EFFECT OF HYDROGEN PEROXIDE 
BLEACHING ON FIBER CHARGE OF 
SOFTWOOD KRAFT PULPS 

By Zheng Dang, Dong Ho Kim, and Art Ragauskas 

IPST @ GaTech 
Atlanta, GA 
January 27, 2005
Outline

– Introduction
– Objectives
– Experimental results
  • Bleaching chemistry
  • Preliminary tests of peroxide bleaching on fully bleached ECF kraft pulp
  • Kinetics study of peroxide bleaching on softwood kraft pulp
  • Experimental matrix of peroxide bleaching
  • Peroxide bleaching on DE pulp
  • Carbohydrates analysis by HAPEC
– Future work
Introduction

– Fiber charge influences the WRV, the wet fiber flexibility, the fiber-fiber bonding, and the physical properties of resultant paper sheet

– Carboxylic group is the only acid groups providing charged site during papermaking process

– Kraft cooking changes the chemical structure structure of wood compositions

– \( \text{H}_2\text{O}_2 \) bleaching is mainly used to degrade chromophoric components in pulps
Objectives

- Explore the bleaching chemistry of hydrogen peroxide
- Develop a comprehensive kinetic study including kappa number, intrinsic viscosity, and carboxylic acid content on fibers during peroxide bleaching
- Develop a process of ClO₂ bleaching followed by peroxide bleaching which leads to the best results regarding final kappa number, final intrinsic viscosity, and fiber charge
- Develop the relationship between the carboxylic acid content and physical strength properties of the paper sheet
- Investigate the effect of kraft cooking conditions on the following peroxide bleaching
### Experimental results

#### Bleaching Chemistry

- Results of conventional peroxide bleaching and pressurized peroxide bleaching

<table>
<thead>
<tr>
<th>Bleaching Conditions</th>
<th>Kappa Number (%Delignification)</th>
<th>Carboxylic acid content of pulp (meq./100g O.D. pulp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brown stock</td>
<td>28.4</td>
<td>8.8</td>
</tr>
<tr>
<td>2.5%P/60°C, 4h</td>
<td>16.5 (41.9%)</td>
<td>10.0</td>
</tr>
<tr>
<td>7.5%P/70°C, 4h</td>
<td>11.5 (59.5%)</td>
<td>9.6</td>
</tr>
<tr>
<td>2.0% P/110°C, 1h</td>
<td>11.1 (60.9%)</td>
<td>8.5</td>
</tr>
<tr>
<td>3.0% P/110°C, 1h</td>
<td>8.2 (71.1%)</td>
<td>7.9</td>
</tr>
<tr>
<td>4.0% P/110°C, 1h</td>
<td>7.1 (75%)</td>
<td>7.8</td>
</tr>
</tbody>
</table>
– Bleaching chemistry (continued)

- $^1$H NMR results of residual lignins isolated from brown stock and peroxide bleached pulps
  - Formyl (RCHO) and acid content (RCO$_2$H) of residual lignins
  - Total phenoxy content (PhOH) and guaiacyl content of residual lignins
– Bleaching chemistry (continued)
  • ¹H NMR results of residual lignins isolated from brown stock and peroxide bleached pulps (continued)
    – Phenoxy content (PhOH) and condensed phenolic content of residual lignins
    – Aromatic, aliphatic, and methoxy group of residual lignins
Preliminary tests of peroxide bleaching on fully bleached ECF kraft pulp

- Condition: 1% H$_2$O$_2$, 2% NaOH, 80°C, 1 hr, and 10% consistency

<table>
<thead>
<tr>
<th>Conditions of H$_2$O$_2$ Bleaching</th>
<th>Carboxylic Acid Content (meq./100g O.D. pulp)</th>
<th>Consumed H$_2$O$_2$ (%)</th>
<th>Freeness (mL)</th>
<th>Tensile Index (Nm/g)</th>
<th>Tear Index (mNm$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original (fully bleached pulp)</td>
<td>3.70</td>
<td>~</td>
<td>694</td>
<td>15.0</td>
<td>11.6</td>
</tr>
<tr>
<td>H$_2$O$_2$ bleaching without MgSO$_4$</td>
<td>4.54</td>
<td>99.5</td>
<td>689</td>
<td>16.2</td>
<td>13.0</td>
</tr>
<tr>
<td>H$_2$O$_2$ bleaching with 0.5% MgSO$_4$</td>
<td>4.60</td>
<td>98.7</td>
<td>684</td>
<td>16.5</td>
<td>13.5</td>
</tr>
</tbody>
</table>
Kinetics study of peroxide bleaching on softwood kraft pulp

- Kappa number variation during peroxide bleaching on brown stock (initial kappa number 31.26)

![Graph showing Kappa number variation during peroxide bleaching.](image-url)
Kinetics study of peroxide bleaching on softwood kraft pulp (continued)

- Intrinsic viscosity variation during peroxide bleaching on brown stock (Initial intrinsic viscosity 1095.34 mL/g)
– Kinetics study of peroxide bleaching on softwood kraft pulp (continued)

• Carboxylic acid group content variation during peroxide bleaching on brown stock (Initial RCOOH 9.232 meq/100 g o.d. pulp)
– Experimental matrix of peroxide bleaching

Condition:
- $\text{H}_2\text{O}_2$ charge 2%, 3%, 4%, and 5%
- NaOH charge 1%, 2%, 3%, and 4%
- 120 min, 60°C, 0.3% DTPA

• Comparison of the results for kappa number
– Experimental matrix of peroxide bleaching
  • Comparison of the results for intrinsic viscosity
– Peroxide bleaching on DE pulp

• Conditions of preparing DE pulp
  – D₁, 0.3% ClO₂; E₁, 0.4% NaOH; D₂, 0.5% ClO₂; E₂, 0.6% NaOH

• Peroxide bleaching on DE pulp
  – 2% NaOH; 2%, 3%, 4%, 5% H₂O₂; 60°C, 120 min.

<table>
<thead>
<tr>
<th>H₂O₂ % on O.D. pulp</th>
<th>NaOH % on O.D. pulp</th>
<th>Kappa Number</th>
<th>Intrinsic Viscosity (mL/g)</th>
<th>Carboxylic acid content of pulp (meq./100g O.D. pulp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
<td>13.75</td>
<td>1047.68</td>
<td>10.906</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>13.71</td>
<td>1042.52</td>
<td>11.105</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>13.68</td>
<td>1014.52</td>
<td>11.133</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>13.45</td>
<td>1011.74</td>
<td>11.249</td>
</tr>
</tbody>
</table>
### Carbohydrate analysis by HAPEC

#### Summary of results

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Mass fractions of polysaccharides (%)</th>
<th>Kappa number</th>
<th>Intrinsic Viscosity (mL/g)</th>
<th>Carboxylic acid content of pulp (meq./100g O.D. pulp)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Glucan</td>
<td>Xylan</td>
<td>Arabinan</td>
<td>Galactan</td>
</tr>
<tr>
<td>Brown stock</td>
<td>77.05%</td>
<td>8.65%</td>
<td>0.74%</td>
<td>0.45%</td>
</tr>
<tr>
<td>Peroxide bleaching¹ @ 15 min</td>
<td>80.44%</td>
<td>8.90%</td>
<td>0.75%</td>
<td>0.42%</td>
</tr>
<tr>
<td>Peroxide bleaching¹ @ 30 min</td>
<td>81.04%</td>
<td>8.95%</td>
<td>0.74%</td>
<td>0.42%</td>
</tr>
<tr>
<td>Peroxide bleaching¹ @ 60 min</td>
<td>81.12%</td>
<td>8.97%</td>
<td>0.75%</td>
<td>0.41%</td>
</tr>
<tr>
<td>Peroxide bleaching¹ @ 120 min</td>
<td>81.59%</td>
<td>8.96%</td>
<td>0.74%</td>
<td>0.40%</td>
</tr>
<tr>
<td>Peroxide bleaching¹ @ 180 min</td>
<td>81.48%</td>
<td>8.96%</td>
<td>0.74%</td>
<td>0.40%</td>
</tr>
<tr>
<td>DE² pulp</td>
<td>77.66%</td>
<td>8.60%</td>
<td>0.68%</td>
<td>0.42%</td>
</tr>
<tr>
<td>Peroxide bleaching³ on DE pulp</td>
<td>79.34%</td>
<td>8.49%</td>
<td>0.67%</td>
<td>0.38%</td>
</tr>
<tr>
<td>Peroxide bleaching⁴ on DE pulp</td>
<td>80.09%</td>
<td>8.71%</td>
<td>0.68%</td>
<td>0.38%</td>
</tr>
<tr>
<td>Peroxide bleaching⁵ on DE pulp</td>
<td>80.97%</td>
<td>8.67%</td>
<td>0.69%</td>
<td>0.39%</td>
</tr>
<tr>
<td>Peroxide bleaching⁶ on DE pulp</td>
<td>80.80%</td>
<td>8.64%</td>
<td>0.69%</td>
<td>0.38%</td>
</tr>
</tbody>
</table>

¹ 3% H₂O₂, 2% NaOH, 0.3% DTPA, 5% Consistency
² D₁, 0.3% ClO₂; E₁, 0.4% NaOH; D₂, 0.5% ClO₂; E₂, 0.6% NaOH
³ 2% H₂O₂, 2% NaOH, 0.3% DTPA, 5% Consistency, 120 minutes
⁴ 3% H₂O₂, 2% NaOH, 0.3% DTPA, 5% Consistency, 120 minutes
⁵ 4% H₂O₂, 2% NaOH, 0.3% DTPA, 5% Consistency, 120 minutes
⁶ 5% H₂O₂, 2% NaOH, 0.3% DTPA, 5% Consistency, 120 minutes
– Carbohydrate analysis by HAPEC (Continued)
  • Intrinsic viscosity versus glucan content of pulps undergoing peroxide bleaching

![Graph showing intrinsic viscosity versus glucan content in pulp](image-url)
Conclusion

- The lignin remaining after a peroxide is becoming increasingly unreactive to hydrogen peroxide.
- Peroxide bleaching has the potential of enhancing fiber-fiber bonding by enhancing carboxylic acid group on fibers.
- pH value during P-stage has a significant effect on delignification.
- Higher temperature during P-stage leads to higher delignification and higher degradation of carbohydrate.
- ClO₂ bleaching process also increases carboxylic acid group.
- Cellulose content increases during a P-stage, but changes a bit after the DE process. Also cellulose degradation occurs at a faster rate than the increase in the cellulose content.
Future work

– Develop the relationship between the carboxylic acid content and physical strength properties of the paper sheet.

– Investigate processes of ClO$_2$ bleaching associated with peroxide bleaching including DEP, PDEP, and Enzymatic treatment with DEP.

– Investigate the effect of kraft cooking conditions on the following peroxide bleaching.