Measurement of dissolved organic substances as a predictive tool to monitor pulp qualities in the alkaline peroxide bleaching of aspen mechanical pulp

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Abstract: Alkaline peroxide bleaching causes pulp yield loss and significantly contributes to enhancing fiber bonding properties thereby improving pulp strength. Previous studies have demonstrated that yield loss is a key factor that has a considerable impact on fiber bonding properties. The present study has found that the quantity and nature of materials dissolved in bleaching have a close correlation to properties of resulting pulps. The implications of this result include using a method of measuring dissolved substances in bleeding filtrates for monitoring pulp quality.

While primarily aiming at increasing pulp brightness, the bleaching process causes an inevitable yield loss, which is generally undesirable. Yield is an important measurement of the selectivity (brightness increase vs. carbohydrate removal) of a bleaching process, which is important to the process economy (lower pulp yield means more wood consumption for a given pulp production). Fundamentally, yield loss reflects the dissolution of pulp components from fibers into water phase. Hemicelluloses, lignin and extractives are the three major components dissolved during the alkaline peroxide bleaching of mechanical pulps. Disolved organic substances from different fiber processing stages can be quantified, for example, as total organic carbon (TOC) in the filtrates (or pressates) or as chemical oxygen demand (COD) of the filtrates (or pressates). According to the law of conservation of mass, TOC or COD measurement may be used to estimate yield loss during pulping and bleaching processes. Our previous study has established a strong, linear relationship between yield loss, TOC and COD in the alkaline peroxide bleaching of aspen CTMP. Yield loss, occurring as a result of the dissolution of pulp materials from fibers, likely involves: (a) oxidative degradation to split lignin end units (e.g chromophoric groups) from the lignin macromolecule; (b) alkaline hydrolysis of ester and lactone groups in hemicellulosics, lignin, pectin and extractives; and (c) solubilization of fragments of these pulp substances. Yield, the degree to which these mechanisms occur collectively, plays a significant role in influencing pulp properties. First, the removal of fiber components, especially lignin, causes the loss of cross-sectional structural integrity of fibers, leading to increased fiber collapse. Second, the removal of hydrophobic substances such as lignin and extractives, in particular from fiber surfaces, renders fibers more hydrophilic, thereby enhancing their tendency to swell and improving the bonding property. Third, the alkaline hydrolysis (b) and the oxidation (a) increase the ion content on fiber surfaces, predominantly through the introduction of carboxylic acid groups, giving effects similar to those in the preceding pathway. It is well documented that the concentration of carboxylic acid groups, particularly on fiber surfaces, has a strong influence on fiber-to-fiber bonding properties.

The changes in pulp physical properties resulting from the above-mentioned mechanisms can be measured, for example, by apparent density and tensile index. Low apparent density (i.e. high bulk) is desirable for aspen BCTMP for most of its end uses. In general, tensile index increases with increasing apparent density. In the production of aspen BCTMP, the bleaching is used not just for developing brightness but for developing strength as well. In the bleaching composition, sodium hydroxide and hydrogen peroxide are the two chemicals that contribute to strength development. It is a quite common industry practice to adjust the caustic-peroxide ratio to optimize the brightness-strength-bulk relationship in order to make a variety of pulp grades to meet various end use requirements. Our early study indicates that the alkalinity plays a more important role in developing physical properties during the alkaline peroxide bleaching of aspen CTMP. This suggests that the alkaline hydrolysis and the solubilization may influence the pulp strengthening to a greater extent.

The objective of the present investigation was to examine the correlation between “what is taken out of the fibers” and “what is put onto the fibers”. In this study, the total dissolved and colloidal organic substances in bleaching pressates were measured as TOC and their anionic portion was measured as cationic demand. The changes on fibers were analyzed by carboxylic acid group content and bonding properties.

Materials and Methods

Pulp

An aspen CTMP (61.6 of ISO brightness and 480 CSF) supplied by a pulp mill in Western Canada was employed in this study.

Bleaching

All the bleaching experiments were performed in polyethylene bags using various amounts of H2O2 and NaOH under the following conditions to attain different brightness levels: 15% pulp consistency, 70°C for 2 hours, 3% Na2SiO3, 0.05%
MgSO₄ and 0.1% DTPA. The bleaching chemicals were commercial products and the charges given on the basis of o.d. pulp. After the required retention time, the spent bleach liquor was separated from the pulp by filtration in a Buchner funnel. The bleached pulp was washed and acidified to about pH 5 by sodium metabisulfite prior to preparation of brightness pads.

Testing and analysis
The brightness values were recorded in a Technibrite Micro TB-1C instrument. The physical properties were measured following the TAPPI standard methods. The pulp yields were calculated from gravimetric measurements using pulp consistency and total weight before and after bleaching.

The carboxylic acid group content was determined according to Katz et al [10].

The amounts of dissolved organic substances were determined as total organic carbon (TOC) on a Dorhman DC-80 TOC analyzer. The inorganic carbon was determined by the reaction with nitric acid to produce CO₂, that was detected by an IR detector. The total carbon analysis was performed by combustion of the sample at 800°C in an atmosphere of oxygen and detection of the CO₂ liberated. The TOC content of the sample was calculated from the difference between the total carbon value and the inorganic carbon content.

The charge density (cationic demand) of the spent bleach liquors was determined by polyelectrolyte titration on a Mutek PCD 03 charge analyzer. This technique involved the use of a cationic titrant, polydiallyldimethylammonium chloride (p-DADMAC, av. Mw ca 100,000-200,000, Aldrich).

The Raman absorbances of the samples pre-filtered with a 0.45 micron filter were measured on a Chromex 2000 Raman Spectrometer. The excited laser was 785nm diode laser. The power at sample was 180mw and the integration time was 120 seconds. The standard 10mm quartz cuvette from Hellma was used as the liquid sample cell.

RESULTS AND DISCUSSION
The pulp was bleached to different brightness levels by applying various amounts of hydrogen peroxide and caustic. Pulp components released from fibers by peroxide bleaching, which have a broad molecular mass distribution ranging from simple molecules to polymers, become dissolved and colloidal substances (DCS) in bleach plant filtrates and are subsequently accumulated in mill process water system. The anionic (virtually carboxylic acid-bearing) portion of the DCS is mainly composed of acetic acid from deacetylation of hemicelluloses, acidic hemicelluloses, lipophilic extractives and acidic lignin degradation products. The anionicity of bleaching filtrates can be determined by polyelectrolyte titration using a cationic polymer and the measurement is defined as charge density or cationic demand.

As shown in Fig. 1, brightness development always accompanied pulp yield loss. Accordingly, the amount of dissolved organic substances was proportional to the magnitude of brightness increase. Unlike a linear relationship between yield and TOC, the amount of accumulated anionic substances increased with the yield loss in an exponential manner, as
shown in Fig. 2. This is because the cationic demand is a direct measurement of the level of anionic charge, but not the quantity, of dissolved organic substances. The equivalent magnitude of yield loss occurring in the initial portion of brightness increase produced less anionicity than that in the final portion of brightness increase. This result suggests that the latter phase of bleaching is far more intensive and produces more carboxylic acids. Figure 1 shows that the formation of anionic substances was accelerated from a brightness of about 80 ISO.

The Raman absorption at 925 cm\(^{-1}\) is assigned to carboxylic compounds. Not surprisingly, Fig. 3 shows a strong correlation between the Raman absorption intensity and the cationic demand of the bleaching pressates. In other words, these two measurements are interchangeable; either of them can be used for quantifying the anionic (carboxylic) dissolved substances in bleaching pressates.

Figure 4 shows that, given an alkali charge, increasing the peroxide charge had little effect on the dissolution of organic substances. The slightly reduced anionicity in this case was likely due to the fact that increasing the peroxide charge lowered the bleach liquor pH thus decreasing the rate of alkaline hydrolysis. On the other hand, at a given peroxide charge, the amount of both total dissolved organic substances and anionic materials was considerably increased with the caustic charge. This result confirms that alkalinity is the most important parameter influencing pulp yield and pulp mechanical properties in the alkaline peroxide bleaching of aspen mechanical pulps. The observation also provides evidence that alkali-induced hydrolysis and solubilization of fiber substances are more important contributions to the dissolution of pulp components.

Peroxide bleaching is a complex process that simultaneously brightens and strengthens pulps. In general, the bleaching improves the fiber-to-fiber bonding property of pulp, consequently leading to

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**FIG. 4.** Effects of \(H_2O_2\) and \(NaOH\) dosages on TOC and cationic demand.

**FIG. 5.** Correlation of TOC and cationic demand to formation of carboxylic acid groups on fibers.
enhanced strength. The improvement in fiber-to-fiber bonding property is the outcome of a number of chemical and morphological changes on the fibers. While the contribution of specific chemical changes to the strengthening is not well established, it appears that the dissolution of certain pulp components in bleaching plays an important role in enhancing the pulp bonding property. The removal of hydrophobic substances, such as lignin and extractives, rendered the fibers more hydrophilic, thereby improving the bonding property. From this standpoint, the dissolution of pulp components to some extent is beneficial to strength development. This conclusion can be validated by the observation that the physical properties are predominately determined by the alkalinity, but little influenced by the peroxide charge, because the former parameter plays a key role in influencing the dissolution of organic substances.

On the other hand, another significant contribution to the enhancement of fiber bonding property is the introduction of carboxylic acid groups onto fibers by bleaching. It is well documented that the concentration of carboxylic acid groups, particularly on fiber surfaces, has a strong influence on fiber-to-fiber bonding properties [5,6]. Alkaline hydrolysis of hemicelluloses and other pulp components is an important source of carboxylic acid formation [4,7] and is virtually an alkaline-catalyzed cleavage of ester linkages, for instance, formation of new uronic acid groups on hemicelluloses and pectin as well as saponification of the steryl ester portion of extractives. Moieties split from the fibers go into the water phase in bleaching, become dissolved organic substances and result in pulp yield loss. The contribution of alkaline hydrolysis to the formation of carboxylic acid groups is evidenced by its relationship with the yield loss and the importance of the effect of alkalinity in bleaching. We have observed that the formation of carboxylic acid groups was increased as a function of caustic charge and little affected by peroxide charge. Moreover, weaker alkalis, such as magnesium hydroxide and sodium carbonate, in bleaching dissolve pulp components and produce carboxylic acid groups to a smaller extent than sodium hydroxide.
Figures 5-7 present the changes in fiber bonding properties as a function of TOC or cationic demand. Pulp carboxylic acid group content, bulk and tensile index reflect the degree of bonding improvement resulting from bleaching from different angles. These three measurements are all relevant to fiber bonding properties and have a close interrelationship: formation of carboxylic acid groups improves bonding; better bonding leads to decreased bulk and increased tensile. From Figs. 5-7, we can see that the pulp carboxylic acid group content, bulk and tensile index have exponential relationships with the total dissolved organic substances and linear relationships with the amount of carboxylic materials in the pressates. It appears that the bleaching coincidentally generated carboxylic acid groups on both fibers and dissolved materials. This observation suggests that the amount of carboxylic acid in liquor is proportional to that on fibers. This linear correlation would allow the estimation of pulp bulk and tensile by measuring the charge density of bleaching pressates. However, such a first order interrelationship was not observed between TOC and bonding properties. This is not surprising because equivalent amounts of dissolved organic materials (TOC) from different brightness levels during bleaching contain different charge densities. In general, materials dissolved in the later portion of brightness increase undergo more intensive reactions and, thus, contain more carboxylic acid groups than those from the earlier portion.

Upon successful completion of the laboratory study, we decided to move to mills to test our methodology. An Albertan BCTMP mill is seriously considering installing an on-line cationic demand measurement for monitoring bleaching performance and pulp quality. As shown earlier, the cationic demand measurement and the Raman absorption at 925 cm⁻¹ give identical results. As a detective instrument, Raman spectroscopy offers more benefits over a charge density analyzer for peroxide bleaching because the former not only measures carboxylic substances but also measures hydrogen peroxide and other species in bleach liquors. Therefore, we conducted a preliminary investigation into implementing the Raman method in the mill. This stage of the investigation was to assess sampling and measuring points in the mill. Table I gives some relevant data.

The mill is operating two-stage peroxide bleaching for all their pulp grades. As the second stage (P2) performs most of the bleaching (brightness gain), we chose P2 for this study. Table I indicates that the Raman absorption intensity is more than double in Line 2 than in Line 1. This is because the aspen pulp gives greater amounts of dissolved hemicelluloses, the major source of carboxylic substances released by peroxide bleaching. This preliminary result gives us confidence in the Raman method as a new instrumentation for peroxide bleaching. As limited numbers of pulp samples for physical property measurements were collected in this mill trip, it is impossible to plot a correlation curve between the Raman measurements and the pulp properties. Further validation work is to be conducted in the mill in the near future, which requires more frequent sampling/testing of both liquor and pulp samples.

### CONCLUSIONS

The present investigation has revealed a strong correlation of bleaching pressates’ TOC and cationic demand with pulp yield and bonding properties. The TOC measurement appears to have a first order linear relationship with yield loss and a second order linear relationship with pulp carboxylic acid group content, bulk and tensile. By contrast, the cationic demand measurement is shown to have a first order linear relationship with pulp carboxylic acid group content, bulk and tensile. In general, either of these liquor sample analyzing techniques can be used for predicting pulp yield and quality, which is alternative to traditional methods involving either gravimetric measurement or tedious handsheet testing. On the other hand, Raman spectroscopy can be a versatile instrumentation method for the peroxide bleaching process; it is capable of providing information about cationic dissolved substances, consistent to those measured by cationic demand, as well as about bleach chemical consumption.

The interrelationships established in this investigation cannot be universal and should be wood species-dependent especially for TOC. TOC only measures the total quantity of dissolved organic substances and does not differentiate between them: lignin, hemicelluloses and extractives. However, their dissolution may have impacts on pulp properties to varying extent.

The ultimate goal of our project would be using on-line measurement of dissolved materials to deliver quick, real-time prediction of pulp quality at the exit of the bleach plant. Further development work is needed toward that direction.

### LITERATURE


**Résumé:** Il est généralement reconnu que le blanchiment au perox- yde alcalin entraîne une perte de rendement de la pâte et contribue de façon importante à l’accroissement de la cohésion entre les fibres, ce qui permet d’améliorer la résistance de la pâte. Des études antérieures ont démontré que la perte de rendement est un facteur clé ayant une inci- dence considérable sur la qualité de la pâte, par exemple les propriétés de cohésion des fibres. La présente étude a indiqué que la quantité et la nature des matières dissoutes lors du blanchiment sont étroitement cor- relation avec les propriétés des pâtes obtenues. Ces résultats indiquent qu’il faut utiliser une méthode de mesure des matières dissoutes dans le pressat (ou le filtrat) du blanchiment pour surveiller la qualité de la pâte.

**Reference:**


**Keywords:** POPULUS, MECHANICAL PULPS, PEROXIDE BLEACHING, ALKALI TREATMENT, PULP PROPERTIES, BLEACHING EFFLUENTS, FIL- TRATES, DISSOLVED SOLIDS, ORGANIC COMPOUNDS

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**TABLE I. Mill data and measurement of Raman peak intensity at 925 cm⁻¹ of samples obtained from 2nd stage perox- ide bleach (P₂) in an Albertan BCTMP mill in August 2001.**

<table>
<thead>
<tr>
<th>Brightness (ISO)</th>
<th>Freeness (CSF)</th>
<th>Bulk (cm³/g)</th>
<th>Breaking length (km)</th>
<th>Raman absorption intensity at 925 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>78.9 - 79.7</td>
<td>608 - 658</td>
<td>3.22 - 3.44</td>
<td>3.09 - 3.49</td>
<td>330 - 812</td>
</tr>
<tr>
<td>78.9 - 79.4</td>
<td>400 - 410</td>
<td>2.83 - 2.85</td>
<td>1.49 - 1.64</td>
<td>328 - 706</td>
</tr>
</tbody>
</table>

**Line 1** | **Line 2**
---|---
**P₂ out** | **P₂ Pressate**
---|---
330 | 812
328 | 706