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MISSION STATEMENT:
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Serving the industry since 1903.
Effects of Extractives from Mountain Pine Beetle-Attacked Lodgepole Pine on Kraft Mills
By L. Allen, A. Gagné, and P. Watson

Les effets des produits d’extraction du pin de Murray attaqué par le dendroctone du pin ponderosa sur les usines de pâte kraft

Abstract: This report addresses the impact of mountain pine beetle infestation on several extractives-related issues in kraft pulp mill operation: extractives in pulp, pitch control, and effluent treatment. The work, funded by the Mountain Pine Beetle Initiative of Natural Resources Canada, involved visits to five western Canadian kraft mills to observe operating conditions, collection of samples for subsequent laboratory measurements, and overall analysis of the combined information. Work in separate reports has shown that the use of infested wood usually causes higher extractives (especially increased resin acid content) in the wood to the digester and this results in an increased solubility of fatty and resin acid soaps in black liquor. Hence the use of infested wood resulted in a greater extractives load to be removed in brownstock washing for good pitch control. Use of green- and red-stage wood did not cause a significant change in the total quantities of extractives in pulp across the bleach plant and at the pulp machine. In the mill using gray-stage wood, the solubility of extractives in black liquor was even higher and brownstock washing was more important for their removal. The quantity of extractives, especially the unsaponifiables, in the final pulp was significantly higher in the mill using gray-stage wood. In this mill, the resin acid concentration in the final effluent was high. The gray-stage results require further confirmation in more mills.


Keywords: MOUNTAIN PINE BEETLE, LODGEPOLE, PINE, WOOD EXTRACTIVES, EXTRACTIVES, PITCH, FATTY ACIDS, RESIN ACIDS, STEROLS, STEROL ESTERS, TRIGLYCERIDES, PITCH CONTROL, PULP AND PAPER PRODUCTION, KRAFT MILLS, EFFLUENT MANAGEMENT, SOAP, SOAP RECOVERY, TALL OIL.

Full peer-reviewed manuscript available at www.paptac.ca

The Half-Life of Biological Knots in Kraft Pulping
By M. MacLeod and A. Dort

Période de demi-vie des nœuds biologiques dans la mise en pâte kraft

Abstract: How many cycles of kraft pulping does it take to reduce biological knots (and the knotter rejects derived from them) to fibrous pulp and dissolved organics? To find out, we experimented with stockpiled knotter rejects and with fresh biological wood knots. With either material, re-cooking knotter rejects begat further knotter rejects. Relative to normal wood chips, biological knots cooked slower and to lower pulp yields; after re-cooking, the pulps became progressively weaker. Knotter rejects from biological knots had a half-life of two complete cooks in bleachable-grade kraft pulping.


Keywords: BIOLOGICAL KNOTS, KNOTTER REJECTS, KRAFT PULPING, DELIGNIFICATION RATE, PULP YIELD, PULP PROPERTIES

Full peer-reviewed manuscript available at www.paptac.ca

Effect of the Final ECF Bleaching Stage on Eucalyptus Kraft Pulp Properties – A Comparison Between Hydrogen Peroxide and Chlorine Dioxide
By P.E.G. Loureiro, P.J. Ferreira, D.V. Evtuguin, M.G.V.S. Carvalho

L’effet du stade final de blanchiment sans chlore élémentaire sur les propriétés de la pâte kraft d’eucalyptus – une comparaison

Abstract: The factors contributing to the differences between chlorine dioxide and hydrogen peroxide final ECF bleaching stages are discussed with respect to the properties of Eucalyptus globulus Kraft pulp. The higher beatability of pulps bleached with a final peroxide stage was assigned to the better fibre swelling capacity. For laboratory beaten fibres, dry zero-span tensile strength is a more suitable predictor of fibre strength than wet zero-span or intrinsic viscosity, at least when comparing pulps with different bleaching history. A comparison between laboratory and industrial bleached pulps is also provided.


Keywords: PULP PROPERTIES; FIBRE SWELLING; FIBRE STRENGTH; FINAL ECF BLEACHING; HYDROGEN PEROXIDE; CHLORINE DIOXIDE

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By: P.E.G. Loureiro, P.J. Ferreira, D.V. Evtuguin, M.G.V.S. Carvalho

Abstract: The factors contributing to the differences between chlorine dioxide and hydrogen peroxide final ECF bleaching stages are discussed with respect to the properties of Eucalyptus globulus kraft pulps. The higher brightness of pulps bleached with a final peroxide stage was assigned to the better fibre swelling capacity. For laboratory beaten fibres, dry zero-span tensile strength is a more suitable predictor of fibre strength than wet zero-span or intrinsic viscosity, at least when comparing pulps with different bleaching history. A comparison between laboratory and industrial bleached pulps is also provided.

The conventional ECF multistage pulp bleaching technology usually comprises 4/5 stages: DEDD/DEDED with or without oxygen pre-delignification. In order to improve some desired properties of fully bleached pulps (brightness retention, structural or physical properties, etc.) the final D bleaching stage may be substituted by hydrogen peroxide (P) [1-4] or by ozone (Z) [5] stages. Both alternative stages (P and Z) are suitable for the effective degradation of quinone type chromophores [6] arising in chlorine dioxide bleaching [7] and co-responsible for the increased brightness retention [8]. Besides improving brightness stability, eucalyptus pulps bleached with a final P stage have also shown better beatability and mechanical/optical properties despite of a lower intrinsic viscosity, when compared with last D bleaching stage [4]. Moreover, it has been reported that the final P stage can increase fibre charge [9], due to the conversion of carbonyl groups to carboxyl moieties in reaction of hydrogen peroxide anion with e.g., quinone structures [10]. On the other hand, D and Z bleaching stages reduce the amount of charge, mainly due to the reactions with hexemuronic acid side groups of xylan [11]. Additionally, these chemicals react with pulp components producing structures with carbonyl groups which can be adverse from the brightness stability point of view. However, very dissimilar results regarding the final Z stage have been reported using softwood [5] and hardwood [1] pulps.

The subject of fibre charge has gained greater attention because the carbonyl groups associated charge promotes fibre swelling [12-13], pulp beatability and improves handsheet strength properties [13], not to mention the impact on wet end chemistry regarding retention mechanisms [14]. The increased fibre charge due to peroxide bleaching has also been shown to reduce the phenomena of hornification [13, 15].

The main goal of this study was to provide more light on the causes for the above reported differences in our previous work [4], regarding brightness retention, beatability and papermaking properties of pulps bleached either with a final D or P stage (DEDD versus DEDP pulps). This goal was extended to a second set of bleached pulps previously studied as well [2]: an industrial fully bleached pulp (DEDED) and an industrial DED pulp further bleached in the laboratory with hydrogen peroxide. In contrast to the former study [4], the peroxide bleached pulp exhibited an opposite trend, despite a lower brightness retention: slightly worse beatability and papermaking properties compared to the industrial DEDED pulp. Therefore, the pulps from both studies were further characterized in this work in terms of specific chemical and physical properties in order to provide more detailed information.

EXPERIMENTAL

All the fully bleached Eucalyptus globulus kraft pulps (without oxygen pre-delignification) used in this work had an ISO brightness of 90±0.5% and were produced in previous studies [2,4]. In the study of Carvalho et al. [4], DED partially bleached pulps with three different initial ISO brightness levels, 84.7% (pulp A), 86.9% (pulp B) and 88.7% (pulp C), were submitted in the laboratory either to a final P stage (DEDP) or to a conventional final D stage (DEDD) – the lower the ISO brightness, the higher the chemical charges applied. In the work of Campos et al. [2], a DEDED industrial kraft pulp (D$_{2nd}$ pulp), was compared with a DEDP bleached pulp (P$_{1}$ pulp), where only the last P stage was carried out in the
PULP PROPERTIES

<p>| Table I: Fibre quality analysis of all pulp beaten to 8000 rev in a PFI mill |
|------------------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Bleached pulp</th>
<th>L^1 (mm)</th>
<th>Coarseness (mg/100m)</th>
<th>Fines content &lt; 200 µm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A ClO_2</td>
<td>0.682</td>
<td>7.6</td>
<td>13.3</td>
</tr>
<tr>
<td>A H_2O_2</td>
<td>0.687</td>
<td>7.8</td>
<td>14.6</td>
</tr>
<tr>
<td>B ClO_2</td>
<td>0.687</td>
<td>7.8</td>
<td>13.3</td>
</tr>
<tr>
<td>B H_2O_2</td>
<td>0.691</td>
<td>7.4</td>
<td>13.3</td>
</tr>
<tr>
<td>C ClO_2</td>
<td>0.687</td>
<td>8.0</td>
<td>13.0</td>
</tr>
<tr>
<td>C H_2O_2</td>
<td>0.692</td>
<td>7.6</td>
<td>12.8</td>
</tr>
<tr>
<td>D ClO_2</td>
<td>0.689</td>
<td>8.0</td>
<td>12.3</td>
</tr>
<tr>
<td>E ClO_2</td>
<td>0.701</td>
<td>8.0</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Coefficient of variation: (1) 0.5%; (2) 1.7%; (3) 2.1%

laboratory.

The pulps were beaten in a laboratory PFI mill according to the ISO 5264/2 procedure. Handsheets for physical properties evaluation were prepared using the ISO 5269/1 procedure. Dry and wet zero-span breaking strength and internal bond strength (Scott test) were measured according to TAPPI T 231, TAPPI T 273 (curiously withdrawn) and TAPPI UM 403 procedures, respectively. The procedure used for determining water retention values (WRV) was that described by Jayne [16]. Fibre length, coarseness and fines content were determined using the Fibre Quality Analyzer (FQA). Pulps carboxyl group's content was assessed by the Wilson method (TAPPI T 237) while the carboxyl groups (in aldehyde form) was determined by spectrophotometry using 2,3,5 triphenyl-2H-tetrazolium chloride (TTC) [17]. Fibres fines set potential was measured by laser doppler electrophoresis using the Zetasizer nano ZS (Malvern Instruments).

RESULTS AND DISCUSSION

Pulps A, B and C

As reported in the work of Carvalho et al. [4], referred above, DEDP pulps have shown higher beatability than DEDD pulps. However, while chloride dioxide charge was linearly correlated with D', brightness, a much higher hydrogen peroxide charge was needed to bleach pulp A in comparison to pulps E and C. Therefore, a final P stage in the ECF bleaching of eucalypt kraft pulps has a higher performance if the ISO brightness after DED is at least 87%. This results in a reasonable chemical consumption and better physical and optical properties, compared to a final D stage. In addition, the higher intrinsic viscosity of the final D pulps did not reflect better strength properties.

Table I shows the FQA results of fibre length, coarseness and fines content. Considering the first group of pulps (A, B and C), no significant differences between pulps after the final D and P stages in terms of length-weighted average fibre lengths (L_p) and coarseness, have been detected that could explain the observed differences in papermaking potential of both pulps. On the other hand, the differences in fines content, presented here as the percentage of fines on an arithmetic basis, have some relevance, mostly considering pulps A and B. The higher beatability of final P pulps may also result in a greater production of secondary fines which improve swelling, as well as fibre-to-fibre bonding due to their bridging effect, thus imparting sheet consolidation [18]. However, fines content does not explain the differences in beatability between both pulps C.

One of the most common methods to assess fibre strength of papermaking pulps is based on the measurement of pulp intrinsic viscosity. Furthermore, the wet zero-span tensile strength test was originally suggested to be the index related to the average axial tensile strength of individual fibres. As can be seen in Table II, wet zero-span values show the detrimental effect of hydrogen peroxide on wet fibre resistance, which is the most truthful property measured by the wet zero-span test (and not the dry fibre resistance), as claimed by Gurnagul and Page [19]. They hypothesized that the drop in zero-span strength (from dry to wet) is dependent on the extent of chemical and mechanical damage caused to the fibres structure during pulping, bleaching and refining, in opposition to the assumption made by Cowan [20] that rewetting a dry sheet would eliminate only the inter-fibre bonding (remaining fibre strength unchanged).

In addition, the loss in strength on rewetting was not related to the degree of polymerization of the cellulose [19]. On the contrary, the results presented here (Figure 1) show that P pulps intrinsic viscosity is linearly correlated with the loss in strength upon rewetting (R^2=0.9994). Final D pulps, having similar intrinsic viscosities (from 970 to 1000 dm^3/glucose) [4], exhibit the same loss in strength. Following Cowan's assumption it would be expected that the highest internal bonding strength evaluated by the Scott test would have the highest drop in zero-span strength from dry to wet conditions. In this study, however, such agreement does not exist (Table II). Mention is due to the small number of points and to this specific comparison of fully bleached pulps with different final stages, thus disallowing wide-ranging conclusions.

Seth and Chan [21] argued that pulp viscosity and wet zero-span are not suitable tests to determine fibre strength, claiming the dry zero-span as the most reliable method as long as the fibres are straightened. Given that beating at moderate consistency tends to straighten fibres, and based on dry zero-span strength, it could be concluded that peroxide-treated pulps have lower fibre strength than the corresponding D pulps, with the exception of pulp C. As a matter of fact, this was seen on the development of tearing strength as a function of the tensile strength with the D pulps having better tearing resistance at 2000 rev [4], with the exception of pulp C final P.

Because the strength of individual fibres has been proposed to be the major fac-
ior contributing to tear strength of well bonded hand sheets [22], the dry zero-span tensile strength may be the most reliable method to assess fibre strength. Seth and Chan [21], for the range of viscosities they studied, also concluded that there was no relationship between pulp viscosity and dry zero-span strength. Nevertheless, for wet zero span and intrinsic viscosity such a relationship has been found (Figure 1), in agreement with some earlier findings [13,23], and also considering the remaining pulps (not shown), besides A, B and C bleached with peroxide. Agarwal and Gustafson [23] found that this relationship was significantly influenced by the occurrence of primary peeling (end-initiated depolymerisation of carbohydrates) and by the presence of hemicelluloses. They also reported that primary peeling probably had a beneficial influence on fibre strength at the expense of a higher yield loss. This is likely the case of the pulps bleached with a final alkaline P stage: comparing pulp C with pulp A, the higher fibre resistance of pulp C (Table II) can be related to superior primary peeling caused by a greater amount of aldehydes groups produced in D stage due to the harsher conditions.

Considering the case of pulps bleached with the final P stage, pulp A possesses the lowest intrinsic viscosity (690 d.m.\(^3\)/kg), the lowest wet zero-span strength (10.9 km), and the highest decrease in strength upon rewetting (37%). It is important to notice that the most severe conditions that were used in the final P stage applied to pulp A (higher \(\text{H}_2\text{O}_2\) and \(\text{NaOH}\) charges) explain the extreme values achieved. At the same time, this pulp has the highest WRV (Table II).

Moreover, as can be seen in Table II, pulps bleached with a final P stage have a higher WRV than those bleached with a final D stage. This higher swelling ability of the former can be the main cause for the observed differences in beatability and papermaking properties. Of course this swelling ability of P pulps, opening up the cell wall fibrous structure, causing debonding and therefore a weakening of the interfibrillar matrix (elastization of the structure), will increase the drop in zero-span tensile strength upon rewetting (supporting Gunnagul and Page theory), and will, at the same time, promote the evidenced higher beatability.

Fibre swelling is a well-known phenomenon which makes fibres more flexible and conformable. The swelling is affected by the electrostatic repulsion between negatively charged moieties in the cell wall and also due to the difference in osmotic pressure that is generated from different concentrations of mobile ions between the interior of the fibre wall and the external solution (Donnan theory), depending on the nature of those counter-ions in the vicinity of the acidic groups [12,13,24].

Fibre charge can be increased by the introduction of carboxyl groups, since these are the only groups capable of ionization without going to extreme values of pH [12]. As already mentioned, hydrogen peroxide is able to produce carboxyl groups during pulp brightening reactions, thus increasing fibre charge. Moreover, in the alkaline conditions of the P stage, carboxylic groups are negatively charged, increasing the electrostatic repulsion between these groups which promotes a better swelling of cell walls. Besides the positive effect of the carboxyl groups on swelling, the effect of \(\text{NaOH}\) charge, pH and ionic strength should also be considered.

In fact, according to Scallan [12], the nature and the amount of carboxylate counter-ions is of great importance because they will control the osmotic pressure inside the fibre wall. Furthermore, a progressive increase in swelling as pH was raised was found by Grignon and Scallan [24] (conversion of the acidic groups from \(\text{H}^+\) to \(\text{Na}^+\) form). As proposed by Laitinen and Scallan [25], the electrolytic swelling due to ion exchange is similar to the swelling created by the mechanical beating, being both additive. Therefore, more swollen pulps, as the alkaline-peroxide bleached pulps, will require less mechanical energy in the beating process to attain a pulp drainability target (Schopper-Riegler or Canadian Standard Freeness level). Their most important drawback can be a more difficult dewatering in the pressing section, although the swelling can be reduced by ensuring that the pulp is more in the calcium form after beating [25].

Table III reveals some differences in oxidised groups and zeta potential between pulps bleached with final P and D stages. For pulp A, where harsh beating conditions were used in either P or D stages, while chlorine dioxide raises the amount of carboxyl groups, hydrogen peroxide raises the carboxyl groups content (comparing pulps C with A). Although it is widely recognized the detrimental effect of carboxyl groups on brightness retention, they do not solely explain the higher brightness stability of pulps bleached with final P stage, as can be seen for both pulps C. This subject remains for the future investigations.

Despite the higher carboxyl groups content, pulps A and C after the final P stage have lower zeta potential absolute values than the corresponding pulps bleached with a final D stage (Table III). However, while the carboxyl groups content presented is a bulk fibre property,
PULP PROPERTIES

<table>
<thead>
<tr>
<th>Bleached Pulp</th>
<th>COOH content (meq/kg odp)</th>
<th>CHO content (mmol/kg odp)</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A ClO₂</td>
<td>74.9</td>
<td>44.6</td>
<td>-23.2</td>
</tr>
<tr>
<td>A H₂O₂</td>
<td>80.8</td>
<td>29.5</td>
<td>-18.9</td>
</tr>
<tr>
<td>B ClO₂</td>
<td>...</td>
<td>...</td>
<td>-23.0</td>
</tr>
<tr>
<td>B H₂O₂</td>
<td>...</td>
<td>...</td>
<td>-18.9</td>
</tr>
<tr>
<td>C ClO₂</td>
<td>69.9</td>
<td>16.5</td>
<td>-20.9</td>
</tr>
<tr>
<td>C H₂O₂</td>
<td>71.8</td>
<td>17.2</td>
<td>-16.1</td>
</tr>
<tr>
<td>D ±w</td>
<td>76.1</td>
<td>14.8</td>
<td>-19.5</td>
</tr>
<tr>
<td>P ±w</td>
<td>74.8</td>
<td>18.4</td>
<td>-15.0</td>
</tr>
</tbody>
</table>

As far as brightness reversion is concerned, despite the higher carbonyl groups content, P ±w showed much lower brightness reversion.

CONCLUSIONS

Compared to the acidic chlorine dioxide stage, an alkaline peroxide stage at the end of the bleaching sequence has shown to be more advantageous regarding beatability, strength and optical papermaking properties, despite the lower intrinsic viscosity and wet zero span values. It was confirmed that the latter properties can be pour fibre strength predictors. In fact, dry zero span provides more reliable information on fibre resistance in well beaten fibres, at least when comparing pulps with different bleaching history. The intrinsic viscosity was correlated with the wet zero-span as well as with the loss in strength upon rewetting the handsheets.

The higher beatability of pulps bleached with a final P stage was assigned to electrolytic fibre swelling caused by a greater amount of carbonyl groups and by the higher osmotic pressure inside the fibre wall (due to carboxylate counter-ions such as Na⁺ from the alkali source). In addition, the higher pH of the peroxide bleached pulps increases the ionization degree of the carbonyl groups thus favouring swelling. However, the swelling degree should be controlled in order to not impair dewatering in the pressing section. According to the zeta potential values, final P pulps have shown improved fines retention.

Regarding brightness reversion and carbonyl and carbonyl groups contents, the results were inconclusive and therefore further investigation is needed.

Comparison between laboratory and industrial pulps need some caution due to the different washing conditions, since there is no carryover in laboratory washings.

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