<td>0.96</td>
</tr>
<tr>
<td>Douglas Fir</td>
<td>$y = 0.17x + 40.49$</td>
<td>0.94</td>
<td>$y = 0.12x + 42.18$</td>
<td>0.89</td>
</tr>
<tr>
<td>SPF</td>
<td>$y = 0.11x + 42.87$</td>
<td>0.82</td>
<td>$y = 0.14x + 42.34$</td>
<td>0.87</td>
</tr>
</tbody>
</table>

### TABLE III. Residual EA (g/L as Na₂O) at 30 kappa.

<table>
<thead>
<tr>
<th>Species</th>
<th>Kraft</th>
<th>KAQ</th>
<th>PS</th>
<th>PSAQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cedar</td>
<td>19.3</td>
<td>19.7</td>
<td>19.3</td>
<td>19.0</td>
</tr>
<tr>
<td>Hemlock</td>
<td>12.6</td>
<td>12.3</td>
<td>13.9</td>
<td>15.0</td>
</tr>
<tr>
<td>Douglas Fir</td>
<td>13.1</td>
<td>13.5</td>
<td>14.5</td>
<td>15.7</td>
</tr>
<tr>
<td>SPF</td>
<td>13.8</td>
<td>14.5</td>
<td>16.0</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Since process chemistry conditions (20% AA, 34% sulphidity) were held constant for both species, the well-known effects of sulphidity and AA on AQ performance [29-31] could be ruled out. As shown in Table III, residual EAs for cooks done at 20% AA were comparable, ranging between 12.3 and 16.5 g/L, depending on the pulping process. Furthermore, while it has been reported that the yield gain provided by AQ is primarily a consequence of faster delignification [26], the pulping rate during kraft cooking was actually accelerated to a slightly greater extent by AQ with Douglas fir than with hemlock - by 14% versus 10%, at the 30 kappa number target. The muted response of Douglas fir to AQ has also been observed during some western mill applications of the additive under kraft.
The relative yield benefits of PS for the four wood species, at 30 kappa number, at a constant PS charge are compared in Fig. 3. The yield gains provided by a 1% PS charge (o.d. wood basis) for Western red cedar, Western hemlock, Douglas fir and Western SPF were 1.44, 1.27, 1.01 and 1.38%, respectively. For comparison, the corresponding yield gain for black spruce was found to be 1.35%.

These results suggest that the yield gain provided by AQ and PS is dependent on factors other than pulping rate. In Fig. 4, the yield gain using AQ, PS and PSAQ...
FIG. 6. The effect of PS addition and cation form on beating requirements to reach 500 CSF freeness. PS pulps beat faster than their kraft counterparts. The values over the bars indicate the percentage reduction in beating energy requirements.

FIG. 7. The maximum tensile for PS pulps was a little higher than that of the kraft control pulps in almost all cases, with Douglas fir showing the largest increase of 8%.

FIG. 8. Initial tensile was higher for PS pulps in sodium form, by as much as 14%. Douglas fir PS pulp in calcium form had a 17% higher initial tensile than its kraft counterpart.

FIG. 9. The effect of PS addition and cation form on tear strength at 500 CSF. PS pulps had a consistent tear penalty (percentage values over the bars) ranging from 7% for SPF to as high as 17% for Western red cedar.

FIG. 10. The effect of PS addition and cation form on tear strength at a constant beating rate of 5,000 PFI revs. Hemlock and SPF sodium pulps are tear deficient relative to the calcium pulp from these species. The percentage values over the bars indicate the tear penalty for the PS pulps.

FIG. 11. Decreased tear correlates with increased yield for the three pure Western wood furnishes over the yield range studied.
with each furnish (for a 1.75% PS charge on wood) is plotted against fibre coarseness; the cedar data are normalized to a 1.75% PS charge on wood. The data indicate that fibre coarseness affects yield gain, with the coarser fibres responding less well to PS and AQ.

Carbohydrates in Western Softwoods: To determine which carbohydrates are responsible for the observed yield increases provided by AQ, PS, and the combined addition of PS and AQ, the 30 kappa number pulps from the four cooking processes with each of the four Western softwood species were analyzed for carbohydrates. The carbohydrate analyses were done at least in triplicate and the average carbohydrate yields for each respective species and cooking process were used in the data interpretation. As the carbohydrate analysis only determines the mass fraction of each carbohydrate in a pulp sample, and not the carbohydrate yield, the reported carbohydrate yields are calculated using the pulp yield measurements in the corresponding pulping experiments.

The effect of the yield-retaining additives on the carbohydrate yield profiles of the four Western wood species is shown in Fig. 5. Since glucose and mannose exist primarily as cellulose and glucomannan polymers in the pulp matrix, these chemical forms—rather than glucose and mannose—are reported in the figure. The cellulose and glucomannan concentrations were obtained using the relationships cellulose = glucose - mannose/3 and glucomannan = 1.33 x mannose [28].

The predominant carbohydrate constituents in the four Western softwoods are cellulose, glucomannan and xylan, with yield increases for PS, AQ, and PSAQ pulping being attributed primarily to the preservation of glucomannan (Fig. 5). Similar observations have been reported previously for black spruce pulp [26]. When applied separately in the kraft process, PS provided 1.4 to 2.3% increases while AQ provided 0 to 0.5% increases in glucomannan. For both additives, the lowest glucomannan yield gains were observed for Douglas fir. The combined application of PS and AQ resulted in 2.1 to 3.0% yield increases in glucomannan, with the lowest benefits again being obtained with Douglas fir.
Figure 5 also shows that the addition of PS and AQ affected cellulose yield. When applied separately in the kraft process, PS provided 0.2 to 0.6% increases while AQ provided 0 to 0.4% increases in cellulose yield; their combined application resulted in 0.6 to 1.2% yield increases. The figure further shows that the concentration of xylan is lowered by PS, and perhaps by AQ. The combination of the two additives decreases the xylan in the pulp by between 0.3 and 0.8% on wood. This decrease in xylan can be attributed to PS-induced destruction during cooking of hexenuronic acid, which protects xylan from peeling reactions [32,33].

Pulp Physical Properties: To assess the changes in pulp properties associated with PS pulping of Western softwoods, the physical properties of the kraft and PS brownstocks generated in cooks with an initial 20% AA charge (22% for Western red cedar) were evaluated. Since pulp properties are affected by cation form, data were obtained for pulps in both sodium and calcium forms. Mill pulps are variable and not usually completely in the Na or Ca form. As expected, several distinct differences in the physical performance of kraft and PS pulps were observed, and these changes were exhibited - to a greater or lesser extent - by the pulps from all four Western softwood species examined. The largest changes were observed in beating requirement, tensile strength, tear strength and Gurley air resistance, and these are discussed in more detail below.

The beating requirements to attain a freeness of 500 CSF, for kraft and PS pulps, in calcium and sodium form, are compared in Fig. 6. As expected from the literature [20], PS pulps were generally found to beat faster than their kraft counterparts. The largest impact on beating was observed with Western red cedar, where for both sodium and calcium pulps, there was a 25% decrease in the beating energy required to attain 500 CSF. The cedar pulp also beat considerably faster than the other three Western softwood species. For hemlock and SPF, calcium pulps were found to beat more slowly than their sodium counterparts. This may be attributed to Ca pulps in unbeaten form having a higher initial freeness [34]. For cedar and Douglas fir, however, beating requirements were independent of the ionic form of the pulp.

The maximum tensile, Fig. 7, for PS pulps was a little higher than that of the kraft controls but the concentration of Douglas fir showing the largest increase of 8%. In all cases, maximum tensile was independent of the ionic form of the brownstock. Initial tensile, as shown in Fig. 8, for PS pulps in sodium form was higher than for the kraft controls, by as much as 14%, while Douglas fir PS pulp in calcium form had a 17% higher initial tensile than its kraft counterpart.

Tear strength losses ranging from 0 to 15% have been reported for Northern spruce and pine polysulphide brownstocks relative to the corresponding kraft pulps [3,7,18-21]. Similar results were observed in our study. The tear strengths at 500 CSF, for kraft and PS pulps, in calcium and sodium form, are compared in Fig. 9. PS pulps had a consistent tear penalty ranging from 7% for SPF to as high as 17% for red cedar. Furthermore, tear strength was independent of the ionic form of the brownstock. This last observation appears to contradict literature reports that the tear strength of spruce-jack pine pulp was higher in its calcium form [35]. The literature data, however, were reported at constant PFI, in contrast to a fixed freeness. A comparison of our tear strength data at a constant PFI value of 5,000 revs, Fig. 10, shows a similar effect for hemlock and SPF as that described in the literature. Figure 11 indicates that the tear changes are predictable for the single species furnishes and are correlated with yield over the range studied.

Another approach for evaluating the tear penalty of PS pulps is to do the tear comparison at constant breaking length. The results are summarized in Table IV and Fig. 12. The tear deficits of the PS pulps are very comparable to those reported at constant freeness (Fig. 9), except for Douglas fir, where no tear deficit was observed. As before, the PS-related tear deficits at constant breaking length were independent of the ionic form of the brownstock. Figure 13 shows that the PS-induced tear deficit at mid-range breaking length appears related to fibre coarseness, with Western red cedar showing the largest tear penalty, and Douglas fir no tear penalty. This difference in conclusion regarding Douglas fir when the comparison is done at constant freeness or constant breaking length appears to be related to the larger maximum tensile advantage of PS pulps than that observed for the other three western species (Fig. 7).

Gurley air resistance data for the sodium and calcium forms of the kraft and PS pulps, from the four Western wood species, are compared in Fig. 14. Gurley air resistance values were different for the four wood species examined as would be expected considering the coarseness range of the fibres. It was highest for Western red cedar at over 150 s/100 mL, and lowest for Douglas fir at 10 s/100 mL. The cost of polysulphide addition on Gurley air resistance was highly variable, with increases of up to 50% observed for hemlock, and decreases in the order of 10% for Douglas fir.

These physical property results are consistent with the changes that are believed to occur through increasing the amount of hemicellulose in the fibre [19,21,22, 36-41]. Increasing yield decreases the number of fibres in a given weight of pulp while greater fibre flexibility and collapsibility increases fibre-fibre bonding of the PS pulps. Such changes should decrease tear, light scattering, and beating requirements, and change Gurley air resistance. This combination of fewer fibres and increased collapsibility may explain why Gurley air resistance can either decrease or increase depending on the coarseness of the different furnishes. Fewer fibres should increase the porosity of the sheet but a more collapsible fibre should decrease it. For Douglas fir, the degree of collapsibility afforded by increasing the hemicellulose content appears to be less than for the other species and because of this the decrease in fibre count outweighs the changes in collapsibility.

SUMMARY

The yield gain provided by a 1% PS charge (o.d. wood basis) at 30 kappa number ranged from 1.0 to 1.4%, Douglas fir responded least to PS, cedar the most. The yield gain provided by 0.5% AQ (o.d. wood basis) at 30 kappa number ranged from 0.2 to 0.8%, Douglas fir responded least to AQ, cedar the most.

Fibre morphology affects yield gain, with coarser fibres responding less well to both PS and AQ.

Glucomannan is the main contributor to the yield increase resulting from adding PS and AQ, while xylan is lost particularly when PS is used.

The change in beating energy required to attain a freeness of 500 CSF for a polysulphide pulp and a kraft pulp was variable. The beating energy needed for a Western red cedar polysulphide pulp was 25% lower than for the kraft counterpart, while no change in beating energy requirements was seen with hemlock in the calcium form.

Initial tensile was higher for PS pulps in sodium form by as much as 14%.

Tear strength at a constant freeness decreased with increasing yield for Western red cedar, Western hemlock and Douglas fir over the yield range studied.

Polysulphide pulps have a consistent tear penalty at constant freeness ranging from 7% for SPF to 17% for red cedar.

The effect of polysulphide addition on Gurley air resistance was highly variable, with increases of up to 50% observed for hemlock, and decreases in the order of 10% for Douglas fir.

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LITERATURE