ANNUAL PROGRAM REVIEW

CHEMICAL PULPING AND BLEACHING

Volume 1

March 23-24, 1999

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DUES-FUNDED PROJECT SUMMARY  
FY 1998-99

Project Title: Chemical Fundamentals of Bleaching  
Project Number: F015  
PAC: Chemical Pulping and Bleaching  
Division: Chemical and Biological Sciences  

Project Staff  
Faculty/Senior Staff: Arthur J. Ragauskas, Lucian A. Lucia, Lenong Allison, Ki-Oh Hwang  
Staff:  
FY 97-98 Budget: $270,000  
Allocated as Matching Funds: N/A  

Time Allocation  
Faculty/Senior Staff: 80%  
Support: 150%  

Supporting Research  
Ph.D. Students: F.S. Chakar and M. Zawadzki  

RESEARCH LINE/ROADMAP:  

Environmental Performance:  
• Reduce emissions of entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule while maintaining global competitiveness.  
• Reduce water usage in bleached kraft pulp production to 2,500 gallons per ton.  

Improved Forest Productivity:  
• Increase the yield of kraft-pulp equivalent fiber by 10%.  

PROJECT OBJECTIVE:  

Provide a fundamental understanding of the physical and chemical reactions that control lignin and carbohydrate degradation during new bleaching sequences. Understand the reasons for selectivity of reactions that occur in selected pulping and bleaching sequences. The research compliments Project F013 research on bleach process technology. Focus areas for this fiscal year are hexenuronic acids, biobleaching, high efficiency peroxide bleaching, oxalic acid formation, and oxygen delignification.
PROJECT BACKGROUND:

Influence of Hexenuronic Acids on Bleaching

The effects of temperature and acid conditions needed to optimize the removal of hexenuronic acid (HexA) were determined. Metal binding studies demonstrated that hexenuronic acids are one of the main components involved in binding non-process elements to kraft pulp fibers. The removal of HexA was shown to significantly improve pulp bleachability of hardwood kraft pulps. Polysulfide kraft cooking showed little influence on the formation of hexenuronic acids, whereas AQ kraft cooks appeared to favor their formation. Preliminary investigations suggested that the effective alkali concentration during pulping influences the formation of hexenuronic acids.

High Efficiency Peroxide Bleaching

Spectroscopic lignin studies of D(EPO) and DE bleached kraft pulps illustrated that condensed phenolic groups are resistant to a Dₗ stage. Residual lignin and peroxide bleaching studies of methylated pulps suggest that alkaline peroxide is more effective at chromophore removal than delignification.

Oxalic Acid Process Chemistry

The insolubility of calcium oxalate in bleach process streams can lead to costly maintenance programs. Although some oxalate originates from woodchips the bulk is generated during bleaching. Literature results suggest that the levels of oxalic acid generated during bleaching can be controlled by process parameters. This new project has begun to explore mill specific properties that influence the level of oxalic acid generated during bleaching.

Biobleaching Studies

New mediators were studied for the laccase/mediator delignification system. For a softwood oxygen delignified kraft pulp, the new mediators allowed for >50% delignification with less than 3% of the typical enzyme charge. Preliminary studies have demonstrated that the laccase/mediator systems are effective for the delignification of high-kappa kraft pulps.

Oxygen Delignification Fundamentals

Singlet oxygen is an electrophilic species with a very high oxidation potential in solution. Its role in oxygen delignification schemes has not been adequately investigated nor understood. It was the purpose of the present investigation to provide insight into its bleaching action on pulps. Initial investigations into the role of singlet oxygen revealed that it is a potent delignifying agent.
that also demonstrates a remarkable capacity to brighten kraft pulps. It can be generated both photochemically and chemically, and is known to react during both oxygen delignification and hydrogen peroxide bleaching.

**SUMMARY OF FY 1998-99 RESULTS:**

**Influence of Hexenuronic Acids on Bleaching**

Research efforts in HexA were focused on exploring the effects of alternative acids at removing HexA and the impact of HexA removal on chlorine dioxide bleachability. The hydrolysis of HexA from an industrial hardwood kraft pulp was examined with five different acids including, formic acid/potassium formate, nitric acid, phosphoric acid, p-toluenesulfonic acid, and the acidic effluent from a D₀ stage. Each of these reagents were reacted with the same hardwood kraft pulp using an initial pH of 3.0 for reaction times of 1, 2, and 5 h at 80°, 90°, and 95°C. The decrease in apparent kappa number varied from 14 – 38% depending on the reaction conditions and acid used. The D₀ effluents were shown to be almost as effective as acid treatment. The effects of using a D₀ effluent as an acid source were confirmed using a series of commercial HW kraft pulps and D₀ effluents. The hot acid treatment was shown to operate independent of consistency effects in the range of 2–10% consistency.

The effects of removing HexA on yield were also examined. Our yield measurements for the hot acid treatment of HW kraft pulps continues to range between 98.0 – 98.4%. Research efforts directed at examining the effects of HexA removal on ECF bleachability employed a pre- and post oxygen delignified industrial hardwood kraft pulp, the pre-O₂ pulp was bleached with DEDED and ADEDED sequence and the post-O₂ pulp was treated with a DED and ADED sequence using a 0.20 k.f. Final brightness values of the HexA free pulps were virtually the same as the control pulps but the former pulps consumed approximately 50% less chlorine dioxide.

**Oxalic Acid Process Chemistry**

Our initial goal in this project was to develop an accurate, reproducible method of measuring oxalic acid content in bleach effluents. With the assistance of the IPST analytical group an oxalic acid analysis procedure was developed that provided satisfactory results using Capillary Ion Electrophoresis. Heat treatment of laboratory D₀ SW kraft pulp effluents increased the amounts of oxalic acid by a factor of 2 whereas for industrial D₀ HW kraft effluents the oxalic acid content increased by approximately 25% or less.

**High Efficiency Peroxide Bleaching**

The bleaching chemistry of an EPO stage was studied by comparing its efficiency against an E and EO stage using a D₀ bleached SW kraft pulp. The effects of alkaline extraction were

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examined at 70°, 80°, and 90°C as a function of time (0.15 – 2 h). All extraction studies indicated that the bulk (> 80%) of the delignification process occurs within the first 15 minutes of an E* stage. The use of peroxide in an EPO stage appears to be principally directed towards brightening chemistry and not towards delignification. Additional studies directed towards evaluating the molecular weight distributions of E* effluents are underway and will be reported in the near future.

**Biobleaching Studies**

Biobleaching studies continue to explore the use of violuric acid as a mediator for laccase catalyzed delignification of kraft pulps. The use of the laccase-violuric acid system on a hardwood kraft pulp was shown to yield a 42% reduction in kappa number after an alkaline extraction stage. The yield after the (LMS)E treatment was determined to be 99.6%.

The sensitivity of the LMS treatment to NPEs was explored by adding metal sulfates to the pulp. These results suggest that the LMS system is sensitive to Cu²⁺, Ni²⁺, and Fe²⁺. Interestingly, the presence of Mn²⁺ or Mg²⁺ was shown not to influence the LMS delignification of kraft pulps.

**Oxygen Delignification Fundamentals**

Currently, research efforts in our sub-objective have been directed toward the study of the pulp reactions of singlet oxygen, a highly reactive and short-lived species of oxygen that is present in oxygen delignification of pulps. Interestingly, very few research efforts have been initiated to determine its effect on pulps during oxygen delignification. Our work has shown that both the photochemical and chemical production of singlet oxygen can induce significant delignification and concomitant brightening of both pre- and post-O₂ kraft softwood pulp, albeit to different extents.

Very remarkably, we were able to substantially delignify pre-O₂ softwood pulps with > 95% visible light (5750 Å) and a small amount of catalyst (0.5% odw). All singlet oxygen runs were done in a quartz round bottom flask containing pulp, which was vigorously stirred and cooled by a fan. The efficiency of delignification for an irradiated softwood kraft pulp containing catalyst is approximately 70%. Control experiments successfully showed that isolated variables of temperature, light, or catalyst do not contribute significantly to delignification.

Chemical singlet oxygen work proved to also be successful, but was limited by the transport of active species to lignin sites. NMR analysis of singlet oxygen treated isolated lignin under homogeneous conditions showed an increase in oxidation sites. Interestingly, the degree of brightening was much more substantial than typically demonstrated by the kappa drop. Viscosity measurements of the pulps suggested that the pulps did not suffer carbohydrate damage (potentially not incurring much yield loss).

Our studies were directed to the economic profitability of the singlet oxygen technique. We performed an intensive singlet oxygen run (high concentration of active species) to determine if we...
could obtain significant delignification and brightness gains in a much shorter period of time than our original studies. The results were very positive, but the major limitation to the economic profitability of the work is the cost of the catalyst.

The rest of our studies focused on comparing the factors involved in singlet oxygen and traditional oxygen delignification technologies. We compared the UV/VIS spectra of the effluent from singlet and traditional oxygen runs, explored the effect of traditional magnesium sulfate protectors, and obtained molecular weights of oxygen delignification effluents to understand the chemistry of the processes. Our intention is to determine how to improve the standard oxygen process operating in mills. We began to investigate the influence of radicals generated in singlet oxygen work and standard oxygen work and concluded that their action must be manipulated to obtain the maximum benefits. We are continuing to explore the importance of radicals in our work with the intention of enhancing delignification while maintaining pulp yields.

DELIVERABLES FOR FY 98-99:

The goals for the remaining three months of 1998-99 are summarized below:

1. Determine the molecular weight distributions of E, EO and EPO effluents from D₀ SW kraft pulp as a function of bleaching time and temperature.
2. Evaluate the effects of varying kappa number and D₀ k.f. on levels of oxalic acid generated during a D₀ stage.
3. Determine the value of magnesium sulfate in oxygen delignification.
4. Explore the effect of controlling the action of radicals in oxygen delignification by employing radical protecting agents.
F015.1 Influence of Hexenuronic Acids (HexA) on Bleaching
by Art J. Ragauskas

BACKGROUND

Hexenuronic acids are unsaturated carbohydrate acids that are formed by base-catalyzed elimination of methanol from 4-O-methyl-D-glucuronoxylans, as shown in Figure 1.1. Research by Clayton (Svensk Papperstidning, Feb., p. 115, 1963) suggested that hexenuronic acids could be formed from hemicelluloses under pulping conditions.

Simulated soda pulping studies with 4-O-methyl-D-glucuronoxylans, isolated from birch, poplar, and elm, demonstrated that this xylan derivative was unstable under these conditions. The investigators noted that the xylan recovered from the alkali cooks was deficient in methoxy and 4-O-methyl-D-glucuronic acids, as summarized in Figure 1.2.
Figure 1.2. Loss of methoxy and glucuronic acid during an alkaline cook at 170°C for white birch 4-O-methylglucuronoxylan.

They, furthermore, suggested that base-catalyzed formation of hexenuronic acids from 4-O-methyl-D-glucuronoxylan could readily explain the experimental observations.


Studies by Vuorinen et al. (Conf. Proceedings from 1996 Int. Pulp Bleach. Conf., 1, p 43, 1996) and Buchert et al. (Tappi J., 78, p 125, 1995) further explored the chemistry of hexenuronic acids in kraft pulps. It was demonstrated that in birch kraft pulps hexenuronic acids contributed up to 50% of the kappa number of a northern Scandinavian kraft pulp and consumed electrophilic bleaching chemicals, such as chlorine dioxide and ozone. Hence, hexenuronic acids play a pivotal role in the bleaching of hardwood kraft pulps. Based on these considerations, the 1996 Spring PAC elected to examine the chemistry of hexenuronic acids in Project F015. Subsequent studies at IPST demonstrated that 35–55% of the kappa number of commercial southern hardwood kraft pulps could be attributed to HexA.

SUMMARY OF PAST RESULTS

FY 1997-98 research efforts established the optimal temperature and pH range for acid catalyzed removal of HexAs. Pulp yield determination for the acid-catalyzed removal of hexenuronic acids
was found to be at least 98.6%, suggesting that the removal of HexAs from HW kraft pulps can be achieved without significant loss of fiber. Preliminary analysis of fiber properties suggested that the hot acid treatment of HW kraft pulp fibers improved intrinsic fiber properties but lowered burst and tensile sheet properties.

HexAs were also found to be a dominant factor controlling the retention of nonprocess elements (NPE) for hardwood kraft pulps. A hot acid treatment of HW kraft pulp fibers (i.e., pH ≈3, 95°-99°C for 1-3 h) not only resulted in the removal of NPEs from the pulp, but also removed the HexAs from the fiber, thereby removing the metal binding sites from HW kraft pulps.

HexA analysis of HW AQ kraft pulps demonstrated that the use of AQ in pulping yields a pulp that is enriched in HexAs. In contrast, the use of polysulfide (PS) during pulping does not impact the formation of HexAs for HW kraft pulps. The combination of AQ-PS in pulping yields HW kraft pulps enriched in HexAs due to the presence of AQ during pulping.

RESEARCH GOALS

FY 1998-99 goals for this section of F015 are listed below:

1. Examine the effect of alternative acidic treatments to remove HexA.
2. Determine the effects of HexA removal on yield and pulp bleachability.
3. Evaluate the effect of consistency on HexA removal for a HW kraft pulp.
4. Study the effects of using a D_0 effluent to remove HexA from HW kraft pulps.

FY 1998-99 RESULTS

Goal 1: Effect of Alternative Acid Treatment

The role of the conjugate base on the overall acid hydrolysis procedure, was examined by performing the hot acid treatment of a hardwood kraft pulp using formic acid, nitric acid, phosphoric acid, and p-toluenesulfonic acid. For each acid, a 3% consistency hardwood kraft pulp was pH adjusted to 3.0 and heated to either 80°, 90°, or 95°C for periods of 1, 2, and 5 h. In addition, a 3% csc HW kraft pulp was acidified to pH 2.2 using a D_0 effluent. This pulp was reacted for 5 h at temperatures of 80°, 90°, or 95°C. In each case, the acid treated pulps were then washed with water and analyzed for kappa and viscosity. The results of these studies are summarized in Table 1.1.
Table 1.1: Results of treating a commercial HW kraft pulp with an acidic aqueous solution.

<table>
<thead>
<tr>
<th>Acid Treatment (initial pH) – Bleaching Temperature(C)</th>
<th>Initial Kappa #: 13.5 Initial Viscosity: 28.7 cP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pulp Properties After Acid Treatment</td>
</tr>
<tr>
<td></td>
<td>1 h</td>
</tr>
<tr>
<td>Formic Acid/Sodium Formate (3) 80°</td>
<td></td>
</tr>
<tr>
<td>90°</td>
<td>12.8</td>
</tr>
<tr>
<td>95°</td>
<td>11.2</td>
</tr>
<tr>
<td>Nitric Acid (3)</td>
<td></td>
</tr>
<tr>
<td>80°</td>
<td>12.0</td>
</tr>
<tr>
<td>90°</td>
<td>10.9</td>
</tr>
<tr>
<td>95°</td>
<td>10.5</td>
</tr>
<tr>
<td>Phosphoric Acid (3)</td>
<td></td>
</tr>
<tr>
<td>80°</td>
<td>12.6</td>
</tr>
<tr>
<td>90°</td>
<td>11.8</td>
</tr>
<tr>
<td>95°</td>
<td>11.2</td>
</tr>
<tr>
<td>p-toluenesulfonic acid (3)</td>
<td></td>
</tr>
<tr>
<td>80°</td>
<td>12.5</td>
</tr>
<tr>
<td>90°</td>
<td>12.0</td>
</tr>
<tr>
<td>95°</td>
<td>10.6</td>
</tr>
<tr>
<td>Do (2)</td>
<td></td>
</tr>
<tr>
<td>80°</td>
<td>-</td>
</tr>
<tr>
<td>90°</td>
<td>-</td>
</tr>
<tr>
<td>95°</td>
<td>-</td>
</tr>
</tbody>
</table>

The results of this investigation demonstrated that the removal of hexenuronic acids from a HW kraft was virtually independent of the acid source. The three key parameters controlling the efficiency of hexenuronic acid removal are the pH of the solution, reaction time and reaction temperature. Based on these results, it is obvious that the use of D_0 effluents to remove hexenuronic acids is a viable, low-cost approach to controlling HexAs in hardwood kraft pulps.

Goal 2: Determine the effects of HexA removal on yield and pulp bleachability.

The effect of the hot acid treatment on pulp yields remains an issue of extreme concern. In the past fiscal year, we had noted experimental yields for treating HW kraft pulps with formic acid/sodium formate buffer (pH 3) at 100°C were usually in the range 98 – 98.6% (i.e., gravimetric yields: % mass pulp recovered/mass of starting pulp). We have continued to determine pulp yields for acid hydrolyzed HW kraft pulps employing either dilute sulfuric acid or D_0 effluents. The results of these studies are summarized in Table 1.2.
Table 1.2. Yield and changes in physical properties of HW kraft pulps treated with a hot acid stage.

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Kappa #</th>
<th>Viscosity/cP</th>
<th>Yield (% mass recovered)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Brownstock -initial</td>
<td>11.4</td>
<td>24.9</td>
<td>98.2 (performed on 30 gr scale)</td>
</tr>
<tr>
<td>- A¹</td>
<td>5.6</td>
<td>22.8</td>
<td>97.8 (performed on 100gr scale)</td>
</tr>
<tr>
<td>- A²</td>
<td>6.2</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>2. O – initial OA¹</td>
<td>8.5</td>
<td>21.8</td>
<td>98.1 (performed on 30 gr scale)</td>
</tr>
<tr>
<td>OA¹</td>
<td>2.8</td>
<td>19.9</td>
<td>98.1 (performed on 100gr scale)</td>
</tr>
<tr>
<td>OA²</td>
<td>3.7</td>
<td>--</td>
<td>98.1 (performed on 100gr scale)</td>
</tr>
<tr>
<td>3. HW Brown. – initial</td>
<td>14.1</td>
<td>29.6</td>
<td>98.4% (performed on 100gr scale)</td>
</tr>
<tr>
<td>- A¹</td>
<td>12.7</td>
<td>--</td>
<td>98.0% (performed on 100gr scale)</td>
</tr>
<tr>
<td>- A²</td>
<td>10.2</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

¹Pulp slurry was adjusted to pH 3 with 4N H₂SO₄, 2% CSC and refluxed for 3 h. ²Pulp was refluxed in D₀ effluent pH 2.8, 3% CSC and refluxed for 3 h.

Interestingly, the use of either sulfuric acid, formic acid/sodium formate, or D₀ effluent provided comparable yields for the hot acid treatments of HW kraft pulps.

The second goal of this subproject was to determine the effects of HexA removal on fully bleached kraft pulps. Two pulps were employed for this study, a pre- and post oxygen delignified HW kraft pulp (see entries 1 & 2 in Table 1.2). The HW kraft pulp was bleached with a DEDED sequence and the post-O₂ was bleached with a DED sequence. Experimental conditions and chemical charges employed are summarized in Table 1.3.

Table 1.3: Bleaching conditions employed to bleach pre- and post-O₂ delignified HW kraft pulps.

<table>
<thead>
<tr>
<th>DEDED and ADEDED</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Brownstock kappa #: 11.4</td>
<td>Brownstock kappa #: after acid hydrolysis: 5.6</td>
<td>A-stage: formic acid/sodium formate pH:3, 3 h.</td>
</tr>
<tr>
<td></td>
<td>D₀: 0.20 k.f. 3.5% CSC, 45 min., 50°C</td>
<td>D₁ Charge: 0.6%; Consistency: 10%; 3 h; 75°C</td>
</tr>
<tr>
<td></td>
<td>D₂ Charge: 0.1, 0.2, 0.4, 0.6%; Consistency: 10%; 3 h; 75°C</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DED and ADED</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Brownstock kappa #: 8.5</td>
<td>Brownstock kappa #: after acid hydrolysis: 2.8</td>
<td>A-stage: formic acid/sodium formate pH:3, 3 h.</td>
</tr>
<tr>
<td></td>
<td>D₀: 0.20 k.f. 3.5% CSC, 45 min., 50°C</td>
<td>D₁ Charge: 0.1, 0.2, 0.4, 0.6%; Consistency: 10%; 3 h; 75°C</td>
</tr>
</tbody>
</table>
The changes in TAPPI brightness and viscosity were followed throughout the bleaching sequences and these data are summarized in Figures 1.3 – 1.4 and Table 1.4.

Figure 1.3: Changes in TAPPI brightness for HW kraft pulp bleached DEDED and ADEDED.
The results of the ECF bleaching studies indicate that acid hydrolyzed kraft pulps yield final brightness properties comparable to the unhydrolyzed kraft pulps. Nonetheless, there is approximately a 50% savings in chemical bleaching agent for the A-stage treated pulps.

As has been previously observed, there is a slight decrease in viscosity after the hot acid treatment of kraft pulps and this was observed again for the pre and post-O2 delignified kraft pulps, as summarized in Table 1.4. The differences in viscosity values do narrow as the pulps are bleached to full brightness but nonetheless the fully bleached A-treated pulps exhibit slightly reduced viscosity values.
Table 1.4: Changes in viscosity for HW kraft pulps bleached DEDED, ADEDED, ODED, and AODED.

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Viscosity/cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brownstock</td>
<td>24.0</td>
</tr>
<tr>
<td>Brownstock(A)</td>
<td>18.7</td>
</tr>
<tr>
<td>DEDED</td>
<td></td>
</tr>
<tr>
<td>D2: 0.1% charge</td>
<td>23.1</td>
</tr>
<tr>
<td>D2: 0.2%</td>
<td>21.6</td>
</tr>
<tr>
<td>D2: 0.4%</td>
<td>21.8</td>
</tr>
<tr>
<td>D2: 0.6%</td>
<td>19.7</td>
</tr>
<tr>
<td>ADEDED</td>
<td></td>
</tr>
<tr>
<td>D2: 0.1%</td>
<td>19.3</td>
</tr>
<tr>
<td>D2: 0.2%</td>
<td>19.0</td>
</tr>
<tr>
<td>D2: 0.4%</td>
<td>18.9</td>
</tr>
<tr>
<td>D2: 0.6%</td>
<td>17.3</td>
</tr>
<tr>
<td>O</td>
<td>21.8</td>
</tr>
<tr>
<td>OA</td>
<td>19.9</td>
</tr>
<tr>
<td>ODED</td>
<td></td>
</tr>
<tr>
<td>D1: 0.1%</td>
<td>21.4</td>
</tr>
<tr>
<td>D1: 0.2%</td>
<td>20.4</td>
</tr>
<tr>
<td>D1: 0.4%</td>
<td>20.4</td>
</tr>
<tr>
<td>D1: 0.6%</td>
<td>19.7</td>
</tr>
<tr>
<td>OADED</td>
<td></td>
</tr>
<tr>
<td>D1: 0.1%</td>
<td>16.1</td>
</tr>
<tr>
<td>D1: 0.2%</td>
<td>16.2</td>
</tr>
<tr>
<td>D1: 0.4%</td>
<td>15.8</td>
</tr>
<tr>
<td>D1: 0.6%</td>
<td>15.2</td>
</tr>
</tbody>
</table>
Goal 3: Evaluate the effect of consistency (csc: 2 and 10%) on HexA removal for a HW kraft pulp.

Previous IPST research studies into the removal of HexAs from kraft pulps were performed at low consistency (ca 2–3%). The effects of consistency on the acid catalyzed removal of HexAs were studied this past fiscal year. Three commercial HW kraft pulps were employed for these studies. In each case, the pulps were exhaustively washed, diluted with water, and adjusted to pH 3 with 4 N H₂SO₄. The three pulps were acid hydrolyzed at 2 and 10% consistency. The acid treated pulps were analyzed for kappa number, Klason lignin, and viscosity. In addition, selected acid hydrolysis effluents were characterized for color and COD. The results of these investigations are summarized in Table 1.5.

Table 1.5: Physical properties of HW kraft pulps and effluents treated with an aqueous pH 3 (dilute H₂SO₄) solution at 2 and 10% consistency at 100°C.

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Kappa #</th>
<th>Viscosity/cP</th>
<th>Klason Lignin</th>
<th>Color¹</th>
<th>COD²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp 1 Brownstock</td>
<td>14.1</td>
<td>29.6</td>
<td>2.10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H⁺ 1 h medium csc</td>
<td>11.5</td>
<td>27.9</td>
<td>1.76</td>
<td>-</td>
<td>620</td>
</tr>
<tr>
<td>H⁺ 2 h medium csc</td>
<td>10.5</td>
<td>26.8</td>
<td>1.75</td>
<td>-</td>
<td>950</td>
</tr>
<tr>
<td>H⁺ 5 h medium csc</td>
<td>8.1</td>
<td>26.1</td>
<td>1.47</td>
<td>-</td>
<td>1200</td>
</tr>
<tr>
<td>H⁺ 5 h low csc</td>
<td>9.1</td>
<td>29.4</td>
<td>1.28</td>
<td>170</td>
<td>270</td>
</tr>
<tr>
<td>Pulp 2 Brownstock</td>
<td>11.6</td>
<td>24.9</td>
<td>1.63</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H⁺ 1 h medium csc</td>
<td>8.0</td>
<td>22.5</td>
<td>0.76</td>
<td>-</td>
<td>1000</td>
</tr>
<tr>
<td>H⁺ 2 h medium csc</td>
<td>6.7</td>
<td>--</td>
<td>--</td>
<td>-</td>
<td>1300</td>
</tr>
<tr>
<td>H⁺ 5 h medium csc</td>
<td>5.5</td>
<td>19.3</td>
<td>1.18</td>
<td>-</td>
<td>1600</td>
</tr>
<tr>
<td>H⁺ 5 h low csc</td>
<td>5.2</td>
<td>19.2</td>
<td>0.98</td>
<td>120</td>
<td>430</td>
</tr>
<tr>
<td>Pulp 3 Brownstock</td>
<td>14.2</td>
<td>36.6</td>
<td>1.63</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H⁺ 1 h medium csc</td>
<td>10.5</td>
<td>35.6</td>
<td>1.62</td>
<td>-</td>
<td>1200</td>
</tr>
<tr>
<td>H⁺ 2 h medium csc</td>
<td>9.8</td>
<td>33.7</td>
<td>1.41</td>
<td>-</td>
<td>1400</td>
</tr>
<tr>
<td>H⁺ 5 h medium csc</td>
<td>8.0</td>
<td>32.9</td>
<td>1.42</td>
<td>-</td>
<td>1500</td>
</tr>
<tr>
<td>H⁺ 5 h low csc</td>
<td>7.5</td>
<td>32.5</td>
<td>1.21</td>
<td>220</td>
<td>380</td>
</tr>
</tbody>
</table>

¹mg/l; ²PCU.

Several important conclusions can be drawn from the data presented in Table 1.5. The most significant conclusion is that for extended hot acid treatments (i.e. 5 h) the removal of HexA can be accomplished equally effectively with low and medium consistency pulp slurries. It is also important to note that the hot acid treatment resulted in reducing the amount of Klason lignin in the pulps and the reduction was proportionate to the reaction time. Clearly, this effect can not be attributed to the removal of HexA and this latter result suggests that a portion of the observed kappa reduction during a hot acid treatment is due to lignin removal in addition to the removal of HexAs.
The relative effectiveness of using $D_0$ effluents as an acid source for a hot acid treatment of hardwood kraft pulps was further examined employing a series of commercial HW kraft pulp and $D_0$ samples. Commercial pulps and $D_0$ mill effluents were provided to the PI from interested PAC members and, in each case, these pulps were exhaustively washed until the effluents were pH neutral and colorless. Table 1.6 provides a brief description of the pulps and effluents provided to the PI.

Table 1.6: Description of commercial HW kraft pulps and bleach effluents provided to PI.

<table>
<thead>
<tr>
<th>Mill</th>
<th>Pulp Sample: kappa number</th>
<th>First Stage Bleach Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Brownstock: 13.7</td>
<td>C/D pH: 2.5</td>
</tr>
<tr>
<td>B</td>
<td>Brownstock: 12.1</td>
<td>$D_0$ pH: 3.4</td>
</tr>
<tr>
<td>C</td>
<td>Pre O2: 11.3</td>
<td>$D_0$ pH: 2.8</td>
</tr>
<tr>
<td>D</td>
<td>Brownstock: 10.9</td>
<td>$D_0$ pH: 2.3</td>
</tr>
<tr>
<td>E</td>
<td>Brownstock: 9.8</td>
<td>$D_0$ pH: 2.3</td>
</tr>
<tr>
<td>F</td>
<td>Post O2: 8.9</td>
<td>$D_0$ pH: 2.6</td>
</tr>
<tr>
<td>G</td>
<td>Post O2: 7.8</td>
<td>Acid pressate pH: 2.6</td>
</tr>
</tbody>
</table>

The washed pulps were then treated with mill bleach effluents at 10% consistency for 2 and 5 hours at 99°C. As a control, all pulp samples were also treated with a dilute sulfuric acid solution (pH: 2.8) at 10% consistency for 2 and 5 hours at 99°C. The resulting pulps were analyzed for changes in kappa number, TAPPI brightness, and viscosity; these results are summarized in Figures 1.5 and 1.6 and Table 1.7.
Figure 1.5. Changes in kappa of HW kraft pulps heated to 99°C in dilute sulfuric acid (pH 2.8) and D₀ effluents for 2 and 5 h.
Figure 1.6. Changes in TAPPI brightness of HW kraft pulps heated to 99°C in dilute sulfuric acid (pH 2.8) and Do effluents for 2 and 5 h.

Table 1.7: Changes in pulp viscosity when heat-treated (99°C) with dilute sulfuric acid (pH 2.8) and Do effluents for 2 and 5 h.

<table>
<thead>
<tr>
<th>Pulp Sample</th>
<th>Pulp Viscosity Values/cP</th>
<th>Initial</th>
<th>2 h H2SO4</th>
<th>2h D0</th>
<th>5 h H2SO4</th>
<th>5 h D0</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>31.2</td>
<td>29.7</td>
<td>26.5</td>
<td>25.6</td>
<td>24.5</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>36.9</td>
<td>30.0</td>
<td>31.5</td>
<td>16.0</td>
<td>28.5</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>29.1</td>
<td>28.3</td>
<td>31.1</td>
<td>26.4</td>
<td>29.8</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>35.9</td>
<td>28.3</td>
<td>21.1</td>
<td>--</td>
<td>14.2</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>24.3</td>
<td>19.8</td>
<td>19.4</td>
<td>13.4</td>
<td>16.7</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>16.2</td>
<td>16.9</td>
<td>16.6</td>
<td>9.2</td>
<td>15.8</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>24.5</td>
<td>14.6</td>
<td>22.0</td>
<td>12.0</td>
<td>18.7</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>32.0</td>
<td>15.8</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

The results of the kappa number analysis indicate that all pulps undergo a reduction in kappa number when heated in either dilute sulfuric acid or first stage bleach effluent. In most cases, the use of a hot sulfuric acid treatment maximized the decrease in kappa number although the difference with the D0 hydrolyzed pulps was frequently less than 1.5 kappa number units. The

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sulfuric acid treatments, therefore, provide a measure of the maximum kappa number reduction for these hardwood pulps whereas the D₆ effluent treatments represent a more practical mill technology approach.

(Note: The use of 5 hours of hot sulfuric acid treatment is undoubtedly excessive and caused significant degradation of pulp viscosities, see Table 1.7. This reaction time was selected as a means for rapidly determining the HexA content of the mill pulps studied.)

Interestingly, almost all pulps exhibited a slight increase in brightness when treated with dilute acid at 99°C for 5 hours (see Fig. 1.6). This latter result suggests that the removal of HexA with a hot acid treatment will not detrimentally impact the optical properties of the pulp.

FUTURE RECOMMENDATIONS

Having established the important role of hexenuronic acids in controlling pulp bleachability of kraft pulps, the next set of goals for this component of F015 should include:
- The identification of optimal HW cooking parameters for HW kraft pulps;
- Characterization of the natural diversity of 4-O-methyl-D-glucuronoxylyans in US hardwood furnishes.

RESEARCH BENEFITS

The anticipated benefits of these studies include:
- Reduced bleaching costs;
- Simplified NPE control.
SUPPORTING LITERATURE

Additional background information on hexenuronic acids in pulp can be found in the following articles:


F015.2 Oxalic Acid Process Chemistry by Art J. Ragauskas

BACKGROUND

Calcium oxalate scaling is a difficult problem to control that can impair the performance of stock pipelines, washing filters, filtrate tanks, refiner plates, evaporators, and heat exchangers. The formation of these deposits is a result of relatively high concentrations of calcium oxalate in process equipment operating in the pH range of 2 – 8. The removal of this material is difficult and results in costly downtime. The goal of this subproject is to determine how process chemistry can be used to control the generation of oxalic acid.

The source of calcium oxalate in modern pulp bleaching operations is ultimately due to the wood. Calcium is introduced into the pulp mill principally from the wood, although some calcium may also be introduced into the process from the mill’s fresh water source. Most softwood and hardwood fiber sources also contain oxalic acid, both in the wood furnish and in the bark. Krasowski and Marton (J. Wood Chem. Technol. 3, no. 4: 445-458 (1983)) reported oxalic acid contents for HW and SW furnish and these results are summarized in Table 2.1.

Table 2.1. Oxalic acid content reported for North American SW and HW wood chips

<table>
<thead>
<tr>
<th></th>
<th>Bark/ (kg/ton)</th>
<th>Wood (kg/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HW</td>
<td>9 -15</td>
<td>0.1 - 0.3</td>
</tr>
<tr>
<td>SW - pine</td>
<td>4 -10</td>
<td>0.1 - 0.4</td>
</tr>
</tbody>
</table>

After kraft pulping operations, the typical concentration of oxalic acid present in SW brownstock typically is 0.1–0.7 kg/ton o.d. pulp. Most of this oxalic acid is from the native wood, although some may be also formed from the degradation of carbohydrates during pulping. Subsequent kraft bleaching operations significantly increase the amounts of oxalic acid present in bleaching liquors.

Depending upon the bleaching technologies employed, Ulmgren and Radestrom (1997 Minimum Effluent Mills Symposium: TAPPI Conf. Proceedings San Francisco, CA: 51-62 (October 23, 1997) have reported that open bleach mills can have oxalate concentration levels of 4 x 10^-2 to 9 x 10^-2 g/L. Clearly, as reduced effluent programs are implemented in modern mill operations, the levels of oxalate will increase. The exact conditions under which calcium oxalate is deposited on operating equipment is dependent upon several parameters, including pH, nature of bleach effluent, and temperature. The typical pH range under which calcium oxalate deposits occur is between 2 and 8. This can be readily attributed to the fact that oxalic acid is a diacid (see Eq. 1) with $pK_a$ values of 1.0 and 3.7 (at 25°C, ionic strength 0.1 mol/L).
Equation 1

\[
\begin{align*}
\text{HO} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{HO} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

oxalic acid

In pure water the solubility of calcium oxalate is approximately \(2 \times 10^{-9} \) M but this is significantly modified by the process streams of a kraft bleaching mill. Recent studies at IPST, STFi, and Paprican are directed at developing computational models that will be able to predict the operational conditions that will lead to calcium oxalate deposition. **The goal of this project is to examine the fundamental chemistry of oxalic acid generation during the bleaching process so as to minimize its formation.**

The generation of oxalic acid (OxA) during bleaching has not been fully explored. Certainly, it is well known that both chlorine dioxide (see Fig. 2.1) and ozone generate OxA during bleaching but the relative amounts generated, rates, and sensitivity to process conditions are not known. A recent M.Sc. thesis by Freiholtz (KTH, Stockholm 1996, Studier av oxalsyrbildning under blekning av sulfatmassa) has shown that ozone generates the highest amount of oxalic acid/unit oxidative charge when applied to a kraft black liquor lignin and compared against chlorine dioxide and peroxide.

Figure 2.1. Oxidative pathway contributing to the formation of oxalic acid during bleaching.

This thesis also suggested that the bulk of the oxalic acid formed during bleaching could be attributed to oxidative reactions with lignin and not with hexenuronic acid.

Elsander et al. (1997 TAPPI Minimum Effluent Mills Symposium: Proceedings, San Francisco, CA: 63-66) have reported that the amounts of oxalic acid generated in the initial stage of bleaching increase as the degree of delignification achieved in the first stage of bleaching is extended. Based on **very limited data** it appears that the O and Z-stages generate the highest amounts of oxalic acid from kraft pulps. A D or P*-stage generates slightly lower amounts of OxA from kraft pulps as summarized in Table 2.2.
Table 2.2. Reported changes in kappa # and amounts of oxalic acid [OxA] generated when bleaching a Scandinavian SW kraft pulp.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(OP)DQ(PQ)</td>
<td>0.48</td>
<td>10</td>
<td>0.36</td>
<td>2.9</td>
<td>0.01</td>
<td>2.8</td>
<td>0.26</td>
<td>1.6</td>
</tr>
<tr>
<td>(OP)PaaQ(PQ)</td>
<td>0.48</td>
<td>10</td>
<td>0.13</td>
<td>6.1</td>
<td>0.03</td>
<td>5.5</td>
<td>0.21</td>
<td>3.6</td>
</tr>
<tr>
<td>(OP)ZQ(PQ)</td>
<td>0.48</td>
<td>10</td>
<td>0.45</td>
<td>5.9</td>
<td>0.36</td>
<td>4.2</td>
<td>0.22</td>
<td>2.6</td>
</tr>
</tbody>
</table>

In addition to the uncertainties associated with amounts of oxalic acid generated during bleaching, Ulmgren and Radestrom (1997 TAPPI Minimum Effluent Mills Symposium: Proceedings, San Francisco, CA: 51-62) have recently shown that prolonged heating of a D$_0$ effluent can increase the amount of oxalic acid present in a bleach effluent. For example, storage of a D$_0$ effluent at 90°C for 5 hours increased the amount of oxalic acid in the effluent by a factor of 4. For the samples reported, the post-bleaching formation of OxA was also shown to be independent of pH in the range of 2.5 to 5. Although the chemical processes contributing to this effect are unknown, it is undoubtedly due to the formation oxidized lignin fragments that undergo slow hydrolysis reactions, which eventually yield OxA.

In summary, it is well known that the deposition of OxA on process equipment can detrimentally impact mill performance and lead to costly mill maintenance programs. The prediction of OxA solubility constants under mill operating conditions is rapidly being developed into stand-alone simulation product and will certainly be commercially available within a few years. The successful application of these mill simulation programs will require in-depth experimental data on how OxA is generated in ECF bleaching technologies and how post-processing of these effluents influence the level of OxA. This subcomponent of FO 15 begins to address these issues.

**SUMMARY OF PAST DFRC RESULTS**

This is a new research component of FO 15 and no previous results are available.

**RESEARCH GOALS**

FY 1998-99 goals for this section of FO 15 are listed below:

1. Examine the influence of sample preparation for measuring oxalic acid in D$_0$ effluents by capillary ion electrophoresis.
2. Measure the concentration of oxalic acid in industrial D$_0$ effluents.
3. Evaluate the effect of heat treatment on oxalic acid generation of D$_0$ effluents.
FY 1998-99 Results

Goal 1: Method development of oxalic acid analysis

Preliminary oxalic acid studies employed a Waters Capillary Ion Analyzer equipped with a 75 \( \mu m \) I.D. x 60cm fused silica capillary. Effluent samples were filtered and acidified prior to analysis. A series of control standards was used to identify and quantify the oxalic acid species. Initial studies using this procedure suffered from a great deal of experimental variability. Subsequent method development work established that the removal of chloride and calcium from the effluent samples prior to analysis significantly improved the overall accuracy of the observed measurements. Calcium was removed using a Dionex OnGuard-H cartridge and the chloride was removed using a Dionex OnGuard-Ag cartridge.

**Experimental Accuracy**

The experimental accuracy of the oxalic acid determinations was evaluated by spiking effluent samples with known amounts of oxalic acid and evaluating these samples by means of Capillary Ion Electrophoresis (CEI). Preliminary OxA studies simply filtered the effluent solutions, acidified, and analyzed the material by CEI. CEI analysis of spiked effluent samples usually detected no more than 80% of the added oxalic acid. The overlapping chloride and oxalic acid signals made integration difficult and unreliable. Potential calcium oxalate precipitates further complicated the overall effluent analysis studies. Purification of the effluent samples by means of ion-exchange columns simplified the CEI analysis of bleach effluents and improved the accuracy of measuring oxalic acid spiked effluent samples. Ion chromatography conditioning of effluent samples prior to CEI analysis typically resulted in detecting > 96% of the oxalic acid added to control effluent samples.

Goals 2 & 3: Measure the concentration of oxalic acid in industrial \( D_6 \) effluents.
Evaluate the effect of heat treatment on oxalic acid generation of \( D_6 \) effluents.

As reported in the Fall 1998 PAC, our initial measurements of oxalic acid in bleach plant effluents were only qualitative since our sample preparation methods and analytical techniques failed to detect more than 80% of oxalic acid present in control bleach effluent samples. Nonetheless, given the practical interest in this field, we elected to pursue some preliminary studies to examine the oxalic acid level of several laboratory prepared \( D_6 \) effluents. As discussed in the introduction, several researchers have noted that the concentration of oxalic acid in bleach plant effluents can be increased with additional heating. Therefore, the concentration of oxalic acid in \( D_6 \) effluents was measured immediately after \( D_6 \) bleaching and after extended heating. The results of our preliminary studies are summarized in Table 2.3.
Table 2.3: Semi-quantitative¹ analysis of oxalic acid in \( D_0 \) bleach effluents² and the effect of heat treatment on oxalic acid content.

<table>
<thead>
<tr>
<th>( D_0 ) Effluent</th>
<th>[Oxalic acid] mg/L</th>
<th>Time/h:</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_0 ) (0.27 kf) from SW Sulfite, kappa # 23.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Effluent heated to 70°C</td>
<td>26.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( D_0 ) (0.25 kf) post-O SW kraft, kappa #15.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Effluent pH 2.6 heated to 70°C</td>
<td>27</td>
<td></td>
<td></td>
<td>47</td>
<td>54</td>
<td>55</td>
</tr>
<tr>
<td>( D_0 ) (0.25 kf) post-O SW kraft, kappa #15.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Effluent pH 2.6 heated to 90°C</td>
<td>27</td>
<td></td>
<td></td>
<td>59</td>
<td>--</td>
<td>61</td>
</tr>
<tr>
<td>( D_0 ) (0.25 kf) post-O SW kraft, kappa #15.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adjusted Effluent pH 11.5 heated to 70°C</td>
<td>27</td>
<td></td>
<td></td>
<td>33</td>
<td>34</td>
<td>61</td>
</tr>
</tbody>
</table>

¹Measurements were accomplished using Capillary Ion Electrophoresis; analysis detected approx. 80-87% of spiked oxalic acid. ²All effluents were lab generated, stored at 0°C prior to oxalic acid analysis.

The studies in Table 2.3 were consistent with the results of Ulmgren and Radestrom, suggesting that some oxidative lignin fragments present in bleach plant effluents can undergo a slow hydrolysis reaction yielding additional oxalic acid. Prior to performing additional oxalic acid analyses of bleach effluents, the procedure was modified to increase its accuracy (see Goals section 1). The use of two ion-exchange resins prior to analysis of bleach effluents improved the detection limits so that > 96% of the oxalic acid spiked into control samples could be detected.

Following these modifications to the oxalic acid analysis procedure, a series of first stage HW kraft bleaching effluents were analyzed. The results of these studies are summarized in Table 2.4. These data indicate that most mills studied had oxalic acid concentrations of approximately 20 mg/L of bleach plant effluent. Mill A had significantly lower values but it remains uncertain if this is due to operational procedures or the sampling point. Several of the effluents exhibited increases in oxalic acid content when heated to 70°C for 1 and 4 hours but the magnitude of the increase was less than what has been reported in the literature or what was reported in Table 2.3. If this is due to an industrial process parameter or, perhaps, due to the fact that only HW bleach effluents were examined is unknown and will require additional investigation.
Table 2.4. Analysis of oxalic acid content from a series of industrial generated HW kraft bleach effluents.

<table>
<thead>
<tr>
<th>Bleach Effluent</th>
<th>[Oxalic Acid] mg/L</th>
<th>Time 0</th>
<th>Heated 70°C 1 h</th>
<th>4 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₀ Mill A</td>
<td>2.6</td>
<td>1.6</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>D/C Mill B</td>
<td>20.6</td>
<td>20.3</td>
<td>20.7</td>
<td></td>
</tr>
<tr>
<td>D₀ Mill C</td>
<td>20.1</td>
<td>21.8</td>
<td>24.9</td>
<td></td>
</tr>
<tr>
<td>D₀ Mill D</td>
<td>20.7</td>
<td>24.8</td>
<td>27.5</td>
<td></td>
</tr>
<tr>
<td>D₀ Mill E</td>
<td>23.3</td>
<td>23.9</td>
<td>24.2</td>
<td></td>
</tr>
</tbody>
</table>

**FUTURE RECOMMENDATIONS**

Our understanding of the chemical reactions/processes contributing to the generation of oxalic acid is ill defined. Effective modeling of oxalic acid in a modern mill will require further insight into its chemistry of formation. To accomplish this goal we propose to investigate:

- The amounts of oxalic acid generated from typical SW and HW kraft furnishes bleached with O, D₀, and Z-stages;
- The effect of heat treatment on laboratory generated bleach effluents;
- The effects of heating industrial D₀ SW and HW kraft bleaching effluents.

**RESEARCH BENEFITS**

The anticipated benefits of these studies include:
- Reduced oxalic acid in bleach plant effluents;
- Reduced down-time associated with removing calcium oxalate scales from process equipment.
SUPPORTING LITERATURE

Additional background literature in oxalic acid in kraft bleach effluents can be found in the following articles:


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SUMMARY OF PAST RESULTS

The goal of this fundamental study is to improve the bleaching efficiency of hydrogen peroxide with kraft pulps. During the past fiscal year we examined the interrelationship between D₀ and a subsequent EPO stage. Changes in lignin functional groups were examined by characterizing the residual lignin after the D₀, E, or EPO stages, along with the lignin structures in the effluents. Residual lignin studies indicated that the D₀ stage caused the greatest changes in residual lignin structure. The D-stage resulted in approximately a 70% reduction in non-condensed phenolics, and a 60% reduction in condensed phenolics in the residual lignin. Accompanying these changes, we also observed minor reductions in the methoxy content of the D-stage residual lignin that were attributed to demethylation chemistry of chlorine dioxide.

The subsequent E stage was found to remove additional free phenolics from the lignin. The usage of an EPO stage instead of an E stage appeared to remove additional uncondensed phenolics rather than condensed phenolics. Both the E and EPO stages enriched the residual lignin with carboxylates, which can be attributed, in part, to oxidative chemistry, saponification of muconic acids, and base-catalyzed quinone rearrangement reactions.

In light of the chemical changes occurring to the residual lignin after a DE and D(EPO) sequence, we wished to explore how process parameters and the molecular weight of lignin influences the performance of an EPO stage.

FY 1998-99 RESEARCH GOALS

Investigate the influence of temperature profiling on an (EO) and (EPO)-stage for a D₀ bleached kraft pulp. The effluents will be characterized for molecular weight and the pulps will be characterized according to lignin content and brightness.

RESULTS

The bleaching chemistry of the EPO stage was investigated using a softwood kraft pulp that was bleached with a standard D₀ stage with a kappa factor of 0.20. The D₀ bleached pulp was washed and immediately subjected to an E, (EO), and (EPO) stage. The bleaching conditions employed for these studies are summarized in Table 3.1. Our initial studies in this field examined the performance of an E, EO, and EPO stage at temperatures of 70°, 80°, and 90°C. The effects of further modifying the temperature profile of an E* (i.e., E or EO or EPO) will be examined in the future, once these initial operating parameters are fully understood.
Table 3.1: Summary of bleaching parameters used for bleaching a SW kraft pulp via DE, D(EO), and D(EPO).

<table>
<thead>
<tr>
<th>Bleaching Stage</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>kf 0.20, csc 3.5%, bleaching time: 45 min, bleaching temp: 50°C</td>
</tr>
<tr>
<td>E</td>
<td>2.23% NaOH, 10% csc, bleaching time: 0.15, 0.50, 1.0, 2.0 h, bleaching temp: 70°, 80°, and 90°C. Terminal pH: 12.0 – 12.2</td>
</tr>
<tr>
<td>EO</td>
<td>2.23% NaOH, 10% csc, 65 psig O₂, bleaching time: 0.15, 0.50, 1.0, 2.0 h, bleaching temp: 70°, 80°, and 90°C. Terminal pH: 11.7 – 12.0</td>
</tr>
<tr>
<td>EPO</td>
<td>2.23% NaOH, 10% csc, 65 psig O₂, 0.6% H₂O₂, bleaching time: 0.15, 0.50, 1.0, 2.0 h, bleaching temp: 70°, 80°, and 90°C. Terminal pH: 11.3 – 11.7</td>
</tr>
</tbody>
</table>

1 starting kappa number: 22.3; viscosity 23.7/cP.

Each of the alkaline extracted pulps was filtered, washed, and analyzed for physical properties (i.e., kappa #, viscosity, and brightness). The E* effluents have been collected and are currently being analyzed for molecular weight distributions. Once the latter studies are completed we should be able to determine to what extent the efficiency of an alkaline extraction stage is controlled by the size of lignin fragments extracted during an E*-stage. This analysis will be completed before the end of this fiscal year.

The physical pulp properties already allow for several interesting conclusions to be made. Examining the delignification properties of an E-stage (see Fig. 3.1) it is apparent that the bulk of the lignin (∼90%) is extracted within the first 15 minutes of an E-stage. The development of brightness during an E-stage also follows the same pattern. Employing 70°C for an E-stage the extraction of a D₀ pulp is completed within an hour. At higher extraction temperatures stages; we observe continued removal of oxidized lignin from the pulp over a period of 2 hours. The higher extraction stage temperatures also yielded a slight improvement on the overall brightness values of the pulp (see Fig. 3.2).

Analysis of the pulps after an EO-stage (see Fig. 3.3) indicated once again that the bulk of the extraction process is completed within the first 15 minutes of the extraction stage (i.e., ∼80% of lignin removed within 15 min). In contrast to the E-stage performed at 70°C, the EO stage at 70°C continued to remove lignin from the pulp even after 2 h. The improved performance of an EO-stage at 70°C minimized the differences in the kappa number of the EO pulps performed at 70°, 80° and 90°C. The differences observed for the D(EO) delignifications were paralleled in the brightness analysis studies (see Fig 3.4). For example, the bulk of the brightness development of an EO stage occurred within the first 15 minutes of an EO-stage. Additional brightness gains were observed for the EO pulps at 70°, 80°, and 90°C over a period of 2 h. Finally, a comparison of the results of E vs. EO indicates that at all temperatures and times the EO-stage outperforms the E-stage, as to be expected.
Following much the same experimental approach, the Dp SW kraft pulp (k.f.=0.20) was extracted using an EPO-stage (see Table 3.1 for experimental conditions) at 70°, 80°, and 90°C. The extracted pulps were analyzed for kappa number and brightness and these results are summarized in Figures 3.5 and 3.6. This analysis indicates that the bulk of the delignification (> 94%) and brightness gains (>85%) achieved in an EPO stage are accomplished within 30 min. Since the final pH for these extractions was approximately 12, clearly the reduced reactivity after the first 30 minutes can not be attributed to a low pH value.

Comparing the delignification results of the EPO stage against those determined for the EO stage suggest that the addition of peroxide provides only a modest decrease in lignin content (≈5% increase in delignification based on kappa #). A comparison of the brightness values after an EO and EPO stage suggests that peroxide provides a significant increase in terms of brightness gains. Typically, the EPO pulps exhibited ≈20% increase in brightness over their analogous EO stages.

The changes in viscosity for the EPO stages are shown in Figure 3.7. It is clear the fibers suffer decreases in viscosity as the fibers are exposed to harsher oxidative conditions, but fortunately these loss in viscosity are small. Figure 3.8 summarizes the changes in viscosity for the DE pulps employing temperatures of 70°, 80° and 90°C for extraction times of 0.25 - 2.00 h. The E-stage pulps do not exhibit as severe a decrease in viscosity values as the EPO pulps.

SUMMARY

The results observed in this study are consistent with previous research studies in peroxide delignification of kraft pulps. Although the ‘kinetics’ of an E* stage were not previously examined we have previously noted that a component of kraft lignin is rapidly oxidized by an alkaline peroxide stage and the remaining material becomes intransigent to routine peroxide conditions. The observed delignification trends of the EO and EPO-stages are consistent with these past observations. The propensity of alkaline peroxide to enhance brightness values was previous noted in M. Zawadzki’s thesis studies and this trend holds for all the EPO conditions studied in this report. The one issue that has not been explored, as of yet, is the influence of molecular weights on the overall efficiency of an E*-stage. The effluents generated from the experiments summarized in Figures 3.1 – 3.6 have been all collected and selected samples are currently being analyzed. It is anticipated that these studies will be completed by the end of this fiscal year.
Figure 3.1. Changes in kappa number for a D₀ treated SW kraft extracted with an E stage at 70°, 80°, and 90°C.

Figure 3.2. Changes in TAPPI brightness for a D₀ treated SW kraft extracted with an E stage at 70°, 80°, and 90°C.
Figure 3.3. Changes in kappa # for a D₁₀ treated SW kraft extracted with an EO-stage at 70°, 80° and 90°C.

Figure 3.4. Changes in TAPPI brightness for a D₁₀ treated SW kraft extracted with an EO-stage at 70°, 80° and 90°C.
Figure 3.5. Changes in kappa # for a D₀ treated SW kraft extracted with an EPO-stage at 70°, 80° and 90°C.

Figure 3.6. Changes in TAPPI brightness for a D₀ treated SW kraft extracted with an EPO-stage at 70°, 80° and 90°C.
Figure 3.7. Changes in viscosity for a D₀ treated SW kraft extracted with an EPO-stage at 70°, 80° and 90°C for 0.25, 0.50, 1.00, and 2.00 h.

Figure 3.8. Changes in viscosity for a D₀ treated SW kraft extracted with an E-stage at 70°, 80° and 90°C for 0.25, 0.50, 1.00, and 2.00 h.
FUTURE RESEARCH RECOMMENDATIONS

The current E* bleaching studies highlight the importance of temperature on the overall efficiency of an E* stage. The future research goals for this component of F015 include:
- Modifying the temperature of an EO and EPO stage after the first 15 minutes of extraction to improve the delignification effects;
- Examining the effects of carryover;
- Examining the effects of delayed peroxide addition for an EPO stage.

RESEARCH BENEFITS

Given the current cost of hydrogen peroxide and chlorine dioxide we anticipate that an optimized EPO stage could reduce chlorine dioxide bleaching costs by at least 15 – 25% for a 5-stage bleaching sequence.

SUPPORTING LITERATURE

Additional background information on peroxide reinforced alkaline extraction can be found in the following articles:


F015.4 Laccase-Mediator Bleaching of Kraft Pulp by Art J. Ragauskas

SUMMARY OF PAST RESULTS

FY 1997-98 research efforts were directed towards evaluating the bleachability of Laccase Mediator System treated (LMS) pulps. Bleaching studies demonstrated that the removal of lignin from a laccase(N-hydroxybenzotriazole) treated pulp could be optimized by employing an EOP-stage. Employing an OL(EOP)LED sequence, a final brightness of +85 was achieved using a SW kraft pulp. Interestingly, the first L(EOP) stage removed 65% of the lignin in the pulp and the second LE removed 35% of the remaining lignin. If two LE stages are used each stage removes approximately 50% of the lignin in the pulp.

Last year’s research efforts also demonstrated that the use of either N-hydroxyacetanilide or violuric acid (see Fig. 4.1) as a mediator for laccase yielded a significantly improved LMS-stage in comparison to the results accomplished with N-hydroxybenzotriazole. The two newly identified mediators can delignify kraft pulps comparable to N-hydroxybenzotriazole but require only 2.5% of the enzyme charge.

![Chemical structures](image)

N-Hydroxybenzotriazole (NHB)  Violuric Acid (VA)  N-hydroxyacetanilide (NHAA).

Figure 4.1. Mediators for laccase-catalyzed delignification of kraft pulps.

FY 1998-99 RESEARCH GOALS

Research goals for this section of F015 are listed below:

1. Evaluate the sensitivity of an LMS-stage to NPEs found in a kraft mill.
2. Measure the yield of an LMS-stage.
RESULTS

Prior PAC reviews of laccase-mediator bleaching technologies had speculated that LMS technologies would be unsuited for future kraft bleaching applications that were operated under low effluent conditions. The underlying hypothesis for this suggestion was that the increased amounts of metals in process streams would inhibit the activity of laccase thereby halting the LMS-process. To examine this issue, a SW and HW kraft pulp were bleached with the LMS system using violuric acid as the mediator. A series of LMS stages were spiked with 1% \( \text{MgSO}_4 \) or a molar equivalent of \( \text{MnSO}_4 \), \( \text{FeSO}_4 \), \( \text{NiSO}_4 \), and \( \text{CuSO}_4 \). The LMS treated pulps were then alkaline extracted, washed and the physical properties were determined. The experimental bleaching conditions are summarized in Table 4.1 and the results of the LMS(E) experiments are summarized in Figures 4.2 – 4.4.

Table 4.1: Summary of bleaching parameters used for LMS bleaching of a SW kraft and HW kraft pulp.

<table>
<thead>
<tr>
<th>Bleaching Stage</th>
<th>Bleaching Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMS</td>
<td>190 Laccase activity measured units/gr od pulp, 10% csc, 3% violuric acid charge, ( \text{O}_2 ) pressure: 135 psig, bleaching time: overnight, bleaching temp: 52°C</td>
</tr>
<tr>
<td>E</td>
<td>2.00% NaOH, 3% csc, reaction time: 2.0 h, bleaching temperature: 70°C</td>
</tr>
</tbody>
</table>
Figure 4.2. LMS(E) delignification of HW kraft pulp with and without 1% MgSO₄, or molar equivalents of MnSO₄, FeSO₄, NiSO₄, and CuSO₄.

Figure 4.3. Changes in viscosity from LMS(E) delignification of HW kraft pulp with and without 1% MgSO₄, or molar equivalents of MnSO₄, FeSO₄, NiSO₄, and CuSO₄.

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The results summarized in Figures 4.2 – 4.4 indicate that the LMS-system is not sensitive to the presence of manganese, magnesium, and iron. LMS delignification was slightly retarded (<35%) in the presence of nickel and copper sulfate. Nonetheless, these results are very promising since Mn, Mg, and Fe are among the dominant metal species present in pulp fibers and effluent process streams. Indeed, the amounts of metals added to the LMS experiments are undoubtedly well in excess of the amounts that would be present in process streams even for mills practicing stringent low effluent practices.

Yield measurements were acquired for the control HW LMS bleaching experiments. The yield after the LMS stage was 99.6% and after the LMS(E) was 99.3%.

**FUTURE RESEARCH RECOMMENDATIONS**

- Identify the lowest oxygen pressure under which an LMS stage can be operated.
- Determine kinetics of LMS delignification.
- Examine use of mediator mixtures to achieve optimal LMS delignification.

Figure 4.4. LMS(E) delignification of SW kraft pulp with and without 1% MgSO₄, or molar equivalents of MnSO₄, and FeSO₄.
RESEARCH BENEFITS

The LMS delignification system provides the potential of developing a low cost oxygen delignification system that exhibits excellent bleaching selectivity. Future LMS systems could provide a cost-effective alternative to $O_2$ delignification systems with improved yield properties.

SUPPORTING LITERATURE

Additional background literature in laccase-mediator bleaching systems can be found in the following articles:


Reid, I.D., “Fate of residual lignin during delignification of kraft pulp by Trametes versicolor”, Applied and Environmental Microbiology 64, no. 6: 2117-2125 (1998).


Oxygen Delignification by Lucian A. Lucia

SUMMARY OF PAST RESULTS

Oxygen delignification continues to attract interest as an economically and environmentally viable pre-bleaching method for the manufacture of pulp. However, its full potential for the delignification of kraft pulps and concomitant preservation of yield and strength are currently not fully realized nor understood. The present project has complemented the current bleaching projects through an exploration of the fundamental chemical parameters governing traditional oxygen delignification technologies. Our first area of study was the generation, implication, and analysis of the role of singlet oxygen, a relatively unstudied and unexploited form of molecular oxygen.

As reported in the November, 1998 PAC Meeting, our studies focused on both the chemical and photochemical generation of singlet oxygen to determine its influence and potential in the delignification and brightening of pulps. Singlet oxygen is an activated form of oxygen that has a transient lifetime (approximately milliseconds in water), yet displays remarkable oxidizing power (one of its forms is about 22 kcal more energetic than molecular oxygen). We were able to generate it by a chemical means using cold pulp saturated with ca. 27% hydrogen peroxide that neutralized a slow addition of sodium hypochlorite, to yield singlet oxygen. We also generated it through ordinary visible light (575 nm) absorption by rose bengal (RB) which was ultimately consumed in the reaction. Both of the singlet oxygen generation methods demonstrated an increased propensity for pulp brightening and bleaching, while viscosity losses were comparable to traditional oxygen technologies. Interestingly, singlet oxygen displays delignification behavior akin to oxygen delignification, while simultaneously demonstrating the brightening ability of hydrogen peroxide.

RESEARCH GOALS FOR FY 98-99

1. Continue the fundamental exploration of the activity of singlet oxygen in pulps to illustrate its role in pulp bleaching.

2. Demonstrate the value of singlet oxygen for pulp bleaching by a comparison to traditional oxygen delignification.

3. Perform an economic feasibility calculation for singlet oxygen implementation as a bleaching technique.

The above research goals have been accomplished and the results of the work will be summarized in this report.

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BACKGROUND

Oxygen delignification is a prebleaching stage that has witnessed increased global popularity, primarily due to its associated economic and environmental benefits. Since its commercial inception in the early 1970s, oxygen delignification has been the subject of many intense research efforts to exploit its maximum potential to delignify while simultaneously preserving pulp yield [1, 2]. Unfortunately, the singular most elusive and poorly understood aspect of oxygen delignification remains its detrimental influence on pulp yield and strength beyond a benchmark delignification threshold of 50%. Despite much scientific inquiry into the latter research issue, researchers in the field cannot surpass the 50% delignification threshold without concurrent losses in pulp strength. Fundamental chemistry-based research is necessary and vital to probing the limiting factors responsible for the less than optimum performance of oxygen delignification technologies.

The purpose of the project under the auspices of the FO15 Chemical Fundamentals of Bleaching program is to develop a fundamental understanding of the chemical reactions between oxygen and the lignin and carbohydrate components of pulp. The knowledge will be essential for developing an oxygen delignification paradigm for the improvement of both pulp delignification selectivity and overall pulp yields.

RESULTS

GOAL 1: Fundamental exploration of the activity of singlet oxygen in pulps to illustrate its role in pulp bleaching.

Introduction to Our Fundamental Research Efforts. Recently, our research efforts have concentrated on the study of the pulp reactions of a highly reactive and short-lived species of oxygen known as singlet oxygen. Singlet oxygen is a transient and highly reactive form of oxygen that exists in an excited state (having excess thermal energy) and behaves as an electrophile, i.e., is electron deficient, very similar to hydroxyl (OH) radicals. In a short communication, Gellerstedt was able to demonstrate through a fundamental study that hydrogen peroxide bleaching generates products directly attributable to the action of singlet oxygen [3]. Singlet oxygen is very reactive toward electron-rich species such as arene systems (e.g., lignin) by engaging in either electron transfer (ET) reactions (Scheme 1, Path A) or addition reactions to form endoperoxides (Scheme 1, Path B).

Both the ET and endoperoxide intermediates proceed to decompose to soluble products such as muconic acids and lower molecular weight carboxylic acids. Singlet oxygen has been shown by the results in our previous experiments to attack both the chromophores and electron-rich structures contained in lignin. It has been recently purported to be a strong bleaching agent for textile fabrics [4]. Interestingly, very few research efforts have probed its role in oxygen delignification technologies.
Recently, several research reports have demonstrated that singlet oxygen is very effective in oxidizing lignin to generate alkali-soluble fragments [5, 6]. Singlet oxygen is generated in oxygen delignification or hydrogen peroxide bleaching by the quenching reaction of two superoxide \( (\text{O}_2^- \rightarrow 2 \text{O}_2) \) molecules. It may also be formed by the exothermic decomposition of endoperoxides or alkyl hydroperoxides (formed in oxygen-based bleaching).

**Research Results (Photochemical Data).** Remarkably, our research has demonstrated that both the photochemical and chemical production of singlet oxygen can induce both delignification and concomitant brightening of pre- and post-\( \text{O}_2 \) kraft softwood pulp in a manner akin to an EOP bleaching stage.

One of our original goals was to determine the influence of both visible and near-UV irradiation on the photochemical production of singlet oxygen through direct lignin carbonyl light absorption resulting in singlet energy transfer to oxygen. We found that direct energy transfer pathways are inefficient as the pulp consistency increases beyond several percent.

We discovered that pulp lignin was virtually undegraded under visible light and 1% consistency. However, by the addition of Rose Bengal (RB), a known highly efficient singlet oxygen sensitizer, we found that delignification and brightness gains were remarkably accelerated. Indeed, the preliminary results were so startling and novel, that we decided to embark upon a patent search for its implementation. We found that sensitized delignification technologies were NEITHER well studied nor characterized. The most similar technology was a patent from International Paper (US Patent # 4,294,654: 1981) describing the delignification of hardwoods initiated by corona discharge light composed of 52% visible light (low energy light) and 48% near-UV light (high energy light) [7]. Very remarkably, we were able to substantially delignify pre-\( \text{O}_2 \) softwood pulps with >95% visible light (5750 Å) and a small amount of RB (0.5% odw). The graph (Figure 5.1) illustrates the potential of singlet oxygen bleaching of a softwood kraft.
pulp. All runs were done in a quartz round bottom flask containing pulp which was vigorously
stirred and cooled by a fan (the temperature was always below about 40°C). Lighting was
provided by a series of 16 "cool-white" fluorescent lamps (each rated at 8W). As shown in
Figure 5.1, the efficiency of delignification for a singlet oxygen-treated softwood kraft pulp is
almost 70%.

Research Results (Chemical Data). Our recent results suggest that chemical singlet oxygen
generation is a practical approach toward inducing simultaneous delignification and brightening
of pre-O₂ pulps over a short time (1 hour). Not surprisingly, it is crucially dependent on the
transfer of the chemicals, much the same way that the efficiency of oxygen delignification is
dependent on the transfer of oxygen. Our preliminary data shows that up to 22% delignification
is possible with minimal loss of viscosity. Control experiments clearly indicate that the
brightening and delignification effects are not simply due to hydrogen peroxide at the
temperature of 8°C. Figure 5.2 below illustrates that at relatively low consistencies (1%), the
delignification is not as effective as at 10% consistency.

The latter finding may reflect diffusional limitations on the activity of singlet oxygen due to the
higher water concentration at lower consistencies (making deactivation of singlet oxygen easier
by water collisions). We attempted to overcome the diffusional limitations, inherent in a
heterogeneous system like pulp, by isolating lignin and conducting homogeneous reactions. We

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dissolved softwood brownstock lignin into 100 mL of a 1/1 dioxane/water solution, added 10 mL of a 30% H₂O₂ solution, cooled to 8°C, added NaOH to get a pH = 10.75, and slowly added 4.7% NaOCl over 1 hour with stirring. The solution was worked up according to standard lab procedures and analyzed by NMR spectroscopy.

A ¹³C NMR indicated that the isolated lignin was enriched in carboxylic acids, similarly to a pulp treated by an oxygen delignification stage (See Figure 5.3 below). It is possible that the increase in muconic acid derivatives of the oxidation partially accounted for the concomitant decrease in aromatic structures. An overall loss of 30% of the lignin macromolecule was achieved by the bleaching experiment. The mass balance is clearly not reflected in the phenolic ratios since both generation and removal of phenolics appear to be comparable despite the oxidation that has occurred. Indeed, oxygen delignification results by Gellerstedt indicate that the number of phenolic sites do not radically change as a result of an oxygen delignification stage. Attempts to increase delignification were clearly a function of efficient delivery of singlet oxygen to the site of oxidation as witnessed in the heterogeneous phase studies above and in the photochemical studies. The later finding exemplifies clearly the limitation to the efficacy of molecular oxygen in traditional oxygen delignification technologies.
GOAL 2: Value of singlet oxygen in bleaching by comparison to traditional oxygen delignification.

*Reactivity Parallels for Singlet Oxygen and Oxygen.* Singlet oxygen has been recently shown to be an effective oxidizing agent for lignin in kraft pulps. However, its abundance and activity in standard oxygen, hydrogen peroxide, and other oxygen-based bleaching technologies is not known. Our studies, however, have shown that the interaction of singlet oxygen with kraft pulps remarkably parallels the delignification ability of traditional oxygen delignification, while mimicking the bleaching ability of a hydrogen peroxide stage.

*Selectivity.* The selectivity of delignification in pulps may be defined, in general, to be the ratio of the change in delignification (kappa) over the change in viscosity. For pre-O₂ pulp, the selectivity of oxygen delignification remains relatively high for the first 50% of the residual lignin removal, after which time it drops drastically, a consequence of severe viscosity attrition.

Singlet oxygen displays noteworthy selectivity for the first 60% residual lignin removal (a selectivity of about 4 is maintained), but drops dramatically after 60% strongly implicating carbohydrate damage (Figure 5.4). Although singlet oxygen does not attack carbohydrates, it nonetheless may be responsible for initiating radical reactions from an electron transfer mechanism or the decomposition of endoperoxides (notorious radical initiators).
Mass Transfer. The delivery of oxygen to lignin sites has long been considered a very important criterion for successful delignification. The mechanism of efficient delivery, however, is somewhat complicated by the transfer of oxygen across three different phases (gas, liquid, and solid matrix). Our work strongly suggests that the availability of oxygen at the site of strongly limiting factor to successful delignification. For example, in Figure 5, one clearly observes that even minor oxygen bubbling significantly enhances the delignification of kraft pulp.

In addition, brightening is increased as a function of increased oxygen, perhaps reflecting the ability of singlet oxygen to remove chromophores and lignin simultaneously. We observed in chemical generation of singlet oxygen that a non-trivial barrier exists for delignification of pulps. The issue of transportation is very pronounced in these studies. We assume that better delignification is evident in the catalyst studies simply because the catalyst is directly adsorbed at the sites where lignin resides and delivers singlet oxygen equivalents onsite.
**Brightening.** Our studies illustrate the tremendous potential of singlet oxygen to brighten pulps. In fact, our patent work, described in the economic analysis (Goal 3 for FY 98-99) of our report, demonstrates that very intense light (by a factor of 10 stronger than our traditional methodology) at low temperatures can significantly brighten pulp after 3 hours (by as much as 20-30 brightness units) as shown in Figure 5.6.

![Figure 5.6. Patent Design Singlet Oxygen Kappa and Brightness Results of SW Kraft Pulp Using a 75W Tungsten Halogen Lamp.](image)

The experimental design and conditions for the previous work are described in the experimental section of this report. Our results were obtained at room temperature with minimal stirring, accounting for an inner pulp distribution of higher kappa, and an outer distribution of lower kappa (due to the proximity of incident light). The greater than 50% delignification at a much more accelerated time frame compared to the visible light studies was very promising and indicated that the kinetics of delignification is clearly a function of concentration of singlet oxygen species. The latter result strongly suggests that the time required for oxygen delignification could be truncated by increasing the efficiency of delivery of reactive oxygen units to lignin sites. In the beginning of these studies, we observed 60% delignification after about 10 hours (also with oxygen bubbling), but recently, we were able to reduce the delignification time by a factor of three by increasing the total output of the light source.

**Effluent.** Most of the work reported has related to the lignin and carbohydrate fractions of pulp. An area that merits further inquiry is the effluent fractions from the delignification studies. A UV/VIS study of the effluents resulting from singlet oxygen and standard oxygen delignification was recently performed to assess the similarities and differences of the removed lignin fragments. A literature report recently appeared on the analysis of the lignin fragments resulting from singlet oxygen treatment of steam-exploded pine lignin [5]. The authors used UV/VIS and Gel Permeation Chromatography to determine the chemical changes accompanying singlet oxygen oxidation of pine lignin. They found that depolymerization of the lignin occurred as supported by reductions in molecular weights (analyzed by GPC) and the disappearance of
longer wavelength bands (UV/VIS). The reaction suggested to account for the depolymerization in the pine lignin is shown in Figure 5.7.

Figure 5.7. Products arising from catalyzed oxidative degradation of a lignin dimer.

Thus, encouraged by the above results, we obtained the UV/VIS spectra of the effluents from both singlet oxygen and traditional oxygen delignification shown in Figure 5.8. Initially, we examined the effect of simply using base (an equivalent amount equal to 4% at 10% cn.) over the course of the experiment with no catalyst. We observed no change in the spectrum.

Figure 5.8. UV/VIS spectra of effluents from singlet and standard oxygen treatments of SW kraft pulps.

We added the catalyst, but did not initiate its activity with light, to observe its effect on the sample over the course of the experiment. Again, we observed only the spectrum attributable to the catalyst (two peaks: on maximum at 550 nm, and another in the deep UV, below 300 nm). We treated both pre-O2 and post-O2 with singlet oxygen and compared the effluents to a traditional oxygen delignification effluent obtained under the following conditions: 2.5% base, 100 psi, 100°C, 2 hrs. retention, slow stirring).
The most prominent difference between the singlet oxygen effluent spectrum (pre-O₂ kraft pulp) and the standard oxygen delignification effluent spectrum is the presence of the longer wavelength absorbing band (300-400 nm) in the standard oxygen. This band strongly suggests that the effluent is enriched with a higher fraction of chromophoric (colored) material. The substance may be a higher molecular weight fraction since its UV/VIS spectrum implies a species with more dispersed electronic distribution. The spectrum of the pre-O₂ fraction has a stronger absorbing band in the UV region (250-300 nm, due to increased chromophore concentrations) and a more intense near UV-visible band (300 nm and greater) suggesting a higher fraction of polymeric lignin units that may account for the colored component of the effluent.

The UV/VIS work demonstrates that at the end of a relatively long (2 hrs.) standard O₂ stage, the lignin is not as depolymerized in solution as that of the singlet oxygen sample. The singlet O₂ stage is able to dramatically reduce the color of the effluent. Yet, the action of the latter stage may be limited in the pulp due to the partitioning of its reactivity between the effluent (effluent lignin) and the solid (lignin in the pulp). We are not clear as to the molecular weights (MW) of the fractions being removed by the singlet O₂ stage. We did perform preliminary MW work on pre-O₂ pulps to determine the MW distributions as a function of time and these results will be discussed shortly.

GOAL 3: Economic feasibility calculation for singlet oxygen implementation as bleaching technique.

Note that the work done thus far has focused on the comparison between singlet oxygen and traditional oxygen delignification technologies. The parallel has been important in our research efforts to understand the oxidizing power and selectivity of singlet oxygen, its contribution to an oxygen stage, and its overall effects compared to oxygen delignification. The economics of delignification using the rose bengal catalyst of the preliminary work are approximately 5 times more energy intensive per ton of pulp delignification than standard oxygen delignification.

Approximately a total of 5% savings in pulp yields, energy, and chemical bleaching (D stages) costs can be realized from the current technology versus oxygen delignification. However, the overall cost of the technology is approximately 50-100 times overall more expensive per ton of pulp due to the exorbitant cost of the catalyst.
Table 5.1: Cost analysis of singlet oxygen technology.

<table>
<thead>
<tr>
<th>ITEM FOR COST ANALYSIS</th>
<th>SAVINGS IN COST (Expressed as Benefit of New Technology)</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp Yield</td>
<td>+2%</td>
<td>higher selectivity</td>
</tr>
<tr>
<td>Chlorine Dioxide</td>
<td>+25%</td>
<td>greater delignification</td>
</tr>
<tr>
<td>Energy</td>
<td>+16%</td>
<td>more efficient use of energy</td>
</tr>
<tr>
<td>Catalyst</td>
<td>-5000%</td>
<td>exorbitant cost of catalyst: cost ca. 50 times higher</td>
</tr>
</tbody>
</table>

It was estimated that given the viscosity retention, 60% delignification, lack of oxygen pressure or cost, and energy savings in heating, the greatest cost consideration would have been a vessel to direct UV light at pulp. Yet, the catalyst is by far the limiting factor in the entire economic analysis. Even at greatly discounted bulk rates (greater than 50%), it is approximately 50 times more expensive than MgSO₄ on a pound per pound basis. Further commercialization work in the area must be directed toward finding catalysts that are at least $1-2/lb in order to provide a satisfactory return on investment. Currently, many visible light absorbing catalysts (dyes) are much more expensive than the target price.

*Exploration of the issue of radicals in oxygen-based pulp bleaching.* Our work has been exploratory in nature to properly examine and compare to oxygen delignification the effect of singlet oxygen on pulps. Note that in all our work controls were done to deconvolute the individual effects of temperature, light, and sensitizer. We were interested in quantifying all contributing effects to the chemical bleaching process we observed. Since the pulp suspension had a temperature of 40-45°C, we mimicked the influence of temperature on the delignification and found that delignification proceeds in a manner consistent with lignin leaching as observed by MaCleod [8]. Interestingly, the effect of light must also be deconvoluted from the temperature effect. The photochemical changes occurring in the lignin are a result of direct absorption (near-UV component) leading to Norrish I type cleavages, *subsequent radical generation*, and potential singlet oxygen sensitization. Although not shown, the catalyst by itself (with no light source) causes virtually no delignification.

Although singlet oxygen does not engage in a thermal radical oxidation process, its by-products can. Its reduction product, superoxide, can easily form alkyl peroxides as a result of addition reactions with lignin. Two pieces of evidence that suggest that singlet oxygen was delignifying pulps were (1) the gradual disappearance of the catalyst and (2) the quenching of the activity of singlet oxygen in pre-O₂ pulps by adding DABCO (2.2.2-DiAzaBiCyclo-Octane).

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We strongly suspected that radical species were being generated in solution during the delignification. It is widely accepted that radical reactions are prevalent during standard oxygen delignification and hydrogen peroxide bleaching, causing unwanted cellulose degradation reactions (hence resulting in a lower strengths and yield). The radical reactions are generally inhibited by the addition of additives such as MgSO₄ or the acid chelation of metals (which contribute to a Fenton-type radical mechanism). MgSO₄ is believed to behave by sequestering metals that can engage in Fenton reactions leading to hydroxy radicals. Nonetheless, its use is more practical than understood, but is believed to suppress radical reactions.

Some of our results strongly suggested that radical mechanisms were operative. For instance, in Figure 5.9, we noticed that brightness (chromophore removal) was directly dependent on whether or not a protector was used.

![Figure 5.9](image)

Figure 5.9. Brightness of Singlet Oxygen Treated SW Kraft Pulps as a Function of Oxygen and MgSO₄.

Remarkably, the greatest gains in brightness were achieved **without a protector** (a difference of almost 30 brightness units!). We examined the viscosity and found it was better maintained with a protector as shown in Figure 5.10.

The above results demonstrate that radical reactions (presumably occurring via Fenton-type reactions) are responsible for the viscosity loss and the brightness gains. Most research efforts focus on eliminating radical-based reactions. Our work with singlet oxygen delignification verifies literature precedent that radicals are simultaneously beneficial and also detrimental. The major problem is controlling the radical reactions for maximum benefit. The detrimental effects are observed during the latter stages of the delignification, suggesting that after a certain amount of lignin is removed (50-70%), carbohydrate damage become very pronounced.

Yet, very interestingly, during the delignification of post-O₂ pulp (chemically modified and low residual lignin), MgSO₄ does not offer significant benefits as observed previously for pre-O₂ pulp. The extent of brightness gain and viscosity loss for post-O₂ pulps is independent of
stabilizer and fairly monotone suggesting that radicals are indiscriminately attacking lignin and carbohydrates. The selectivity is therefore severely compromised in the post-O \(_2\) pulp, perhaps as changes and found that maximum carbohydrate protection was obtained with MgSO\(_4\).

![Viscosity Data as a Function of Oxygen and MgSO\(_4\).](image)

The above results demonstrate that radical reactions (presumably occurring via Fenton-type reactions) are responsible for the viscosity loss and the brightness gain. Most research efforts focus on eliminating radical-based reactions. Our work with singlet oxygen delignification verifies literature precedent that radicals are simultaneously beneficial and also detrimental. The major problem is controlling the radical reactions for maximum benefit. The detrimental effects are observed during the latter stages of the delignification, suggesting that after a certain amount of lignin is removed (50-70%), carbohydrate damage become very pronounced.

Yet, very interestingly, during the delignification of post-O \(_2\) pulp (chemically modified and low residual lignin), MgSO\(_4\) does not offer significant benefits as observed previously for pre-O \(_2\) pulp. The extent of brightness gain and viscosity loss for post-O \(_2\) pulps is independent of stabilizers and fairly monotone suggesting that radicals are indiscriminately attacking lignin and carbohydrates. The selectivity is, therefore, severely compromised in the post-O \(_2\) pulp, perhaps as a result of lower residual content, more resistant lignin structures, or both. The most important message is the ubiquitous and dual nature of the radical reactions: they both accelerate delignification, but also increase carbohydrate damage. Research must be developed to study their reactivities and manipulate them to improve selectivity.

Addition of radical scavengers to limit degree of polysaccharide degradation. The previous studies strongly implicated the importance of radicals to the overall bleaching response of the kraft pulps. The reactivity appears to be a function of radical specificity in the early bleaching phase, but tends to lose selectivity after a given amount of time (for pre-O \(_2\) pulps). We were interested in determining whether the oxidative abilities of radicals present in oxygen-based
delignification technologies could be limited and still provide maximum delignification and carbohydrate preservation benefits. To explore the previous hypothesis, we embarked on a study of the rationale behind adding stabilizers ("protectors") to bleaching sequences.

The following are known as the "activated" oxygen species believed to have a role in pulp delignification processes:

\[
\cdot \text{OH} \quad \cdot \text{OOH} \quad \text{O}_2^- \quad \text{O}_2 \quad \text{H}_2 \quad \text{O}_2
\]

The species that is believed to be the most detrimental to the carbohydrate fraction is the first activated oxygen species shown, OH (hydroxy radical). The next three successive species (perhydroxyl radical, superoxide anion, and perhydroxyl anion) are believed to engage in addition reactions that generate alkylperoxide species, that proceed to decompose by ring opening, bond cleavage, or further reactions with base or oxygen species.

Despite the very significant bleaching response of pulps to the last oxygen species, the amount of singlet oxygen is probably not high in a typical thermally controlled standard oxygen delignification stage. Since this work has already shown that radical reactions are both beneficial and detrimental, we were interested in the possibility of performing a preliminary analysis of the importance of magnesium sulfate in a typical oxygen stage. Our results showed that magnesium sulfate does not influence the delignification, but provides a small measure of protection for the pulp viscosity. We did all work without any prior chelation steps, operating under the best economic scenario. Shown in the table below is the oxygen work with magnesium sulfate that benchmarks all of our work directed for the study of the importance of radicals in oxygen delignification.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Kappa Number</th>
<th>Viscosity</th>
<th>Percent Delignification</th>
<th>Percent Viscosity Drop</th>
<th>Selectivity (Δκ/Δη)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-O₂ Kraft Pulp</td>
<td>23.6</td>
<td>30.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>None</td>
<td>12.3</td>
<td>23.1</td>
<td>47.88</td>
<td>23.3</td>
<td>2.06</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>12.4</td>
<td>24.1</td>
<td>47.46</td>
<td>19.93</td>
<td>2.38</td>
</tr>
</tbody>
</table>

Table 5.2: Effect of magnesium sulfate on the selectivity of oxygen delignification of SW kraft pre-O₂ pulp.
Notice that the gain in viscosity is roughly 3% with the addition of magnesium sulfate and the selectivity is increased by 0.25%. The species used was southern softwood having the following metal distribution shown in Figure 5.11:

![Figure 5.11. Metals profile in a pre-O2 SW kraft pulp before and after metal chelation.](image)

The major detrimental cation in pulp is very likely manganese ($\text{Mn}^{2+}$). Although, we didn't employ a chelation stage, we used 0.5% MgSO$_4$ which gives a mass ratio of $\text{Mg}^{2+}/\text{Mn}^{2+}$ of 116/1, a ratio very favorable for inhibiting manganese catalyzed radical reactions. Yet, it appears that the protector is not providing a satisfactory level of protection. It may be possible that manganese is still acting to degrade the pulp despite the level of magnesium sulfate (or iron is playing a very potent role that cannot be avoided regardless of chelation). It is still debatable how important or effective the protector is in various situations. To further explore the extent of radical reactions that occur despite the protector, we embarked upon a novel course of action based on literature precedent: we employed organic residues as radical scavengers to determine their effect on the course of the reactions. Y. Ni published a report from the recent TAPPI Pulping Conference in Montreal indicating that oxygen effluent may help preserve viscosity [9]. We decided to employ an inexpensive organic additive whose identity will not be disclosed pending confidentiality agreements or research interest from the PAC.

We decided to employ an organic additive to test the assumption that it would be readily incorporated into the lignin polymer due its chemical structure. Its ability to potentially facilitate interactions in lignin is due to a phenomenon known as $\pi$-$\pi$ stacking. It may also act to scavenge radicals. The table below illustrates its effect in oxygen delignification (2 hrs, 100 psi, 95C):
Notice that the additive increases the selectivity of the delignification by over 30%. The delignification is reduced somewhat, implying that while the additive is maintaining the pulp viscosity, it is doing so by reducing the radicals that depolymerize lignin. The effect is expected since the organic additive consumes the radical species that act to delignify and degrade carbohydrates. The dual nature of the activity of pulp radicals during delignification has received more support during these studies. The question of "directing" their action so as to maximize delignification, while minimizing pulp yield losses is perhaps one of the most important to answer for increasing the potential of oxygen-based bleaching technologies. Since the activities of MgSO\textsubscript{4} and the organic additive should differ (but with a common purpose of protecting the pulp), we decided to observe the effect on the pulp if both were added simultaneously. Surprisingly, we found that we obtained tremendous improvements in selectivity. Figure 5.12 illustrates the gains in viscosity.

Table 5.3: Comparison of the protecting abilities of magnesium sulfate and an organic additive in SW kraft pre-O\textsubscript{2} pulps.

<table>
<thead>
<tr>
<th>Additive (0.5%, odp)</th>
<th>Final Kappa ($K_o = 23.6$)</th>
<th>Viscosity</th>
<th>Percent Delignification</th>
<th>Percent Viscosity Drop</th>
<th>Selectivity Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>12.3</td>
<td>23.1</td>
<td>47.88</td>
<td>23.26</td>
<td>2.06</td>
</tr>
<tr>
<td>MgSO\textsubscript{4}</td>
<td>12.4</td>
<td>24.1</td>
<td>47.46</td>
<td>19.93</td>
<td>2.38</td>
</tr>
<tr>
<td>Organic Additive</td>
<td>12.6</td>
<td>26.0</td>
<td>46.61</td>
<td>13.62</td>
<td>3.42</td>
</tr>
</tbody>
</table>

Figure 5.12. Viscosities and kappas of SW kraft pulps as a function of protector.

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The selectivity coefficients are shown in the following table.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>2.05</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>1.89</td>
</tr>
<tr>
<td>Organic Additive</td>
<td>2.76</td>
</tr>
<tr>
<td>MgSO₄/Additive</td>
<td>18.73</td>
</tr>
</tbody>
</table>

Table 5.4: Selectivity coefficients obtained from the magnesium sulfate, organic additive, and magnesium sulfate/additive systems.

Using a relatively low amount of additives (MgSO₄/additive, total of 1% on odt), we were able to raise the selectivity by almost 10 fold. These results are preliminary and have not been optimized for maximum effect, but it is worthwhile to note that the combined action of the additives is synergistic, and not additive. We believe that MgSO₄ may be responsible for partially sequestering metals, and that additive is responsible for reacting with radicals that are generated in solution. At this point in our studies, it is difficult to provide an accurate assessment of their protective behavior during oxygen delignification, but it is certainly worthwhile pursuing these studies. Further studies will include applying similar and inexpensive radical scavengers to evaluate their ability to protect lignin and thus derive a more comprehensive picture of the action of these compounds during oxygen delignification.

**Influence of lignin molecular size on extractability.** From the UV/VIS spectroscopic studies of the oxygen delignification and singlet oxygen work, we were interested in developing an understanding of the relationship of extracted lignin molecular weights on the efficiency of oxygen delignification. It was known for instance, that during singlet oxygen treatment of isolated lignin, lignin is efficiently depolymerized. In fact, our UV/VIS data tended to suggest that singlet oxygen generates smaller fragments than a standard oxygen delignification stage. We embarked upon an exploratory study of the molecular weight distributions of lignin as a function of oxygen delignification time. Fractions from 30, 60, and 120 minutes from an oxygen delignification run (3% NaOH, 100 psi, 95C, no additive) were analyzed by Total Organic Carbon (TOC) data. Two principal effluent fractions eluted; a very low molecular weight fraction (weights up to 5,000 D) and a much higher molecular weight fraction were found (25,000 D). Interestingly, a greater proportion of the larger molecular weight fractions came off in the early part of the runs, which gradually changed over the course of the experiments. The bulk of the smaller fractions came off near the end of the run, but it is not clear if these are the majority from the residual lignin or oxidized effluent lignins. The work demonstrates that larger polymeric lignin components can be removed rapidly, but proceed to become increasingly smaller in weight as a function of time. The results are consistent with the UV/VIS data of the pre-O₂ effluents in which the larger fractions may impart the colored component to the effluent. The larger weights may also interfere with further lignin extraction by consuming oxygen, thus
generating more radicals, or increasing the viscosity of the effluent, lessening the facility of other lignin fragments to escape.

PROPOSED FUTURE WORK

The issue of improving oxygen delignification technologies demands increased fundamental efforts. A natural extension of the work described in this report includes:

1.) continue to explore the role of oxygen reactive species in oxygen delignification,
2.) mechanisms to improve the yield,
3.) examine the role of organic and inorganic radical inhibitors to improve the selectivity of oxygen delignification,
4.) and mechanisms to enhance greater delignification while preserving yields of conventional pulps.

Experimental

Materials: All pre-O₂ and post-O₂ pulps were obtained from North American pulping and oxygen delignification operations, washed thoroughly when received, crummed, and stored at 2-3°C. All chemicals (chemical additives, caustic, etc.) were purchased from chemical vendors and used as received unless otherwise specified.

Singlet Oxygen Bleaching: All work was done in a 1L round bottom flask that was stirred by a mechanical motor. The pulp consistencies were 1%, all water was millipore, triply-distilled. Pulps were irradiated without any prior treatment. The catalyst was added as 0.5% odp. Base concentrations were 10% odp which corresponds to about 1% on for a 10% consistency pulp. Pulps were thoroughly washed of effluent and catalyst after reaction, airdried, and tested for kappa and viscosity. The patent design consisted of a Sylvania Tungsten Halogen Lamp (75W) that was inserted into a glass jacket, and the entire assembly immersed into a pulp suspension of standard conditions for singlet oxygen bleaching. The entire reaction system was cooled with ice and bubbled with oxygen (minimal stirring was possible).

Chemical Oxygen Bleaching: All work was done in small reaction vessels with varying consistencies and vigorous magnetic stirring. Pulps were immersed in 27% hydrogen peroxide solution at 8°C, mixed, and reacted drop-wise with a sodium hypochlorite solution. The evolution of oxygen gas was observed during the reaction. All hypochlorite was consumed by the excess hydrogen peroxide solution to ensure no bleaching effects due to hypochlorite. Pulps were filtered off, washed thoroughly, air dried, and base extracted (standard conditions in a typical bleaching stage).
Oxygen Delignification: All work was done according to standard procedures in a 300 mL PARR Reactor. The conditions used were typically 2-3% caustic charge, 100 psi oxygen pressure, 90-100°C, and 10% consistency. No magnesium sulfate was added unless otherwise specified. The pulp was gently stirred and after a requisite amount of time, removed, washed, and air dried.

SUPPORTING LITERATURE

Additional background information relating to oxygen-based bleaching chemistry and mill applied technologies can be found in the following references:

Practical Method for Studying NPEs [Nonprocess Elements] in a Kraft Mill

Chromophore Changes During Oxygen Delignification of a Radiata Pine [Pinus radiata] Kraft Pulp

Effluent Quality Characteristics at North American Kraft Mills Employing Complete Substitution Bleaching

Analysis of Kappa Variability in a Kamyr Digester and Oxygen Reactor

Kraft Cooking with Varying Alkali Concentration-Influence on TCF Bleachability

New Chemicals Cause Dramatic Changes in Bleaching Sequences

Bleached chemical pulp from Eucalyptus grandis wood produced by peroxyformic acid pulping and photochemical bleaching
Ruggiero, Reinaldo; Machado, Antonio E.H.; da Silva Perez, Denilson; Grelier, Stephane; Nourmamode, Aziz; Castellan, Alain. Holzforschung, 52, No. 3325-332.

Role of Singlet Oxygen in Bleaching of Papermaking Fibers
Lele, I.; Fejes, F.; Kovács, I.; Rusznák, I.; Csiszár, E. Papiripar, 41, No. 392-97 (June 1997).
Mechanism of Hydrogen Peroxide Bleaching

Singlet-Oxygen-Induced Bleaching of High-Yield Pulp Sheets

BIBLIOGRAPHY


DUES-FUNDED PROJECT SUMMARY
FY 1998-99

Date: March 4, 1999
Project Title: Environmentally Compatible Production of Bleached Chemical Pulp
Project Code: BLECH
Project Number: F013
PAC: Chemical Pulping and Bleaching
Division: Chemical and Biological Sciences
Project Staff
  Faculty/Senior Staff: T.J. McDonough, C.E. Courchene, A. Ragauskas
  Staff: M. Turner, B. Carter A. Shaket, N. Rawat, J.-C. Baromès
FY 98-99 Budget: $245,721
  Allocated as Matching Funds:
    Project 4120: $36,000
    Project 4201: $15,000

Time Allocation
  Faculty/Senior Staff: 0.5
  Support: 1.9

Supporting Research
M.S. Students: Carter Johnson, Tim Jacoby
Ph.D. Students: Aric Bacon
External:
  Project 4201, “Bleach Plant Capital Reduction with Rapid D₅ and Simplified Bleaching” (U.S. D.O.E Agenda 2020 Capital Effectiveness)
  Project 4159, “High Efficiency ClO₂ Delignification” (U.S. D.O.E. Agenda 2020 Environmental)

RESEARCH LINE/ROADMAP: Environmental Performance/RM5 - Reduce Emissions

PROJECT OBJECTIVE:
Define pulping and bleaching technology that will decrease or eliminate the release of byproduct organic chlorine compounds without sacrificing bleached pulp quality.

PROJECT BACKGROUND:
Prior work on this project has included investigations in the area of environmentally compatible manufacture of bleached chemical pulp. These have included studies of peroxide delignification of kraft pulps, ECF bleaching
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process behavior, effects of kraft, oxygen and ClO\textsubscript{2} delignification on pulp physical properties, and Rapid D\textsubscript{o} mill trials and laboratory studies. Additional objectives of this project have been leveraged through contribution of matching effort in support of related externally funded projects. These have included work on environmental aspects of ECF bleaching, bleachability as related to pulping conditions, improving the efficiency of ClO\textsubscript{2} delignification, and development of low-capital bleaching processes based on Rapid D\textsubscript{o} and simplified bleaching. Recent investigations within these projects have included vapor phase ClO\textsubscript{2} delignification, effects of cooking liquor concentration profiling on bleachability, effects of pulping conditions on hardwood bleachability, and effects of bleach plant washer inefficiency on effluent characteristics.

Experiments in which kraft pulping conditions were systematically varied over a wide range showed that modern chelation-peroxide technology is capable of extensively delignifying southern pine kraft regardless of pulping conditions.

In a comparison of effects of carryover and D\textsubscript{1} stage pH in ECF and (DC)-based bleaching, we showed that, at low KF, carryover has about the same effect on D\textsubscript{o} and (DC) bleaching. However, at high KF, carryover has significantly less effect on D\textsubscript{o} than on (DC). Final brightness is higher for D\textsubscript{o} than for (DC) when carryover is high, and the optimum D\textsubscript{1} exit pH is higher at low KF than at high KF, and higher in the presence of carryover than in its absence.

A subproject was initiated to characterize the effects of delignification and bleaching processes on fiber properties. The initial work was defined to include conventional kraft batch pulping, oxygen delignification, and both CED and DED bleaching.

From a mill trial of the Rapid D\textsubscript{o} concept, it was concluded that the industrial scale mixers, both static and dynamic, can give sufficiently good mixing to make Rapid D\textsubscript{o} bleaching industrially feasible.

Work on a several externally funded projects moved us toward goals that were closely aligned with the goals of Project FO 13. Laboratory studies showed that Rapid D\textsubscript{o} bleaching is applicable to conventional and Lo-Solids\textsuperscript{TM} pulps and to pulps prepared at unusually low kappa number levels. Laboratory vapor phase ClO\textsubscript{2} delignification experiments showed that, in bleaching hardwood pulps, vapor phase delignification is remarkably more efficient, but generated markedly larger quantities of AOX than the conventional process. Qualitatively similar observations were made with regard to the softwood pulps, but the trends were generally less pronounced than in the case of the hardwood pulps. Differences in the structure of hardwood pulp residual lignin after conventional and vapor phase bleaching were studied and found to be slight, indicating that the superior bleaching efficiency of the vapor phase process is due to diminished importance of reactions that occur between active chlorine compounds and dissolved organic byproducts. In an effort to assign a cause for the superior bleachability of pulps made by modified pulping processes, we conducted systematic bleaching studies of southern pine pulps prepared with controlled liquor concentration profiles. No effects of the profiles used were found and a study of more extreme profiles was initiated.

We conducted a systematic study of AOX, BOD, and COD released by bleaching southern pine kraft pulp in the D\textsubscript{o}(EPO)D\textsubscript{0} sequence. Modest but significant effects were observed. Hardwood bleachability studies indicated that EA and pulping temperature affect the nature and bleachability of the pulp produced. High EA and high temperature pulping emerged as a very attractive option for maple.

**SUMMARY OF RESULTS**

Work on this project during the past year has encompassed research in the following areas:

1. Partial substitution of ozone for chlorine dioxide in the first stage of softwood kraft pulp bleaching sequences
2. Partial substitution of ozone for chlorine dioxide in the first stage of hardwood kraft pulp bleaching sequences
3. Effects of digester conditions on the bleachability of southern pine kraft pulp
4. Hydrogen peroxide delignification of softwood kraft brownstock
5. Effects of pulping and bleaching processes on pulp and fiber properties

Work on the partial substitution of ozone for chlorine dioxide in the first stage of softwood kraft pulp bleaching sequences encompassed a study of the response of southern pine kraft pulp to delignification with combinations of the two oxidants. The experimental design used was a two-level factorial in three variables -- order of addition, time delay before addition of the second chemical, and concentration of ozone in the gas stream fed to the bleaching process.
reactor. The O\textsubscript{3}/ClO\textsubscript{2} stage was followed by an (EPO) stage conducted under constant conditions. Combinations of O\textsubscript{3} and ClO\textsubscript{2} were slightly less effective than an equivalent amount of pure ClO\textsubscript{2} in the first stage of bleaching southern pine kraft brownstock that has not previously been oxygen delignified. Adding the ClO\textsubscript{2} before the O\textsubscript{3} (using D/Z instead of Z/D) gave a slightly lower kappa number and a lower viscosity, both the kappa number and the viscosity being measured after the (EPO) stage. Regardless of which chemical was added first, a delay of only one minute before adding the second gave a kappa number only slightly higher than when addition of the second chemical was delayed for 15 minutes. In addition, the shorter delay gave a higher viscosity. Using an O\textsubscript{3}-containing gas stream that contained 6% O\textsubscript{3} gave a viscosity that was slightly lower than when the O\textsubscript{3} concentration was only 2%. Considering the size of the various effects, it was concluded that reasonably good combinations of post-extraction kappa number and viscosity can be obtained by first injecting O\textsubscript{3} at a 6% concentration in O\textsubscript{2} and, after a delay of only one minute, adding ClO\textsubscript{2}. This operating strategy gave kappa number 6 and viscosity 17 mPa.s, while the use of an equivalent amount of pure ClO\textsubscript{2} gave kappa number 4 and viscosity 21 mPa.s. In the bleaching of pulp which had been previously delignified with oxygen but was otherwise similar, the response of the pulp was different. The combination of O\textsubscript{3} and ClO\textsubscript{2} was nearly as effective as an equivalent amount of pure ClO\textsubscript{2}. Changing the order from Z/D to D/Z slightly decreased the kappa number but did not affect the viscosity. Regardless of which chemical was added first, a delay of only one minute before adding the second gave virtually the same kappa number and viscosity after extraction as when addition of the second chemical was delayed for 15 minutes. Using ozone at a concentration of 6.5% gave a lower kappa number and a higher viscosity than when the concentration was only 2%. It was concluded that good combinations of post-extraction kappa number and viscosity can be obtained by first injecting O\textsubscript{3} at a 6% concentration in O\textsubscript{2} and, after a delay of only one minute, adding ClO\textsubscript{2}. In the present study, this operating strategy gave kappa number 4 and viscosity 16 mPa.s, while the use of an equivalent amount of pure ClO\textsubscript{2} gave kappa number 3 and viscosity 18 mPa.s.

Application of combinations of O\textsubscript{3} and ClO\textsubscript{2} to hardwood pulp was investigated in experiments with a mill kraft pulp made from mixed southern U.S. hardwood (mainly gum and oak). A few experiments were also done on pulp sampled after the oxygen delignification stage at the same mill. The main objective of the experiments was to determine the effects of mixing speed and substitution level on the kappa number, viscosity and brightness of the pulp after the subsequent oxygen- and peroxide-reinforced extraction (EPO) stage. Substitution of O\textsubscript{3} for 25–75% of the ClO\textsubscript{2} in the first stage had little or no effect on either the viscosity or the kappa number of the pulp after the extraction stage, provided that the ozone was efficiently mixed with the pulp. However, increasing the substitution level from 25% to 75% decreased the brightness at a given kappa number by approximately 5 points.

In continuing studies of the effects of pulping conditions on bleachability, a series of experiments was done to assess the effects of varying pulping conditions over a wide range on the response of southern pine kraft pulp to delignification with ClO\textsubscript{2} and alkali. Lignin removal during bleaching was favored by high alkali charge and high sulfidity during pulping. Unbleached brightness was higher when cooking was continued to lower kappa numbers. At a given kappa number the brightness was increased by using higher alkali charge, higher sulfidity and lower liquor-to-wood ratio. The negative direction of the last effect suggests that re-deposition of lignin is not a major factor in determining unbleached brightness and that the higher brightness at lower liquor-to-wood ratio is due to higher residual alkali concentration. Increasing sulfidity had a beneficial effect on DE bleach response that was additive with the beneficial effect on unbleached brightness. This may be due to a decrease in the formation of inter-unit carbon-carbon bonds, as a result of increased rates of interception of reactive intermediates by hydrosulfide ion. At low pulping temperature (165°C), cooking with high EA charge caused slightly less COD to be released during bleaching. Pulp from low-EA, high-temperature cooks released less TOC during bleaching, but not less COD. This suggests that the TOC released from such pulps is less oxidized and therefore has a higher COD per unit of TOC.

Delignification of kraft brownstock with hydrogen peroxide instead of oxygen has been re-examined, in the light of recent advances in technology for effectively removing trace metal impurities from the unbleached pulp with chelating agents. In an earlier study, we showed that some pine brownstocks were readily delignified by as much as 70% with 3% hydrogen peroxide after an effective chelation stage. Since then, we have followed up with some additional work to determine dose-response relationships, and to investigate possibilities for improving the effectiveness of the peroxide stage. It was concluded that combinations of advanced chelation and peroxide stages (QP partial sequences) may be useful as a low-capital alternative to oxygen delignification of softwood kraft brownstock. A charge of 1% H\textsubscript{2}O\textsubscript{2} can remove about one-third of the lignin in unbleached softwood kraft pulp, following an efficient chelation stage. It was also shown that loss of pulp viscosity during peroxide delignification...
can be completely eliminated by addition of manganese ion. This may occur through trapping of hydroxyl radicals by Mn$^{2+}$ and generation of the delignifying species, superoxide radical anion, by Mn$^{3+}$ oxidation of hydroperoxide anion, followed by dissociation of the resulting perhydroxyl radical. Superoxide radical anion also reacts with Mn$^{3+}$ and hydroxyl radical to form molecular oxygen, effectively decomposing hydrogen peroxide. This decomposition limits the extent of delignification and compromises the immediate practical application of manganese addition in peroxide delignification stages. However, new insights provided by the observation and its likely mechanism increase the chances that further research will yield useful results.

In a joint project between the Chemical and Biological Sciences (CBSD) and Fiber and Paper Physics (FFPD) Divisions, effects of delignification and bleaching processes on fiber properties are being characterized. Work to date has included conventional kraft batch pulping, oxygen delignification, and both CED and DED bleaching. There did not appear to be significant differences in the pulp and handsheet properties measured between CED and DED bleaching nor were there any significant differences in PFI refineability. At a lower kappa no. for the brownstock, the freeness reduction with refining was greater. The strength of the unrefined kraft-oxygen brownstocks was significantly lower than that of the kraft pulps but this is probably attributable to curl imparted in the oxygen delignification processing. Refining reduced the strength differences between the pulps but the kraft-oxygen pulps did not meet the strength of the kraft 28 pulp from which they were made. Extending the kraft delignification down to kappa 17 resulted in a somewhat lower strength which was nevertheless comparable to the kraft-oxygen pulps. Increasing the oxygen delignification beyond 50% resulted in a somewhat lower strength.

**GOALS FOR FY 98-99:**

1. Complete the study of effects of modern delignification technologies on pulp and fiber properties that was initiated during FY 97-98. Initiate a follow-up study considering such effects as extended digester delignification and subsequent delignification with oxygen, ozone, chlorine dioxide, alkaline hydrogen peroxide and their combinations.

2. Complete a study of predictors of ease of delignification by (1) an oxygen stage and (2) a D(EO) sequence at several extents of delignification. Use a set of softwood and hardwood pulps representing a wide range of bleachabilities to evaluate a defined set of candidate predictors.

3. Evaluate and develop modern chelation-peroxide technology as a substitute for oxygen delignification.

4. Report laboratory work to date on ozone bleaching kinetics.


**DELIVERABLES FOR FY 98-99:**

Report on completed study of effects of modern delignification technologies on pulp and fiber properties and proposal of a follow-up study considering such effects as extended digester delignification and subsequent delignification with oxygen, ozone, chlorine dioxide, alkaline hydrogen peroxide and their combinations.

Evaluation of a defined set of candidate predictors of ease of delignification by (1) an oxygen stage and (2) a D(EO) sequence at several extents of delignification.

Brownstock chelation-peroxide technology for use as an alternative to oxygen delignification.

Report on ozone bleaching kinetics


**SCHEDULE:**

See attached Gant chart.
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Project: 803013w
Date: Thu 3/4/99

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Project: 803f013w
Date: Thu 3/4/99

Task
Progress
Milestone
Summary
Rolled Up Task
Rolled Up Progress
Rolled Up Milestone
Project F013

Environmentally Compatible Production of Bleached Chemical Pulp

March, 1999

Summary

Work on this project during the past year has encompassed research in the following areas:

1. Partial substitution of ozone for chlorine dioxide in the first stage of softwood kraft pulp bleaching sequences
2. Partial substitution of ozone for chlorine dioxide in the first stage of hardwood kraft pulp bleaching sequences
3. Effects of digester conditions on the bleachability of southern pine kraft pulp
4. Hydrogen peroxide delignification of softwood kraft brownstock
5. Effects of pulping and bleaching processes on pulp and fiber properties

Work on the partial substitution of ozone for chlorine dioxide in the first stage of softwood kraft pulp bleaching sequences encompassed a study of the response of southern pine kraft pulp to delignification with combinations of the two oxidants. The experimental design used was a two-level factorial in three variables -- order of addition, time delay before addition of the second chemical, and concentration of ozone in the gas stream fed to the bleaching reactor. The O₃/C₅O₂ stage was followed by an (EPO) stage conducted under constant conditions. Combinations of O₃ and C₅O₂ were slightly less effective than an equivalent amount of pure C₅O₂ in the first stage of bleaching southern pine kraft brownstock that has not previously been oxygen delignified. Adding the C₅O₂ before the O₃ (using D/Z instead of Z/D) gave a slightly lower kappa number and a lower viscosity, both the kappa number and the viscosity being measured after the (EPO) stage. Regardless of which chemical was added first, a delay of only one minute before adding the second gave a kappa number only slightly higher than when addition of the second chemical was delayed for 15 minutes. In addition, the shorter delay gave a higher viscosity. Using an O₃-containing gas stream that contained 6% O₃ gave a viscosity that was slightly lower than when the O₃ concentration was only 2%. Considering the size of the various effects, it was concluded that reasonably good combinations of post-extraction kappa number and viscosity can be obtained by first injecting O₃ at a 6% concentration in O₂ and, after a delay of only one minute, adding C₅O₂. This operating strategy gave kappa number 6 and viscosity 17 mPa.s, while the use of an equivalent amount of pure C₅O₂ gave kappa number 4 and viscosity 21 mPa.s. In the bleaching of pulp which had been previously delignified with oxygen but was otherwise similar, the response of the pulp was different. The combination of O₃ and C₅O₂ was nearly as effective as an equivalent amount of pure C₅O₂. Changing the order from Z/D to D/Z slightly decreased the kappa number but did not affect the viscosity. Regardless of which chemical was added first, a delay of only one minute before adding the second gave virtually the same kappa number and viscosity after extraction as when addition of the second chemical was delayed for 15 minutes. Using ozone at a concentration of 6.5% gave a lower kappa number and a higher viscosity than when the concentration was only 2%. It was concluded that good combinations of post-extraction kappa number and viscosity can be obtained by first injecting O₃ at a 6% concentration in O₂ and, after a delay of only one minute, adding C₅O₂. In the present study, this operating strategy gave kappa number 4 and viscosity 16 mPa.s, while the use of an equivalent amount of pure C₅O₂ gave kappa number 3 and viscosity 18 mPa.s.

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Partial Substitution of Ozone for Chlorine Dioxide in the First Stage of Softwood Kraft Pulp Bleaching Sequences
T.J. McDonough, M. Turner and C.E. Courchene

Introduction
The literature suggests that ozone can be effectively used to replace part of the ClO₂ in the first stage of bleaching kraft pulps by ECF sequences. This may be an attractive alternative for mills that wish to convert to ECF bleaching but lack sufficient ClO₂ generating capacity. Accordingly, we undertook a laboratory evaluation of the response of kraft pulp to delignification with combinations of the two oxidants. We chose southern pine pulp as the raw material, since southern pine is widely used by many mills to make bleachable grades and may be expected to approximate the behavior of other softwood species in this application.

Since the literature does not make it clear whether adding O₃ before ClO₂ is more effective than the reverse order of addition, nor whether the time interval between additions is important, we included these variables in the study. In addition, we wished to determine whether the concentration of ozone in the gas stream to the reactor had an effect. The experimental design used was a two-level factorial in these three variables, order of addition, time delay before addition of the second chemical, and concentration of ozone in the gas stream fed to the bleaching reactor, other conditions being maintained constant. The O₃/ClO₂ stage was followed by an (EPO) stage, also conducted under constant conditions. The pulp emerging from the (EPO) stage was characterized in terms of kappa number, brightness and viscosity.

Results and Discussion
In all experiments, a kappa factor (KF) of 0.20 was used, and in all but the controls, 50% of the ClO₂ normally required for this KF was replaced with ozone, on an oxidizing equivalent basis. Since the equivalent weights of ClO₂ and O₃ are 13.5 and 8, respectively, 1 kg of O₃ replaced 13.5/8 = 1.69 kg ClO₂.

The time interval between the two chemical additions was either 1 minute or 15 minutes. After addition of the second chemical the reaction was continued for 15 min. The pH of the pulp was adjusted before chemical addition, to ensure that the pH would be 2.5-3 when O₃ was added and that the terminal pH would be approximately 2.5.

D/Z and Z/D on Brownstock
The results of experiments on kraft brownstock are contained in Table I. The combined performance of the oxidative first stage and the reinforced alkaline extraction stage were evaluated by measuring kappa no., brightness and viscosity after the extraction stage. The kappa number of the pulp was reduced from 24 to 3.6 in the control D(EPO) partial sequence, while at the same time the brightness was increased to 63 and the viscosity was reduced from 24 to 21. When half of the ClO₂ was replaced by ozone, the decrease in kappa number was somewhat smaller, the kappa number after extraction being in the range 5.3 – 6.4. Similarly, the brightness increase was smaller, the final brightness being in the range 54 – 59, and the viscosity decrease was larger, the viscosity after extraction being in the range 15 - 18. Within these ranges, there were significant effects of the three experimental variables. These effects were evaluated by analysis of variance of the results of the 2³ factorial experiment, as described below.

Kappa Number
Analysis of the kappa number data, neglecting interaction effects, showed that two of the three variables were statistically significant at a confidence level greater than 90%. These were order of addition (94%
confidence) and time delay (98% confidence). D/Z gave an extracted kappa number that was, on average, 0.4 units lower than Z/D. This is consistent with the expectation that ClO₂ should be more effective when applied to pulp in which the phenolic hydroxyl groups (lignin structural features that are vulnerable to attack by ClO₂) are still intact, as opposed to lignin in which these groups have been destroyed by prior exposure to O₂. Delaying addition of the second chemical for 15 min gave a kappa number that was 0.5 units lower than when the delay was only one minute.

Table I. (D/Z)(EPO) and (Z/D)(EPO) Bleaching of Southern Pine Kraft Brownstock

<table>
<thead>
<tr>
<th>Time Before Chemical</th>
<th>Ozone</th>
<th>Ozone</th>
<th>Kappa</th>
<th>Brightness</th>
<th>Viscosity,</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Added First</td>
<td>Conc. In</td>
<td>Substitution,</td>
<td>Added</td>
<td>Gas, wt%</td>
<td>Total</td>
</tr>
<tr>
<td>First</td>
<td>Conc., min</td>
<td>%</td>
<td>Chemical</td>
<td>First</td>
<td>Time, min</td>
</tr>
<tr>
<td>0.2 0 n.a. n.a. 45</td>
<td>2.5</td>
<td>3.6</td>
<td>62.9</td>
<td>20.6</td>
<td></td>
</tr>
<tr>
<td>50 ClO₂ 1 2.1</td>
<td>16</td>
<td>4</td>
<td>2.3</td>
<td>5.8</td>
<td>57</td>
</tr>
<tr>
<td>15 2.4</td>
<td>30</td>
<td>4</td>
<td>2.4</td>
<td>5.3</td>
<td>58.7</td>
</tr>
<tr>
<td>1 5.8</td>
<td>16</td>
<td>4</td>
<td>2.5</td>
<td>6.1</td>
<td>54.8</td>
</tr>
<tr>
<td>15 5.4</td>
<td>30</td>
<td>4</td>
<td>2.7</td>
<td>5.5</td>
<td>56.7</td>
</tr>
<tr>
<td>O₂ 1 2.2</td>
<td>16</td>
<td>3</td>
<td>2.5</td>
<td>6.4</td>
<td>54.8</td>
</tr>
<tr>
<td>15 2.1</td>
<td>30</td>
<td>3</td>
<td>2.5</td>
<td>6</td>
<td>55.1</td>
</tr>
<tr>
<td>1 5.9</td>
<td>16</td>
<td>3</td>
<td>2.6</td>
<td>6.2</td>
<td>53.9</td>
</tr>
<tr>
<td>15 5.8</td>
<td>30</td>
<td>3</td>
<td>2.6</td>
<td>5.6</td>
<td>56.5</td>
</tr>
</tbody>
</table>

Notes: 1. Unbleached pulp: southern pine, kappa no. 24.2; viscosity 21.0 mPa.s
2. D/Z stage conditions: 3.5% cons'y, 25°C, CRS reactor; mixing speed 1500 rpm during O₂ addition
3. (EPO) stage conditions: 10% cons'y, 70°C, 60 min, O₂ press. 60-0 psig over first 30 min
4. (EPO) stage chemical charges, % o.d. pulp: NaOH, 2.75; H₂O₂, 0.5

In spite of the statistical significance of these effects, it is noteworthy that they are so small. One practical implication is that, as far as delignification is concerned, it doesn’t matter very much which chemical is added first. Similarly, a retention time of only one minute before adding the second chemical gives only slightly less delignification than when the retention time is 15 minutes. It is also noteworthy that increasing the ozone concentration in the gas stream from 2% to 6% had virtually no effect. Finally, it is important to note that, regardless of order, delay or ozone concentration, substituting O₂ for half of the ClO₂ caused a small but significant loss in extent of delignification. This observation differs from that made earlier by Chirat and Lachenal.

Viscosity

A similar analysis of the post-extraction viscosity data of Table I showed statistically significant effects of order of addition (98% confidence), time delay before addition of the second chemical (97% confidence) and ozone gas concentration (98% confidence). D/Z gave an extracted viscosity that was, on average, 2 units lower than Z/D. This can be explained as being due to the smaller amount of lignin present at the time of ozone addition in the former sequence, and the consequently increased vulnerability of the cellulose. Delaying addition of the second chemical for 15 min gave a viscosity that was 0.9 units lower than when the delay was only one minute. A high ozone concentration in the gas stream (6%) gave a viscosity that was 1.0 unit lower than when the concentration was only 2%.

The effects of order and delay on viscosity parallel the corresponding effects on kappa number. Increasing the delay causes decreases in both kappa number and viscosity, the relative sizes of these decreases being given by the slope of the lines in Figure 1. Changing the order from Z/D to D/Z decreases the kappa

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number while at the same time causing a decrease in viscosity that is greater than the viscosity decrease that results when the same kappa number decrease is obtained by increasing the delay. In other words, \((Z/D)(EPO)\) gives a higher viscosity at a given kappa number than \((D/Z)(EPO)\). Similarly, lower ozone concentration in the gas stream gives a higher viscosity at a given kappa number than high ozone concentration. This is because increasing ozone concentration has no effect on kappa number, but decreases viscosity. It may be concluded from this analysis that, within the range investigated, the best results will be obtained by applying \(O_3\) first, adding \(ClO_2\) 15 minutes after \(O_3\), and applying \(O_3\) as a low-concentration mixture with \(O_2\). From a more practical point of view, because the effects of concentration and delay are both relatively small, it may be concluded that an \(O_2\) stream containing \(O_3\) at higher concentration can be used with a delay of only one minute between chemical additions. Ozone should nevertheless be added before \(ClO_2\).

![Figure 1. Viscosity vs. kappa number for \((D/Z)(EPO)\) and \((Z/D)(EPO)\) bleaching of southern pine kraft brownstock. The variation in kappa number is due to changes in the elapsed time between \(ClO_2\) and \(O_3\) additions.](image)

Brightness
The brightness of the pulp was affected by the experimental variables in ways which correlate directly with the corresponding effects on kappa number. As in the case of kappa number, the only significant variables were order of addition (92% confidence) and time delay (91% confidence). \(D/Z\) gave a brightness that was, on average, 1.7 points higher than \(Z/D\). Delaying addition of the second chemical for 15 min gave a brightness that was 1.7 points higher than when the delay was only one minute.

Figure 2 shows that the relationship between brightness and kappa number is relatively unaffected by the variables investigated, although the data suggest that decreasing the \(O_3\) concentration may increase the brightness at a given kappa number.
A second set of experiments, exactly analogous to those described above, were conducted on a sample of the same pulp which had been oxygen delignified prior to ($D/Z$)(EPO) or ($Z/D$)(EPO) bleaching. The results are shown in Table II. The oxygen stage was conducted at 10% consistency and 110°C with an oxygen pressure of 60 psig and a caustic charge of 2% NaOH, with addition of 0.05% MgSO₄. The oxygen delignified pulp had a kappa number of 11.8 and a viscosity of 18.4. The kappa number was reduced from 11.8 to 3.3 in the control $D_0$(EPO) partial sequence, while at the same time the brightness was increased to 68 and the viscosity was reduced to 17.5. When half of the ClO₂ was replaced by ozone, the decrease in kappa number was only slightly smaller, the kappa number after extraction being in the range 3.4 - 4.4. Similarly, the brightness increase was only slightly smaller, the final brightness being in the range 62 - 68. The viscosity decrease was larger than in the case of $D_0$(EPO) bleaching, the viscosity after extraction being in the range 13-16. Within these ranges, there were again significant effects of the three experimental variables.

![Figure 2. Brightness vs. kappa number for ($D/Z$)(EPO) and ($Z/D$)(EPO) bleaching of southern pine kraft brownstock.](image)

**Figure 2.** Brightness vs. kappa number for ($D/Z$)(EPO) and ($Z/D$)(EPO) bleaching of southern pine kraft brownstock.

**Kappa Number**

Analysis of the kappa number data of Table II showed that two of the three variables were statistically significant at a confidence level greater than 90%. These were order of addition (98% confidence) and ozone concentration (91% confidence). $D/Z$ gave an extracted kappa number that was, on average, 0.5 units lower than $Z/D$. An ozone concentration of 6.5% gave a kappa number that was 0.3 units lower than when the concentration was only 2%. Comparison of these effects with those described above for the same pulp without oxygen delignification shows that the response of the two pulp types is somewhat different. Increasing the delay time caused a small but significant decrease in kappa number for the brownstock, but
had no significant effect on the kappa number in the case of the oxygen delignified pulp. Ozone concentration had no effect on kappa number in the former case while in the case of the oxygen delignified pulp increasing the ozone concentration significantly decreased the kappa number after extraction.

Table II. (D/Z)(EPO) and (Z/D)(EPO) Bleaching of Oxygen-Delignified Southern Pine Kraft Pulp

<table>
<thead>
<tr>
<th>Kappa Substitution, %</th>
<th>Ozone Chemical Added Time Before</th>
<th>Ozone Conc. In</th>
<th>Total Viscosity, mPa.s</th>
<th>Time, min</th>
<th>pH in</th>
<th>pH out</th>
<th>Kappa No.</th>
<th>Brightness</th>
</tr>
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<tbody>
<tr>
<td>0.2</td>
<td>0 n.a.</td>
<td>45</td>
<td></td>
<td>2.7</td>
<td>3.3</td>
<td>67.8</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>ClO₂</td>
<td></td>
<td></td>
<td>2.3</td>
<td>2.6</td>
<td>3.8</td>
<td>64.7</td>
<td>13.2</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>15</td>
<td>16</td>
<td>4</td>
<td>4</td>
<td>62.3</td>
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<td>2.6</td>
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</tr>
<tr>
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<td>15</td>
<td>6.5</td>
<td>30</td>
<td>3</td>
<td>2.6</td>
<td>4.3</td>
<td>64.8</td>
</tr>
</tbody>
</table>

Notes: 1. O₂-delignified pulp: mill southern pine, kappa no. 11.8; viscosity 18.4 mPa.s
2. D/Z stage conditions: 3.5% cond'y, 50°C, CRS Reactor, mixing speed 1500 rpm during O₂ addition
3. (EPO) stage conditions: 10% cond'y, 70°C, 60 min, O₂ press. 60-0 psig over first 30 min.
4. (EPO) stage chemical charges, % o.d. pulp: NaOH, 1.5; H₂O₂ 0.5

As in the case of the brownstock, the effects, though statistically significant, are small. They may not significantly constrain bleach plant design, since delay time is unimportant and Z/D works almost as well as Z/D. The existence of a positive effect of ozone concentration on delignification is fortunate, since using a high concentration may also be expected to decrease ozone generation and equipment costs. Comparison with the D₀(EPO) control shows that, unlike brownstock, the oxygen delignified pulp responds almost as well to the D/Z and Z/D stages as to the D₀ stage.

Viscosity

Analysis of the post-extraction viscosity data of Table II showed that, of the three variables investigated, only ozone concentration had a significant effect (91% confidence). An ozone concentration in the gas stream of 6.5% gave a viscosity that was 1.4 units higher than when the concentration was only 2%.

The relationships between viscosity and kappa number after bleaching the oxygen delignified pulp are shown in Figure 3. Changing the order from Z/D to D/Z slightly decreases the kappa number but does not affect the viscosity. Increasing the ozone concentration has beneficial effects on both kappa number and viscosity, while the time delay before adding the second chemical affects neither viscosity or kappa number. As a result of these effects, there is a significant beneficial effect of increasing ozone concentration on viscosity at any given kappa number within the range studied. This is a desirable result, in view of the desirability of high concentrations from a plant design standpoint. It differs from the result obtained with untreated brownstock. In that case, increasing ozone concentration had a small detrimental effect on viscosity at a given kappa number. After oxygen delignification, and within the range investigated, the best results will be obtained by applying ClO₂ first, adding O₂ 1 minute after ClO₂, and applying O₂ as a high-concentration mixture with O₂. Fortuitously, these conditions are also favored by plant design consideration.

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Brightness
The brightness of the oxygen delignified pulp was not significantly affected by the experimental variables, but did exhibit the expected correlation with kappa number, as shown in Figure 4. This figure suggests that using low concentration ozone after ClO₂ may lead to lower brightness.

Comparison of the Responses of Brownstock and Oxygen Delignified Pulp
As indicated above, oxygen delignification significantly affected the response of the pulp to D/Z and Z/D bleaching. Partial substitution of ozone for ClO₂ is not as effective in the bleaching of brownstock as it is after an oxygen delignification stage. Figure 5 shows that (D/Z)EPO or (Z/D)(EPO) bleaching of oxygen delignified pulp gave significantly lower extracted kappa number than the corresponding treatment of brownstock. The viscosities thus obtained are only slightly lower, at a viscosity that is only slightly lower than those obtained with brownstock, and are probably sufficiently high that no detrimental effect on pulp strength is to be expected. After oxygen delignification, the viscosity and kappa number of the (D/Z)(EPO) and (Z/D)(EPO) pulps compare reasonably well with the corresponding properties of the D₀(EPO) control pulp. The corresponding comparison is not as favorable in the case of pulp which has not been oxygen delignified.

Figure 6 shows that oxygen delignification does not have any major effect on the relationship between brightness and kappa number.

![Figure 3. Viscosity vs. kappa number for (D/Z)(EPO) and (Z/D)(EPO) bleaching of oxygen delignified southern pine kraft pulp.](image-url)
Figure 4. Brightness vs. kappa number for (D/Z)(EPO) and (Z/D)(EPO) bleaching of oxygen delignified southern pine kraft pulp.

Figure 5. Viscosity vs. kappa number for (D/Z)(EPO) and (Z/D)(EPO) bleaching of untreated and oxygen delignified southern pine kraft pulps.
Figure 6. Brightness vs. kappa number for (D/Z)(EPO) and (Z/D)(EPO) bleaching of oxygen delignified southern pine kraft pulp.

Conclusions

Under the conditions of this study, combinations of O$_3$ and ClO$_2$ are slightly less effective than an equivalent amount of pure ClO$_2$ in the first stage of bleaching southern pine kraft brownstock that has not previously been oxygen delignified. This is true when the kappa factor is 0.20, 50% of the ClO$_2$ is replaced by the theoretically equivalent amount of O$_3$ (0.6kg O$_3$/kg ClO$_2$) and the first stage is followed by an (EPO) stage. Adding the ClO$_2$ before the O$_3$ (using D/Z instead of Z/D) gives a slightly lower kappa number and a lower viscosity, both the kappa number and the viscosity being measured after the (EPO) stage. Regardless of which chemical is added first, a delay of only one minute before adding the second gives a kappa number only slightly higher than when addition of the second chemical is delayed for 15 minutes. In addition, the shorter delay gives a higher viscosity. Using an O$_3$-containing gas stream that contained 6% O$_3$ gave a viscosity that was slightly lower than when the O$_3$ concentration was only 2%. Considering the size of the various effects, it may be concluded that reasonably good combinations of post-extraction kappa number and viscosity can be obtained by first injecting O$_3$ at a 6% concentration in O$_2$ and, after a delay of only one minute, adding ClO$_2$. In the present study, this operating strategy gave kappa number 6 and viscosity 17 mPa.s, while the use of an equivalent amount of pure ClO$_2$ gave kappa number 4 and viscosity 21 mPa.s.

In the bleaching of pulp which has been previously delignified with oxygen but is otherwise similar, the response of the pulp is different. The combination of O$_3$ and ClO$_2$ is nearly as effective as an equivalent amount of pure ClO$_2$. Changing the order from Z/D to D/Z slightly decreases the kappa number but does not affect the viscosity. Regardless of which chemical is added first, a delay of only one minute before adding the second gives virtually the same kappa number and viscosity after extraction as when addition of the second chemical is delayed for 15 minutes. Using ozone at a concentration of 6.5% gives a lower kappa number and a higher viscosity than when the concentration is only 2%. It may be concluded that good combinations of post-extraction kappa number and viscosity can be obtained by first injecting O$_3$ at a 6%
concentration in O₂ and, after a delay of only one minute, adding ClO₂. In the present study, this operating strategy gave kappa number 4 and viscosity 16 mPa.s, while the use of an equivalent amount of pure ClO₂ gave kappa number 3 and viscosity 18 mPa.s.
Partial Substitution of Ozone for Chlorine Dioxide in the First Stage of Hardwood Kraft Pulp Bleaching Sequences
T.J. McDonough, A. Shaket and C.E. Courchene

Introduction
Application of combinations of O₃ and ClO₂ to hardwood pulp was investigated in experiments with a mill kraft pulp made from mixed southern U.S. hardwood (mainly gum and oak). A few experiments were also done pulp from pulp sampled after the oxygen delignification stage at the same mill. The main objective of the experiments was to determine the effects of mixing speed and substitution level on the kappa number, viscosity and brightness of the pulp after the subsequent oxygen- and peroxide-reinforced extraction (EPO) stage. In all experiments, a kappa factor of 0.20 was used and washer inefficiency was simulated by carrying 1% black liquor solids into the first stage and carrying 10% of the filtrate from the first stage into the (EPO) stage.

Results and Discussion
Figure 7 shows the results of varying the mixer speed and substitution level on the kappa number after the extraction stage. In obtaining the data shown in Figure 7, we had intended that the second set of four experiments (representing the four combinations of the two substitution levels, 25% and 75%, with the two mixer speed levels, 500 and 1500 rpm) be exact replicates of the first such set of four. However, after noting that the (EPO) stage exit pH was lower than desired in the first set, we decided to increase the caustic charge, from 1% to 1.25%. Surprisingly, this apparently resulted in an increase in extracted kappa number when the substitution level was only 25%, although it had little effect at 75% substitution. It

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appears likely that the difference between replicates at 25% substitution was not due to the change in (EPO) stage pH but was rather due to experimental error associated with accurately delivering the small amount of ozone required at the low substitution level.

This observation aside, it is clear from Figure 7 that there was a significant effect of increasing the mixer speed from 500 to 1500 rpm, especially when 75% of the ClO\textsubscript{2} had been substituted by ozone, and that there was no significant effect of substitution when the mixer speed was sufficiently high. The latter observation is more apparent in Figure 8, which plots extracted kappa number against substitution for experiments conducted at 1500 rpm. It may be concluded that substantial fractions of the ClO\textsubscript{2} in a hardwood kraft pulp delignification stage may be replaced with ozone without decreasing the extent of delignification achieved.

![Graph](graph.png)

Figure 8. Effect of ozone substitution on kappa number after \((D/Z)(EPO)\) delignification of hardwood kraft pulp.

The effects of substitution and mixer speed on viscosity are illustrated by the data of Figure 9. Neither variable had much effect on viscosity, although the data suggest that it may be possible to increase viscosity by decreasing the pH of the (EPO) stage when the substitution is low. The most important conclusion to be drawn from Figure 9 is that substitution of ozone for a large fraction of the ClO\textsubscript{2} has no detrimental effect on viscosity in the bleaching of hardwood pulp. The viscosity of the unbleached pulp was 32 mPa\textsecond, so the observed values after \((D/Z)(EPO)\) represent a modest loss. No corresponding measurement of D(EPO) viscosity is available for comparison, but the corresponding D(EPO) pulp after completing the D(EPO)DED sequence had a viscosity of 20.4 mPa\textsecond. This supports the conclusion that substituting O\textsubscript{3} for ClO\textsubscript{2} had no detrimental effect on pulp viscosity.

The corresponding effects on pulp brightness after the (EPO) stage to some extent paralleled those on kappa number. However, increasing the substitution level from 25% to 75% decreased the brightness at a given kappa number by approximately 5 points, as shown in Figure 10.
Figure 9. Effects of mixer speed, ozone substitution and (EPO) stage exit pH on pulp viscosity after (D/Z)(EPO) delignification of hardwood kraft pulp.

Figure 10. Brightness-kappa-number relationships after (D/Z)(EPO) delignification of hardwood kraft pulp.
Conclusions
In the D0(EPO) bleaching of hardwood kraft pulp, substitution of O₂ for 25–75% of the ClO₂ in the first stage has little or no effect on either the viscosity or the kappa number of the pulp after the extraction stage, provided that the ozone is efficiently mixed with the pulp. However, increasing the substitution level from 25% to 75% decreased the brightness at a given kappa number by approximately 5 points.
Effects of Digester Conditions on the Bleachability of Southern Pine Kraft Pulp

T.J. McDonough, A.J. Bacon and M. Turner

Introduction

As described in previous reports on this project, we have shown that there are relationships between pulping conditions and the bleaching behavior of the resulting pulps. For example, in the bleaching of hardwood pulps, increasing the effective alkali charge increases the brightness achievable in a 3-stage sequence by 4-5 points.2 In a related project, we have shown that similar, if less pronounced, effects exist in the bleaching of softwoods and that the response of softwood pulp to oxygen delignification can be adversely affected if the effective alkali charge and sulfidity are too low.

The purpose of the work described here was to assess the effects of varying pulping conditions over a wide range on the response of the resulting pulp to delignification with ClO₂ and alkali. The pulps were prepared in an M/K Systems digester under varied conditions of liquor-to-wood ratio, effective alkali (EA) charge, sulfidity, temperature and H-factor. We chose relatively mild conditions for these bleaching stages, in an effort to maximize the likelihood of detecting effects of the pulping variables. Thus, we used a relatively low kappa factor, 0.15, and a simple extraction with alkali, rather than an extraction fortified with oxygen and/or peroxide. The DE-delignified pulps were characterized by measuring the kappa number and brightness of each, and the combined filtrates from the two bleaching stages were characterized by determinations of chemical oxygen demand (COD) and total organic carbon (TOC).

Results and Discussion

The pulping conditions used and the properties of the resulting pulps are shown in Table III, while the bleaching results are contained in Table IV. In spite of efforts to choose H-factors that would result in similar unbleached kappa numbers, this was made difficult by the extremely wide range of pulping conditions employed, and a range of kappa numbers was obtained. This was taken into account during the analysis of the data by including unbleached kappa number as one of the independent variables and employing multiple regression techniques.

Kappa Number After DE

Figure 11 shows the kappa number after DE bleaching as a function of unbleached kappa number and pulping conditions. Multiple regression analysis and deletion of non-significant terms gave the equation shown on the figure. In this equation, the variable XS is defined so that it is a linear function of sulfidity, taking a value of -1 when the sulfidity is 16% and +1 when the sulfidity is 39%. Similarly, the variable XEA has a value of -1 when the EA charge is 15% and +1 when the EA charge is 21%. The equation indicates that when both of these variables are increased from their low values to their high values, the kappa number obtained after DE bleaching may be expected to decrease by 0.6 units. At the lower end of the unbleached kappa number range, this amounts to a reduction in the DE kappa number of slightly less than 10%. It is concluded that lignin removal during DE bleaching is favored by high alkali charge and high sulfidity during pulping.

Unbleached Pulp Brightness

Analysis of the post-extraction brightness data must take into account the fact that unbleached pulp brightness is affected by changes in pulping variables, as shown in Figure 12. Multiple regression analysis of the unbleached brightness data gave the equation shown on the figure. In this equation, the variable XLW is defined so that it is a linear function of liquor-to-wood ratio, L/W, taking a value of −1 when L/W is 4.6 and +1 when L/W is 7.4. The equation reveals significant positive effects of EA charge (99.99+% confidence) and sulfidity (98.7% confidence), as well as negative effects of unbleached kappa number (99.99+% confidence) and liquor-to-wood ratio (99.1% confidence). The effects of EA and unbleached kappa number are well-known, but the smaller effects of sulfidity and liquor-to-wood ratio are not believed to have been previously reported. The negative direction of the latter effect is somewhat surprising, in view of the expectation that higher lignin concentration would result in lower brightness due to more extensive re-deposition. The existence of the opposite effect suggests that re-deposition is not a major factor and that the higher residual alkali concentration at lower liquor-to-wood ratio may lead to higher brightness. The combined effects of the significant pulping variables amount to as much as 6 points in brightness at any given unbleached kappa number within the range investigated.

Table III. Conditions used to prepare pulps and unbleached pulp properties.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Liquor-to Wood Ratio</th>
<th>Effective Unbl. Alkali, % o.d.w.</th>
<th>Sulfidity, %</th>
<th>Temp., °C</th>
<th>Kappa Number</th>
<th>Viscosity, mPa.s</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>7.38</td>
<td>21</td>
<td>39</td>
<td>175</td>
<td>29.3</td>
<td>45.8</td>
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<td>21</td>
<td>16</td>
<td>175</td>
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<tr>
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<td>42.1</td>
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<td>25.0</td>
<td>38.5</td>
</tr>
</tbody>
</table>

Brightness After DE

The effects of the pulping variables on pulp brightness after the DE stages are illustrated in Figure 13. Multiple regression analysis of the DE brightness data revealed significant positive effects of EA charge (99.99+% confidence) and sulfidity (99.99+% confidence), as well as negative effects of unbleached kappa number (99.99+% confidence) and the interaction between sulfidity and liquor-to-wood ratio (L/W, 94% confidence). The interpretation of the interaction effect is that the positive effect of sulfidity is greater at low L/W than at high L/W. The combined effects of the significant pulping variables are greater after DE

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### Table IV. DE Bleaching Results

<table>
<thead>
<tr>
<th>Unbl. Kappa Number</th>
<th>DE Kappa</th>
<th>DE Brtns. kg/admt</th>
<th>COD, kg/admt</th>
<th>TOC, kg/admt</th>
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</thead>
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<tr>
<td>16</td>
<td>25.0</td>
<td>8.2</td>
<td>39.5</td>
<td>40.9</td>
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</tbody>
</table>

Figure 11. Kappa number after DE bleaching of pulps prepared under different conditions of effective alkali charge and sulfidity. The lines represent values calculated from the regression equation with XS=XEA=1 (solid line, corresponding to filled, triangular data symbols) and XS=XEA=-1 (dashed line, corresponding to open, circular data symbols). EA = effective alkali charge, % o.d.w.; S = sulfidity, % act. alk.
Figure 12. Brightness of unbleached pulps prepared under different conditions of effective alkali charge, liquor-to-wood ratio and sulfidity. The solid lines represent values calculated from the regression equation with $XLW = -1$ and $XS = 1$ with $XEA = 1$ (upper solid line, corresponding to open triangles) and $XEA = -1$ (lower solid line, corresponding to open squares). The dashed lines were calculated for $XLW = 1$ and $XS = -1$ with $XEA = 1$ (upper, filled diamonds) and $XEA = -1$ (lower, filled circles). $L/W =$ liquor-to-wood ratio, other variable names as in Fig. 11.

bleaching than before. They amount to nearly 7 points in brightness at any given unbleached kappa number within the range investigated. Bleaching slightly diminishes the effect of EA and enhances the effect of sulfidity. The brightness difference between low-EA and high-EA pulps is less after DE bleaching than in the unbleached state. By contrast, the brightness difference between low-sulfidity and high-sulfidity pulps is greater after DE bleaching than in the unbleached state. In other words, increasing the sulfidity has a beneficial effect on DE bleach response that is additive with the beneficial effect on unbleached brightness. This was also apparent from a separate analysis aimed at relating the brightness after DE to the unbleached brightness and the pulping variables. This analysis produced an equation with only two statistically significant independent variables — unbleached brightness and sulfidity — that nevertheless fit the data quite well ($R^2 = 0.94$). It showed that, for any given unbleached brightness, the DE brightness of high sulfidity pulps is 1.7 units higher than low-sulfidity pulps.

The present results do not allow the observed effects to be associated with specific chemical changes. However, it seems reasonable to hypothesize that higher sulfidity improves bleachability by decreasing inter-unit carbon-carbon bond formation. This could occur, for example, as a result of increased rates of interception of reactive intermediates (such as quinone methides) by the hydrosulfide ion. Similar mechanisms could be proposed for brightness improvement through the prevention of chromophore formation.

Measurements of bleaching effluent characteristics were of interest in this study because of the possibility of identifying significant influences of pulping conditions on the environmental parameters of the bleach plant. In addition, such measurements can provide clues as to the mechanisms of observed effects and can...
Figure 13. Brightness of DE-bleached pulps prepared under different conditions of effective alkali charge, liquor-to-wood ratio and sulfidity. The solid lines represent values calculated from the regression equation with \( XLW = -1 \) and \( XS = 1 \) with \( XEA = 1 \) (upper solid line, corresponding to open triangles) and \( XEA = -1 \) (lower solid line, corresponding to open squares). The dashed lines were calculated for \( XLW = 1 \) and \( XS = -1 \) with \( XEA = 1 \) (upper, filled diamonds) and \( XEA = -1 \) (lower, filled circles). Variable names as in as in Fig. 11 and 12.

serve as indicators of effects on bleaching yield. Accordingly, we measured the chemical oxygen demand (COD) of the combined bleaching filtrates, as well as their total organic carbon (TOC) contents. The measurements were performed after mixing D and E stage filtrates in proportions representative of the relative volumes generated, as calculated from the respective stage consistencies (3.5 and 10%).

Multiple regression analysis of the COD data, with cooking conditions and kappa number decrease as independent variables, gave the equation shown and plotted in Figure 14. In the equation, the variable \( XT \) is defined so that it is a linear function of cooking temperature, \( T \), taking a value of -1 when \( T \) is 165°C and +1 when \( T \) is 175°C. There were significant effects of kappa number decrease (99.99+% confidence) and EA charge, which also exhibited a significant interaction with temperature (98.3% confidence). The interaction effect arises from the fact that the negative effect of alkali is greater at low temperature. In other words, cooking with high EA charge causes slightly less COD to be formed when the pulp kappa number is decreased by a given amount, but only if the cooking temperature is not too high.

Analysis of the corresponding TOC data gave somewhat different results, as shown in Figure 15. The only statistically significant factor (other than kappa decrease) was the interaction between EA charge and temperature (99.8% confidence) but the effect was in the opposite direction to that observed for COD. It reflects an increase in TOC release during bleaching when the EA charge is increased at low cooking temperature, and a decrease in TOC when the EA charge is increased at high temperature. Examination of the individual data points suggests possible undue influence by the high-EA, low-temperature data point at high kappa decrease (the rightmost open triangle in Figure 15). Omitting it diminishes the measured effect of alkali at low temperature. This suggests that the low-EA, high-temperature pulp differs from the rest by
releasing less TOC during bleaching. This is apparently inconsistent with the observed effects of cooking conditions on COD release. Pulp from low-EA, high-T cooks releases less TOC during bleaching, but not less COD. This suggests that the TOC released from such pulps is less oxidized and therefore has a higher COD per unit of TOC.

![Figure 14. COD of combined filtrates from bleaching of pulps prepared under different conditions of effective alkali charge and temperature. The lines represent values calculated from the regression equation shown with XEA = -1 and XT = -1 (upper, dashed line, corresponding to open circles); XEA = -1 and XT = 1 (solid line, corresponding to filled circles); XEA = 1 and XT = -1 (line of dots and dashes, corresponding to open triangles); and XEA = 1 and XT = 1 (dotted line, corresponding to filled triangles). T = temperature, °C. Other variable names as in as in Fig. 11-13.](image)

**Conclusions**

1. Lignin removal during DE bleaching is favored by high alkali charge and high sulfidity during pulping.

2. Unbleached softwood kraft pulp brightness is higher when cooking is continued to lower kappa numbers. At a given kappa number the brightness may be increased by using higher alkali charge, higher sulfidity and lower liquor-to-wood ratio. The negative direction of the last effect suggests that re-deposition of lignin is not a major factor in determining unbleached brightness and that the higher brightness at lower liquor-to-wood ratio is due to higher residual alkali concentration.

3. Increasing sulfidity has a beneficial effect on DE bleach response that is additive with the beneficial effect on unbleached brightness. This may be due to a decrease in inter-unit carbon-carbon bond, as a result of increased rates of interception of reactive intermediates by hydrosulfide ion.

4. At low pulping temperature (165°C), cooking with high EA charge causes slightly less COD to be released during bleaching.

5. Pulp from low-EA, high-temperature cooks releases less TOC during bleaching, but not less COD. This suggests that the TOC released from such pulps is less oxidized and therefore has a higher COD per unit of TOC.
Figure 15. TOC of combined filtrates from bleaching of pulps prepared under different conditions of effective alkali charge and temperature. The lines represent values calculated from the regression equation shown with $X_{EA} = X_T = -1$ or $X_E = X_T = 1$ (solid line, corresponding to open circles and filled triangles); and $X_{EA} = -1$ and $X_T = 1$ or $X_{EA} = 1$ and $X_T = -1$ (dotted line, corresponding to filled circles and open triangles). Variable names as in Fig. 11-14.
Hydrogen Peroxide Delignification of Softwood Kraft Brownstock
T.J. McDonough, C.E. Courchene and M. Alger

Introduction
Bleach plant modifications that will decrease loadings of AOX and other mill effluent parameters are of interest to many mills, as a result of the need to comply with stricter environmental regulations. Oxygen delignification can effectively improve bleach plant effluent quality by decreasing the residual lignin content of the unbleached pulp, but the necessary equipment is expensive, in part because of the need for a pressurized reactor. Delignification with hydrogen peroxide instead of oxygen, if sufficiently effective, would accomplish the same degree of delignification without requiring a pressurized reactor and would require correspondingly less capital expenditure, especially if existing equipment could be utilized. Although this is not a new idea, it bears re-examination, in the light of recent advances in technology for effectively removing trace metal impurities from the unbleached pulp with chelating agents. Combinations of advanced chelation and peroxide stages (QP partial sequences) have been thoroughly investigated for use following oxygen delignification, but there has been relatively little investigation of their use instead of oxygen delignification.

As part of a study aimed at defining relationships between pulping conditions and bleachability, we have previously subjected pulps prepared under a variety of digester conditions to peroxide delignification. The results, as described in the March 1998 PAC report, showed that the more responsive pulps were readily delignified by as much as 70% with 3% hydrogen peroxide after an effective chelation stage. Since then, we have followed up with some additional work to determine dose-response relationships, and to investigate possibilities for improving the effectiveness of the peroxide stage.

Results and Discussion
Figure 16 shows the results of delignifying four different southern pine kraft pulps with H\textsubscript{2}O\textsubscript{2} and NaOH after chelation with 0.5% EDTA at pH 6 and 90\(^\circ\)C and 10% consistency for 60 min. The peroxide stages were, unless otherwise noted, done at 80\(^\circ\)C for 4 h at 10% consistency, exit pH 11.5 – 12, in the presence of 0.5% MgSO\textsubscript{4} and 0.2% DTPA. The different pulps responded differently to delignification with 3% H\textsubscript{2}O\textsubscript{2}, with degrees of delignification ranging from 54% to 68%. Pulp X, from which 68% of the lignin was removed, was a 28 kappa laboratory pulp. Pulp B, 60% delignified, was a 29 kappa lab pulp. Pulp A, 54% delignified, was a 24 kappa mill pulp. Pulp C, also 54% delignified was a 34 kappa lab pulp. These data suggest that delignification, expressed as a percentage, is greater for lab pulps than mill pulps, and greater for lower-kappa pulps.

When the peroxide charge was decreased, the response was dependent on alkalinity. When the alkalinity was maintained sufficiently high, the response of the 24 kappa mill pulp (Pulp A) fell off only gradually when decreasing the charge from 3% H\textsubscript{2}O\textsubscript{2} to 2%, but more sharply in going from 2% to 1%. Delignification fell to 49% at a charge of 2% H\textsubscript{2}O\textsubscript{2}, and to 36% at a charge of 1% H\textsubscript{2}O\textsubscript{2}. In the case of pulp C, which differed by having a higher unbleached kappa number (34) delignification fell approximately linearly, to 42% and 29% as the H\textsubscript{2}O\textsubscript{2} charge was progressively decreased to 1%. It may be concluded that a charge of 1% H\textsubscript{2}O\textsubscript{2} can remove about one-third of the lignin in unbleached softwood kraft pulp, following an efficient chelation stage.

Like oxygen delignification, peroxide delignification reduces pulp viscosity. However, the viscosity loss is unlikely to limit the extent of delignification practiced, which is more likely to be fixed by the cost of H\textsubscript{2}O\textsubscript{2}. Figure 17 shows the kappa viscosity relationships for the bleaching of Pulps A (kappa 24) and C (kappa 34). The latter pulp's initially higher viscosity decreased much more rapidly with decreasing kappa number, so that the two pulps, after delignification to kappa 16, had similar viscosities, approximately 21 mPa.s. Experience indicates that such a viscosity reduction would not be accompanied by a bleached pulp strength reduction. Pulp A lost viscosity only gradually at kappa numbers down to 12.
Figure 16. Delignification of four different southern pine kraft pulps with H$_2$O$_2$ following chelation with EDTA. All pulps except pulp A, which was a mill pulp, were made in the laboratory. The kappa numbers of Pulps A, B, X, and C were, respectively, 24, 29, 28 and 34.

Figure 17. Viscosity vs. kappa number in the delignification of southern pine kraft pulps with H$_2$O$_2$ following chelation with EDTA. Pulp designations as in the caption for Figure 16.

Earlier work in our laboratory$^4$ showed that addition of manganese ion, as Mn$^{2+}$, had the surprising effect of preventing viscosity loss during H$_2$O$_2$ delignification without serious loss of delignification. Figure 18 shows the


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results of experiments with Mn addition during the current investigation, for comparison with the results presented
above. The data in this figure for pulps A and C are the same as those described above. The remaining data points
are from experiments in which the unbleached pulp was first acid-washed (H$_2$SO$_4$, pH 1.5, 2% consistency, 30 min,
50°C), and then equilibrated with a solution of MnCl$_2$ at 1% consistency, overnight at 5°C. The concentration of
the solution was chosen to result in a Mn content of 40 – 130 ppm in the pulp after dewatering to 20% consistency.
Delignification was reduced from 54% to 39%, while viscosity loss was completely eliminated. This confirms the
results we reported earlier, except that the loss in delignification was slightly greater than expected on the basis of
the earlier results. It is hypothesized that the added manganese ion rapidly converts the
H$_2$O$_2$ to one or more species
that are highly reactive towards lignin but unreactive towards carbohydrate. The following mechanism is proposed:

\[
\begin{align*}
H_2O_2 + Mn^{2+} & \rightarrow HO\cdot + HO^- + Mn^{3+} \quad (1) \\
HO\cdot + Mn^{2+} & \rightarrow HO^- + Mn^{3+} \quad (2) \\
H_2O_2 + HO^- & \rightarrow HO_2^- + H_2O \quad (3) \\
HO_2^- + Mn^{3+} & \rightarrow HO_2\cdot + Mn^{2+} \quad (4) \\
HO_2\cdot + HO^- & \rightarrow O_2 + H_2O \quad (5) \\
O_2\cdot + Lignin & \rightarrow \text{Oxidized Lignin} \quad (6) \\
O_2\cdot + HO\cdot & \rightarrow O_2 + HO^- \quad (7) \\
O_2\cdot + Mn^{3+} & \rightarrow O_2 + Mn^{2+} \quad (8)
\end{align*}
\]

Previously, we observed that viscosity retention increased with increasing levels of Mn$^{2+}$ addition, until a level of
Mn$^{2+}$ addition was reached that completely eliminated viscosity loss. (In the present study the levels of Mn$^{2+}$
addition were above the critical level.) The above mechanism explains this observation in terms of efficiency of
hydroxyl radical scavenging by Mn$^{2+}$ (Equation 2), which prevents hydroxyl radical attack on cellulose. Ionization
of H$_2$O$_2$ furnishes hydroperoxide anion (Equation 3), which is oxidized to the perhydroxyl radical by Mn$^{3+}$
(Equation 4). The latter is acidic (pK$_a$ = 4.8) and immediately dissociates to form superoxide radical anion, O$_2\cdot$
(Equation 5), which is proposed to be the active delignifying species (Equation 6). Superoxide also leads to
decomposition, by conversion of peroxic oxygen to molecular oxygen (Equations 7 and 8), which results in loss of
peroxide and the observed decrease in extent of delignification. Attempts will be made to use the insight provided by
these observations to increase the effectiveness of metal-ion-modified peroxide delignification systems.

Figure 19 shows the results of a series of experiments with Mn$^{2+}$ addition to acid-washed pulp similar to those
described above, except that the retention time in the peroxide delignification stage was varied. The complete
prevention of viscosity loss by manganese is apparent. It is also apparent that the rate of delignification in this
system is slow after the first few minutes. It is noteworthy that only a trace of residual peroxide remained after 5
minutes and that the peroxide was completely absent after 15 minutes. It may be concluded that much of the
observed decrease in kappa number is not due to oxidation, but rather to diffusion of oxidized lignin fragments from
the fiber wall.
Figure 18. Viscosity vs. extent of delignification in the delignification of southern pine kraft pulps with H₂O₂ following chelation with EDTA (Pulps A and C) or acid washing and Mn⁺² addition (Pulp C, AW + Mn). Pulp designations as in the caption for Figure 16.

Figure 19. Kappa number and viscosity vs. retention time in the delignification of southern pine kraft pulps with H₂O₂ following acid washing and Mn⁺² addition. Pulp designations as in the caption for Figure 16.

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Conclusions

1. Combinations of advanced chelation and peroxide stages (QP partial sequences) may be useful as a low-capital alternative to oxygen delignification of softwood kraft brownstock. A charge of 1% $\text{H}_2\text{O}_2$ can remove about one-third of the lignin in unbleached softwood kraft pulp, following an efficient chelation stage.

2. Loss of pulp viscosity during peroxide delignification can be completely eliminated by addition of manganese ion. This may occur through trapping of hydroxyl radicals by $\text{Mn}^{2+}$ and generation of the delignifying species, superoxide radical anion, by $\text{Mn}^{3+}$ oxidation of hydroperoxide anion, followed by dissociation of the resulting perhydroxyl radical. Superoxide radical anion also reacts with $\text{Mn}^{3+}$ and hydroxyl radical to form molecular oxygen, effectively decomposing hydrogen peroxide. This decomposition limits the extent of delignification and compromises the immediate practical application of manganese addition in peroxide delignification stages. However, new insights provided by the observation and its likely mechanism increase the chances that further research will yield useful results.
Effects of Pulping and Bleaching Processes on Pulp and Fiber Properties
C. Courchene, J. Waterhouse, T. McDonough, M. Bliss, B. Carter

Introduction
A joint project between the Chemical and Biological Sciences (CBSD) and Fiber and Paper Physics (FFPD) Divisions has been underway to characterize the effects of delignification and bleaching processes on fiber properties. The initial work has been defined to include conventional kraft batch pulping, oxygen delignification, and both CED and DED bleaching.

Kraft pulps from southern pine chips have been prepared at Kappa nos. of 110, 28, and 17. The kappa 28 pulp has been further delignified in a medium-consistency oxygen stage to kappa nos. of 20, 15, 12, and 10. The 28 and 17 kraft pulps and the four oxygen-delignified pulps were bleached with both a CED and a DED sequence with a constant kappa factor and ClO₂ charge in D₁.

The fiber and handsheet properties from both the brownstock and bleached pulps were measured by FFPD on both an unrefined and refined (PFI mill - 3000 revolutions) samples. The evaluation by the FFPD is reported under the dues-funded project F024.

Results and Discussion

Pulping
Kraft pulps were prepared from a sample of southern pine chips acquired from a mill and screened on a Williams round hole chip screen at IPST. The +1/4" and -1" fractions were retained for all cooks. Pulping was done in a 10 L M/K digester with external liquor circulation and heating. All cooks were done at a 4:1 liquor:wood ratio, heat-up from 100 to 170°C in 90 minutes, and time at 170°C varied for a desired H-factor. The cooking results are shown in Table IV.

<table>
<thead>
<tr>
<th>Active Alkali %</th>
<th>Sulfidity %</th>
<th>H-factor</th>
<th>Total Yield %</th>
<th>Screened Yield %</th>
<th>Kappa No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.5</td>
<td>30</td>
<td>400</td>
<td>56.7</td>
<td>52.8</td>
<td>110</td>
</tr>
<tr>
<td>18.8</td>
<td>30</td>
<td>1250</td>
<td>44.0</td>
<td>43.6</td>
<td>28.1</td>
</tr>
<tr>
<td>25.0</td>
<td>25</td>
<td>1250</td>
<td>42.4</td>
<td>42.0</td>
<td>17.0</td>
</tr>
</tbody>
</table>

After cooking the chips were removed from the digester in a basket. The kappa 110 chips were defibered by refining in a 12" laboratory disc refiner at 0.020" gap. The other pulps were defibered by diluting in a tank and agitating. The defibered pulps were then screened on a Sprout Waldron flat screen with 0.006" slots. The accepts and rejects were collected separately and the dry weight determined for screened yield and % reject determinations. Multiple cooks at kappa 28 were done to provide enough pulp for a series of oxygen delignification runs. The kappa 110 pulp was included in this study by FFPD for a comparison and not much comment is made about it here.

Oxygen Delignification
The kappa 28 kraft pulp was further delignified with a medium-consistency oxygen stage in a pressurized peg mixer with a horizontal rotating shaft. The constant conditions were 10% consistency, 100°C, 90 psig O₂, and 0.05% Mg²⁺.
Multiple runs were done at each caustic level with the pulp composited for additional testing and bleaching. The results are shown in Table V.

Table V. Oxygen Delignification Results

<table>
<thead>
<tr>
<th>NaOH %</th>
<th>Delignification %</th>
<th>Composite Kappa No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>27.4</td>
<td>20.4</td>
</tr>
<tr>
<td>1.45</td>
<td>44.1</td>
<td>15.7</td>
</tr>
<tr>
<td>2.30</td>
<td>56.9</td>
<td>12.1</td>
</tr>
<tr>
<td>2.70</td>
<td>61.9</td>
<td>10.7</td>
</tr>
</tbody>
</table>

Bleaching

Bleaching of the 28 and 17 kappa kraft pulps and each of the oxygen-delignified pulps was done with both CED and DED sequences with the bleaching conditions shown in Table VI.

Table VI. Bleaching Conditions

<table>
<thead>
<tr>
<th>Consistency, %</th>
<th>C or D</th>
<th>E</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>45</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Time, min.</td>
<td>30</td>
<td>60</td>
<td>180</td>
</tr>
<tr>
<td>Chemical</td>
<td>0.2 KF</td>
<td>0.55x act. Cl₂</td>
<td>1.2% ClO₂</td>
</tr>
</tbody>
</table>

Pulp Properties

Pulp properties measured on the unrefined samples are shown in Table VII.

Based on the final brightness values, the CED sequence is more effective than DED at an equivalent total active chlorine applied. The brightness for the kappa 28 DED appears lower than expected and needs to be confirmed. It appears that following oxygen delignification, the DED sequence may be even less effective than CED. This is believed to result from the similar reactions of oxygen and chlorine dioxide with phenolic hydroxyl groups on lignin that would make ClO₂ less effective when it follows an oxygen stage.

The bleached pulp viscosities decrease with the brownstock kappa number and are higher for the DED sequence than the CED. The viscosity vs. brownstock kappa no. is shown in Figure 20 and indicates the viscosity is primarily a function of the degree of delignification. The kraft pulp at 17.1 kappa has a lower kappa-viscosity relationship than the kraft-oxygen pulps. The DED pulps have a higher viscosity than the CED pulps for each brownstock.

All of the pulps were subjected to an ion exchange procedure with calcium ions so that they would have a common ionic nature for refining and physical testing. The ion exchange procedure involved an acid wash with HCl followed by soaking in a solution of 0.1M Ca²⁺ at a pH of 9.5. The metal ion content of the pulps was measured by ICP after an acid digestion. The Ca²⁺ content for each pulp is shown in Figure 21 for each pulp sample. For the brownstock kraft pulps, the Ca²⁺ content is directly related to the lignin content. For the kraft-oxygen pulps, the Ca²⁺ content is also related to the lignin content but the Ca²⁺ content is higher at a given kappa no. than it is for the kraft pulps. Bleaching with CED or DED reduces the Ca²⁺ content with the DED pulps having a somewhat higher amount.
The carboxyl content of the pulps was determined by a conductometric titration and is shown in Figure 22. The kraft-oxygen pulps have a higher carboxyl at a given kappa number than the kraft pulps. There does not appear to be a distinct difference in carboxyl content between CED and DED bleaching. The Ca\textsuperscript{2+} content appears to be generally correlated with the carboxyl content for the brownstocks.

**Refining**

The initial characterization of the pulps has been done with one level of refining at 3000 revolutions in a PFI mill according to CPPA procedure C.7. The measured pulp properties are shown in Table VIII.

The freeness (CSF) values of the initial and refined pulps are shown in Figure 23. The change in freeness after refining increases as the initial pulp kappa number decreases. There does not appear to be a difference in the refined freeness for the fully bleached pulps compared to the brownstock with the exception of the refined kappa 10.7 DED pulp. The lower freeness of this pulp is reflected in the higher fines content of 10.4% compared to 7-9% for the other refined pulps as shown in Table VIII. The fines were determined with the Britt jar procedure (TAPPI T261) with a 200 mesh screen.

The water retention value (WRV) as determined by TAPPI UM 256 was measured for both the whole pulps and samples where the fines were removed by the Britt jar. The WRV results for the whole pulps are shown in Figure 24. For the unrefined kraft brownstock pulps, the WRV increases with a decreasing kappa no. The unrefined oxygen-delignified pulps have a lower WRV than the corresponding kraft pulps but this difference seems to be gone after refining. The unrefined bleached pulps have a somewhat higher WRV than the brownstocks. Refining increases the WRV by approximately 20-30% for the kraft and bleached pulps and about 30-33% for the kraft-oxygen pulps.

The fines-free pulps were stained with both an iron and a palladium colloid. This procedure has been used to highlight changes in both internal and external fiber structures. The much smaller iron colloid is capable of penetrating cracks in the cell wall while the larger palladium colloid will attach to fiber surfaces. Following the staining procedure, the amount of iron or palladium in the samples was determined by ICP measurements and the results are shown in Table VIII. Some of the analyses have not yet been completed. For the unrefined kraft pulps, the iron content increase while the palladium content decreases with decreasing kappa no. The iron and palladium contents of the kraft-oxygen pulps do not appear to be related to the brownstock kappa no. As expected, the iron and palladium contents are significantly increased with refining due to increased internal cell wall fracture and external fibrillation. The increase on refining is not as great for the high kappa (110) pulp that refines more slowly than the other pulps as shown by the much higher refined freeness.

**Handsheet Properties**

Standard handsheets (60 g/m\textsuperscript{2}) were prepared from each of the brownstock and bleached pulps. The handsheet properties are shown Table IX.

The sheet densities were determined from soft-platen caliper measurements. The unrefined bleached pulps have higher densities than the brownstock pulps but the refined pulps do not show any difference. The increase in sheet density from refining is 30-35% for the brownstock and 20-30% for the bleached pulps.

The scattering coefficient as a function of sheet density is shown in Figure 25. As expected, the trend is for the scattering coefficient to decrease with increasing sheet density. The decrease in scattering coefficient with increasing sheet density is greater for the unrefined samples than it is for the refined samples.

The tear index values for each of the pulp samples are shown in Figure 26. For the unrefined pulps, the tear index is highest for the kappa 28 pulp. The kraft-oxygen brownstock pulps have a lower unrefined tear index than the kraft pulps but this difference is not evident after refining. Curl measurements that were made on some of the pulps show that the kraft-oxygen pulps have a considerably higher degree of curl that was induced in the fiber from the processing equipment used for the oxygen delignification. The lower tear and tensile seen for the unrefined kraft-oxygen brownstocks is likely due to this excessive amount of curl. Bleaching does not result in any loss of tear

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strength. The tear of the kraft-oxygen pulps actually increases after bleaching probably due to the relaxation of the curl from the additional processing. The loss of tear strength after refining increases with decreasing brownstock kappa no.

The tensile index values are shown in Figure 27. The tensile index for the unrefined pulps is highest for the kappa 17.1 kraft pulp followed by the kappa 28.1 kraft pulp. The unrefined kraft-oxygen pulps have a significantly lower tensile strength possibly due to the increased curl. The scattering coefficients for the kraft-oxygen pulps do not indicate that there is a reduction in bonding compared to the kraft pulps. The tensile index increases for these kraft-oxygen pulps following bleaching but is still significantly lower than the kraft pulps. After refining, the kappa 28 kraft pulp has the highest tensile strength followed by the kappa 17.1 pulp. The improvement in tensile strength after refining is highest for the kraft-oxygen pulps but the absolute tensile strength is still lower than the kraft pulps.

The tear index values plotted as a function of the tensile index are shown in Figure 28 which highlights the differences between the unrefined kraft and kraft-oxygen pulps. The kappa 28.1 kraft pulp has the highest strength followed by the kappa 17.1 kappa pulp. Refining reduces the differences between the kraft and kraft-oxygen pulps but they still exhibit a lower tensile strength at a given tear index. The tear-tensile strength is the lowest for the refined kraft-oxygen pulps at 12.1 and 10.7 kappa indicating that there is a strength penalty when pushing the delignification beyond 50%.

Additional handsheet testing is being done with measurements of zero-span tensile strength for both dry and wet-pressed handsheets. The results so far are shown in Table IX but they are not complete enough for any conclusions. Fiber length measurements are also being completed.

**Conclusions**

Some of the testing remains to be done and analysis of the results is still ongoing. From the results so far, the following preliminary conclusions can be made. For bleaching, a CED sequence is more effective than a DED sequence at an equivalent total chlorine applied. The effectiveness of the DED sequence appears to be reduced even more when it follows oxygen delignification. The bleached pulp viscosities decrease as the degree of kraft cooking or oxygen delignification is increased though the kappa-viscosity relationship is different for the kraft and kraft-oxygen pulps. The bleached viscosity for the DED sequence is slightly higher than the CED sequence.

There does not appear to be any significant differences in the pulp and handsheet properties measured between CED and DED bleaching nor are there any significant differences in PFI refineability. At a lower kappa no. for the brownstock, the freeness reduction with refining is greater. The strength of the unrefined kraft-oxygen brownstocks is significantly lower than the kraft pulps but this is mostly attributable to the high degree of curl imparted in the oxygen delignification processing. Refining reduces the strength differences between the pulps but the kraft-oxygen pulps do not meet the strength of the kappa 28 pulp from which they were made. Extending the kraft delignification down to kappa 17 results in a somewhat lower strength but it is comparable to the kraft-oxygen pulps. Increasing the oxygen delignification beyond 50% results in a somewhat lower strength.
## Table VII. Pulp Properties

**Brightness, ISO Viscosity, cps**

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Kappa no.</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>28.1</td>
<td>84.0</td>
<td>75.9</td>
</tr>
<tr>
<td>Kraft</td>
<td>17.0</td>
<td>86.9</td>
<td>84.7</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>20.4</td>
<td>88.3</td>
<td>81.2</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>15.7</td>
<td>88.6</td>
<td>83.1</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>12.1</td>
<td>90.8</td>
<td>84.1</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>10.7</td>
<td>89.9</td>
<td>85.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Kappa no.</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>28.1</td>
<td>22.8</td>
<td>26.6</td>
</tr>
<tr>
<td>Kraft</td>
<td>17.0</td>
<td>11.0</td>
<td>12.5</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>20.4</td>
<td>17.1</td>
<td>20.3</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>15.7</td>
<td>17.0</td>
<td></td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>12.1</td>
<td>10.1</td>
<td>13.0</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>10.7</td>
<td>9.8</td>
<td>11.9</td>
</tr>
</tbody>
</table>

**Ca²⁺ Content, ppm**

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Kappa no.</th>
<th>Brownstock</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>110</td>
<td>4360</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>28.1</td>
<td>1680</td>
<td>907</td>
<td>1290</td>
</tr>
<tr>
<td>Kraft</td>
<td>17.0</td>
<td>903</td>
<td>647</td>
<td>764</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>20.4</td>
<td>1720</td>
<td>663</td>
<td>755</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>15.7</td>
<td>1610</td>
<td>613</td>
<td>745</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>12.1</td>
<td>1425</td>
<td>706</td>
<td>740</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>10.7</td>
<td>1420</td>
<td>700</td>
<td>717</td>
</tr>
</tbody>
</table>

**COOH Content, meq/g**

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Kappa no.</th>
<th>Brownstock</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>110</td>
<td>0.175</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>28.1</td>
<td>0.077</td>
<td>0.030</td>
<td>0.041</td>
</tr>
<tr>
<td>Kraft</td>
<td>17.0</td>
<td>0.049</td>
<td>0.036</td>
<td>0.039</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>20.4</td>
<td>0.081</td>
<td>0.046</td>
<td>0.041</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>15.7</td>
<td>0.078</td>
<td>0.036</td>
<td>0.046</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>12.1</td>
<td>0.072</td>
<td>0.050</td>
<td>0.034</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>10.7</td>
<td>0.067</td>
<td>0.044</td>
<td>0.043</td>
</tr>
</tbody>
</table>

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Table VIII. Unrefined and Refined Pulp Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Fines, % 200 mesh</th>
<th>Brownstock</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp</td>
<td>Kappa no.</td>
<td>0</td>
<td>3000</td>
<td>0</td>
</tr>
<tr>
<td>Kraft</td>
<td>110</td>
<td>731</td>
<td>669</td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>28.1</td>
<td>743</td>
<td>400</td>
<td>723</td>
</tr>
<tr>
<td>Kraft</td>
<td>17.0</td>
<td>727</td>
<td>342</td>
<td>738</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>20.4</td>
<td>753</td>
<td>364</td>
<td>728</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>15.7</td>
<td>740</td>
<td>338</td>
<td>733</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>12.1</td>
<td>732</td>
<td>296</td>
<td>730</td>
</tr>
<tr>
<td>Kraft-O₂</td>
<td>10.7</td>
<td>755</td>
<td>347</td>
<td>740</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>WRV whole pulp, g H₂O/g</th>
<th>Brownstock</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp</td>
<td>Kappa no.</td>
<td>0</td>
<td>3000</td>
</tr>
<tr>
<td>Kraft</td>
<td>110</td>
<td>1.70</td>
<td>2.17</td>
</tr>
<tr>
<td>Kraft</td>
<td>28.1</td>
<td>1.83</td>
<td>2.41</td>
</tr>
<tr>
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<td>17.0</td>
<td>1.87</td>
<td>2.33</td>
</tr>
<tr>
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<td>20.4</td>
<td>1.53</td>
<td>2.31</td>
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<tr>
<td>Kraft-O₂</td>
<td>15.7</td>
<td>1.55</td>
<td>2.32</td>
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<tr>
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<td>12.1</td>
<td>1.59</td>
<td>2.37</td>
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<tr>
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<td>10.7</td>
<td>1.55</td>
<td>2.27</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Fe colloid, g/g</th>
<th>Brownstock</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp</td>
<td>Kappa no.</td>
<td>0</td>
<td>3000</td>
</tr>
<tr>
<td>Kraft</td>
<td>110</td>
<td>12400</td>
<td>27700</td>
</tr>
<tr>
<td>Kraft</td>
<td>28.1</td>
<td>16800</td>
<td>42100</td>
</tr>
<tr>
<td>Kraft</td>
<td>17.0</td>
<td>21100</td>
<td>38600</td>
</tr>
<tr>
<td>Kraft-O₂</td>
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<td>18200</td>
<td>41100</td>
</tr>
<tr>
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<td>15.7</td>
<td>20400</td>
<td>51100</td>
</tr>
<tr>
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<tr>
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<td>20100</td>
<td>42500</td>
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Table IX. Handsheet Properties

<table>
<thead>
<tr>
<th>Handsheet Properites</th>
<th>Brownstock</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³ Pulp Kappa no.</td>
<td>0</td>
<td>3000</td>
<td>0</td>
</tr>
<tr>
<td>Kraft 110</td>
<td>0.427</td>
<td>0.665</td>
<td></td>
</tr>
<tr>
<td>Kraft 28.1</td>
<td>0.544</td>
<td>0.861</td>
<td></td>
</tr>
<tr>
<td>Kraft 17.0</td>
<td>0.547</td>
<td>0.851</td>
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</tr>
<tr>
<td>Kraft-0₂ 20.4</td>
<td>0.562</td>
<td>0.835</td>
<td></td>
</tr>
<tr>
<td>Kraft-0₂ 15.7</td>
<td>0.630</td>
<td>0.948</td>
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</tr>
<tr>
<td>Kraft-0₂ 12.1</td>
<td>0.635</td>
<td>0.913</td>
<td></td>
</tr>
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<td>Kraft-0₂ 10.7</td>
<td>0.580</td>
<td>0.865</td>
<td></td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Scattering Coefficient</th>
<th>Brownstock</th>
<th>CED</th>
<th>DED</th>
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</thead>
<tbody>
<tr>
<td>Pulp Kappa no.</td>
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<td>3000</td>
<td>0</td>
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<tr>
<td>Kraft 110</td>
<td>20.3</td>
<td>15.3</td>
<td></td>
</tr>
<tr>
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<td>23.5</td>
<td>13.1</td>
<td></td>
</tr>
<tr>
<td>Kraft 17.0</td>
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</tr>
<tr>
<td>Kraft-0₂ 20.4</td>
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<td>22.1</td>
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<td></td>
</tr>
<tr>
<td>Kraft-0₂ 12.1</td>
<td>23.3</td>
<td>13.9</td>
<td></td>
</tr>
<tr>
<td>Kraft-0₂ 10.7</td>
<td>24.6</td>
<td>15.3</td>
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</tr>
</tbody>
</table>

<table>
<thead>
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<th>CED</th>
<th>DED</th>
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Figure 20. Viscosity vs. Brownstock Kappa No.

Figure 21. Ca^{2+} Content of Pulp Samples, ppm

Figure 22. Carboxyl Content of Pulp Samples

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Figure 23. CSF Values for Unrefined and Refined Pulps
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Figure 24. Water Retention Values for Unrefined and Refined Whole Pulps

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Figure 25. Scattering Coefficient vs. Sheet Density
Figure 26. Tear Index for Unrefined and Refined Pulps

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Figure 27. Tensile Index for Unrefined and Refined Pulps

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Figure 28. Tear Index vs. Tensile Index

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