4-acetamido-TEMPO-mediated oxidation of wood chips and thermomechanical pulp in large scale

Presented by David Myja
Co-authors : Éric Loranger and Robert Lanouette

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Why did we work with TEMPO?

TEMPO oxidation

- Low oxidation
  - Increase paper strength (mainly tensile resistance)
  - New grade of use for TMP?

- High oxidation
  - Improve nanofiber production in water
  - Many possible applications:
    - Paper reinforcement
    - Medicine
    - Electronic paper
    - Humidity sensor
    - ...

What’s next?

Scale up

How?

Implantation at different step in the TMP production process
Studied treatments

On softwood chips:
- Impregnation with TEMPO medium (TC)
- Large batch reactor oxidation (BTC)

Reference:
- Untreated chips (C)

Then:
- Primary and secondary refining
  - Disc gap from 0.15 to 1.00 mm

On softwood primary TMP:
- Replace water during the refining by TEMPO medium (TP)
- High consistency reactor treatment (HCTP)
- Large batch reactor oxidation (BTP)

Reference:
- Untreated primary pulp (P)

Then:
- Secondary refining
  - Disc gap from 0.15 to 1.00 mm
Analysis on primary pulp from softwood chips

- Refining energy consumption
- Freeness
- Fiber length (ww)
- Fine content (lw)
- Shive content
- Carboxylic group content of:
  - Pulp
  - Shives
  - Fibers
Analysis on secondary pulp

Refining energy consumption

Carboxylic group content

- < 1500 mmol/kg
  - Freeness
  - Fiber length (ww)
  - Fines content (lw)
  - Handsheets:
    - ISO brightness
    - Tensile index
    - Tear index

- > 1500 mmol/kg
  - Nanofiber percent
Pulp bleaching

Secondary pulp with freeness between 100 et 200 mL

Chelation of metal ions with DTPA

Hydrogen peroxide bleaching

4 gram handsheets:
ISO brightness
Yellowness (b*)
### Observations on primary pulp from chips

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Disc gap</th>
<th>Specific energy</th>
<th>Freeness</th>
<th>Fiber Length (ww)</th>
<th>Fines content (lw)</th>
<th>Shives content</th>
<th>Carboxylic group content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mm</td>
<td>MJ/kg</td>
<td>mL</td>
<td>mm</td>
<td>%</td>
<td>%</td>
<td>mmol/kg</td>
</tr>
<tr>
<td>C1</td>
<td>1.00</td>
<td>2.27</td>
<td>715</td>
<td>2.21</td>
<td>61.0</td>
<td>24.1</td>
<td>120 41 145</td>
</tr>
<tr>
<td>TC1</td>
<td>1.00</td>
<td>2.43</td>
<td>702</td>
<td>2.25</td>
<td>61.8</td>
<td>27.1</td>
<td>220 45 285</td>
</tr>
<tr>
<td>BTC-1</td>
<td>1.00</td>
<td>1.13</td>
<td>425</td>
<td>1.11</td>
<td>69.5</td>
<td>47.5</td>
<td>545 89 958</td>
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<tr>
<td>BTC-2</td>
<td>0.70</td>
<td>2.19</td>
<td>297</td>
<td>1.21</td>
<td>71.0</td>
<td>40.9</td>
<td>605 69 977</td>
</tr>
<tr>
<td>BTC-3</td>
<td>0.15</td>
<td>4.27</td>
<td>217</td>
<td>1.62</td>
<td>64.3</td>
<td>21.2</td>
<td>675 58 841</td>
</tr>
</tbody>
</table>
Observations on secondary pulp from chips

- C2
- TC2

Graphs showing the relationship between specific energy (MJ/kg) and:
- Freeness (mL)
- Fiber length (mm)
- Fines content (lw, %)

Graphs indicate a decrease in freeness, fiber length, and fines content as specific energy increases.
Observations on secondary pulp from chips

- Tensile index (N.m/g)
  - Specific energy (MJ/kg)

- Tear index (mN.m²/g)
  - Specific energy (MJ/kg)

- ISO Brightness (%)
  - Specific energy (MJ/kg)

- C2
- TC2
## Bleaching effect on untreated and impregnated with TEMPO medium chips

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Before hydrogen peroxide bleaching</th>
<th>After hydrogen peroxide bleaching</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ISO Brightness (%)</td>
<td>Yellowness (b*)</td>
</tr>
<tr>
<td>C2-2</td>
<td>51.8</td>
<td>13.3</td>
</tr>
<tr>
<td>TC2-3</td>
<td>47.2</td>
<td>14.2</td>
</tr>
</tbody>
</table>
Conclusions on chips treatments

• Harmful effect of chips impregnation with TEMPO mixture
  → Not recommended

• Chips batch oxidation effective and change refining effects
  → Further investigation needed
Observations on secondary pulp from primary TMP with a carboxylic group content under 1500 mmol/kg
Observations on secondary pulp from primary TMP with a carboxylic group content under 1500 mmol/kg
Bleaching effect on untreated, refined with TEMPO medium and oxidized in high consistency reactor primary TMP

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Before hydrogen peroxide bleaching</th>
<th>After hydrogen peroxide bleaching</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ISO Brightness (%)</td>
<td>Yellowness (b*)</td>
</tr>
<tr>
<td>P-3</td>
<td>55.3</td>
<td>13.0</td>
</tr>
<tr>
<td>TP-4</td>
<td>30.8</td>
<td>21.4</td>
</tr>
<tr>
<td>HCTP-5</td>
<td>38.1</td>
<td>17.3</td>
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</table>
Observations on secondary pulp from primary TMP with a carboxylic group content higher than 1500 mmol/kg

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Disc gap</th>
<th>Specific energy</th>
<th>Pulp carboxylic group content</th>
<th>Nanofiber percent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mm</td>
<td>MJ/kg</td>
<td>mmol/kg</td>
<td>%</td>
</tr>
<tr>
<td>BTP-1</td>
<td>1.00</td>
<td>0.63</td>
<td>1840</td>
<td>12.3</td>
</tr>
<tr>
<td>BTP-2</td>
<td>0.50</td>
<td>3.21</td>
<td>2005</td>
<td>23.8</td>
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<tr>
<td>BTP-3</td>
<td>0.15</td>
<td>4.80</td>
<td>2095</td>
<td>27.2</td>
</tr>
<tr>
<td>BTP-IKA</td>
<td>/</td>
<td>57.11</td>
<td>1975</td>
<td>19.9</td>
</tr>
</tbody>
</table>
Conclusions on primary pulp treatments

• High consistency treatment is better than to replace water in the refiner but harshly affect the paper optical properties
  → Further investigation needed (Better control of the pH?)

• High efficiency dispersion when refining highly oxidized pulp
  → Recommended to be used as disperser
Global conclusions

- Highly oxidized pulp obtained only with batch treatment of primary TMP
- Batch treatment of chips should be further investigate
- Difficulties to control oxidation conditions during impregnation, inside refiner or high consistency reactor treatments decrease their efficiency
- Refiner is clearly viable for large scale nanofiber producer
Thank you

Presented by David Myja
Ph.D. student
Université du Québec à Trois-Rivières
david.myja@uqtr.ca