Comparison of brightening kinetics in the final hydrogen peroxide stage of \( \text{DE}_{\text{DP}} \text{DP} \) and \( \text{OQ(PO)} \text{DP} \) bleaching sequences

Comparação da cinética de branqueamento no estágio final de peróxido de hidrogênio das sequências de branqueamento \( \text{DE}_{\text{DP}} \text{DP} \) e \( \text{OQ(PO)} \text{DP} \)


1) CIEPQPF, Department of Chemical Engineering, University of Coimbra, 3030-790 Coimbra, Portugal
2) CICECO, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

São Paulo, October 14th, 2008
**Motivation & Objectives**

- Why a final P stage is used instead of the conventional D stage in the ECF bleaching of eucalypt kraft pulps?
  
  **DEDD versus DEDP**
  
  - Lower brightness reversion
  - Higher pulp beatability
  - Better papermaking properties

  But DED ISO brightness > 87%
  If Target is 90±0.5%

- What is the effect of pulp bleaching history on the brightening performance of the final P stage?

---


**Figure 1.** Chemical charges needed to attain 90±0.5% ISO brightness versus D₄ pulp brightness. Carvalho et al. 2008. Tappi J. 7(8):8-13;
Figure 1. Intrinsic viscosity and brightness reversion (PC number).


Figure 3. Tensile index versus PFI revolutions.

**Motivation & Objectives**

- Understanding the effect of pulp bleaching history:
  - Comparison of the *brightening kinetics* in the final P stage of two different partially bleached industrial kraft pulps:

    \[ \text{OQ(PO)D versus DE}_{\text{OPD}} \]

- Development of mathematical kinetic models – ongoing research

*Figure 2. Pulp drainability (Schopper-Riegler method) versus PFI revolutions.*

Carvalho et al. 2008. Tappi J. 7(8):8-13;
**Intro: Bleaching Principles**

- **Final Hydrogen Peroxide bleaching stage**
  - **Brightening reactions:**
    - Alkaline conditions: \( \text{HOOH} + \text{HO}^- \rightarrow \text{HO}^+ + \text{H}_2\text{O} \)
    - Brightening agent

  - Chromophoric type structures:
    - Lignin derived
      - ![Chemical structures](image)

      - Tubino and Filho 1998. O Papel LIX(2):44-54;

- **Final Hydrogen Peroxide bleaching stage**
  - **Decomposition reactions:**
    - *Base-catalyzed:* \( \text{HOOH} + \text{HO}^- \rightarrow \text{HO}^+ + \text{O}_2 + \text{H}_2\text{O} \) (pH > 11.6)
    - *Metal-catalyzed:* e.g., \( \text{HOOH} + \text{M} \rightarrow \text{M}^+ + \text{HO}^+ + \text{HO}^- \) – Transition metal
      - Transition metals: Mn, Fe, Cu

  - Many pathways proposed in the literature – complex phenomena!

  - **Avoid radicals generation – a must!**
    - Prevent loss of viscosity and yield!
Intro: Bleaching Principles

- Metals management
  - Pre-treatments: Acid wash – A stage (also \( D_{HT} \))
    - Less selective
  - Chelation – Q stage
    - Eventual Mg replenishment
  - Additives in the P stage
    (e.g. MgSO\(_4\), EDTA or DTPA)

Mn – the most detrimental metal

Mg – polysaccharides “protector” \( \Rightarrow \) role of Mg(OH)\(_2\)

Important parameter: \( D_{FT} \rightarrow 30 \) \( \Rightarrow \) ensure effective \( H_2O_2 \) bleaching \( (T \leq 90^\circ C) \)

Devenyns et al. 1994. 3rd EWLP, Stockholm

Experimental

- Materials
  - Industrial samples of *Eucalyptus globulus* kraft pulps partially bleached with the sequences: \( DE_{OFD} \) and \( OQ(PO)D \)

- Methodology
  - Further washed in the laboratory

Preliminary study
  - Best stabilizing system to avoid hydrogen peroxide decomposition and preserve pulp quality?

Kinetic study
  - Chemicals consumption
  - Pulp intrinsic viscosity

Inti
Experimental

Bleaching conditions:

<table>
<thead>
<tr>
<th>Bleaching variable</th>
<th>Preliminary studies</th>
<th>Kinetic studies</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O}_2 ) (% odp)</td>
<td>DE(_{\text{ODP}}): 1.0</td>
<td>0.5 – 2.0</td>
</tr>
<tr>
<td>Na(_{2}\text{O}) (% odp)</td>
<td>0.60</td>
<td>0.8 – 0.9</td>
</tr>
<tr>
<td>DTPA (% odp)</td>
<td>0.05-0.20</td>
<td>0.05</td>
</tr>
<tr>
<td>EDTA (% odp)</td>
<td>0.05-0.20</td>
<td>--</td>
</tr>
<tr>
<td>Mg(_2\text{SO}_4 ) (% odp)</td>
<td>0.025-0.100</td>
<td>--</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>70</td>
<td>70 – 90</td>
</tr>
<tr>
<td>Time (min)</td>
<td>30</td>
<td>0 – 180</td>
</tr>
<tr>
<td>Consistency (%)</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

Starting pulps:

- Reaction times of the kinetic studies: 1, 5, 15, 30, 60, 120, 180 min;
- 20 g od pulp in a water bath;
- All reagents were pre-heated to the desired temperature.

Results & Discussion

Preliminary study: Best stabilizing system to avoid hydrogen peroxide decomposition and preserve pulp quality?

<table>
<thead>
<tr>
<th>Stabilizer charge (% odp)</th>
<th>DE(_{\text{ODP}}) (1.0% odp ( \text{H}_2\text{O}_2 ) charge)</th>
<th>OQ(PO)DP (0.5% odp ( \text{H}_2\text{O}_2 ) charge)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(_2\text{SO}_4 )</td>
<td>DTPA</td>
<td>EDTA</td>
</tr>
<tr>
<td>0.050</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.250</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.200</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.050</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.250</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.100</td>
<td>0.100</td>
<td>--</td>
</tr>
<tr>
<td>0.050</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.250</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.050</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.100</td>
<td>0.100</td>
<td>--</td>
</tr>
</tbody>
</table>
Results & Discussion

Metal contents

- DEPOD pulp has a higher content of Ca, Mg, and Mn than OQ(PO)D pulp.
- DTPA is very efficient in Mn removal.
- Fe is not equally removed in both pulps.

All Mg/Mn ratios higher than 30!
OQ(PO)DP pulps have higher Mg/Mn ratio → Higher bleachability of OQ(PO)D pulps?
Results & Discussion

- Brightening kinetics

  - Figure 1. ISO brightness gain kinetics in the final P stage of the sequences DEQPO DP and OQPO DP with 0.5% dwp H₂O₂ at 70 and 90°C.

  - OQ(P)O DP pulp has faster brightness gain (or evolution)
  - DEQPO DP pulp brightening at 90°C is limited by decomposition of H₂O₂ → Brightness ceiling

- H₂O₂ consumption kinetics

  - Figure 3. Hydrogen peroxide consumption kinetics in the final P stage of the sequences DEQPO DP and OQPO DP with 0.5% dwp H₂O₂ at 70 and 90°C.

  - Higher H₂O₂ consumption with the DEQPO DP
  - The OQPO DP pulp allows higher reaction times at 90°C → Continuous brightening
Results & Discussion

- **NaOH consumption kinetics**
  - Figure 5: Sodium hydroxide consumption kinetics in the final P stage of the sequences DE, DP and OQ/PO/DP with 0.5% edp H<sub>2</sub>O<sub>2</sub> at 70 and 90°C.
  - Figure 6: Sodium hydroxide consumption kinetics in the final P stage of the sequences DE, DP and OQ/PO/DP with 2.0% edp H<sub>2</sub>O<sub>2</sub> at 70 and 90°C.

- The OQ/PO/DP pulp has higher NaOH consumption.

Discussion

- Pulp bleachability comparison
  - Figure 7: Bleachability of the final P stage for the sequences DE, DP and OQ/PO/DP with 0.5% edp H<sub>2</sub>O<sub>2</sub> at 70 and 90°C.
  - Figure 8: Bleachability of the final P stage for the sequences DE, DP and OQ/PO/DP with 2.0% edp H<sub>2</sub>O<sub>2</sub> at 70 and 90°C.

- OQ/PO/DP pulp has higher bleachability than DE/DP pulp.
- The highest temperature positively affect OQ/PO/DP pulp bleachability for the highest charge.
Results & Discussion

Why such differences?

- $\Delta E_{0p}D$ pulp
  - Higher $H_2O_2$ consumption
  - Lower brightness gain

The higher bleachability of OQ(PO)D pulps may explain why

- Decomposition reactions are more significant

Further study

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$H_2O_2$ Consumption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
</tr>
</tbody>
</table>

Results & Discussion

Further understanding the pulp history effect on the brightening performance of $H_2O_2$

The role of quinones

These kind of chromophoric structures survive until the end of the bleaching sequence.


They negatively affect pulp bleachable in ClO$_2$ based ECF sequences.

Lach, W. Bleaching with $H_2O_2$ and $ClO_2$.

These structures are produced in D and O stages, but the D$_3$ stage raises dramatically the amount of quinones.


DE$_{0p}D$ vs. OQ(PO)D

Higher amount of quinoid chromophores in the DE$_{0p}D$ pulp is expected.
Conclusions

- The best stabilizing system in the final P stage was dependent on the pulp history:
  - DE₂₆D pulp: DTPA
  - OQ(PO)D pulp: DTPA+MgSO₄
- DTPA is very efficient in reduction hydrogen peroxide decomposition (Mn removal);
- OQ(PO)D pulps have lower Mn content and higher Mg/Mn, due to the Q stage;
- OQ(PO)D pulp has higher bleachability than DE₂₆D pulp;
- The efficiency of accelerating brightening reactions by raising the temperature to 90°C in the final P stage strongly depends on pulp history;
- The decomposition reactions are more significant with the DE₂₆D pulp - after 60 min at 90°C, peroxide is almost depleted and no further brightness increase is achieved;
- At 80°C, with the OQ(PO)D pulp, it is possible to reach a retention time of 180 min with a continuous brightening evolution;
- For the DE₂₆D pulp longer times than 60 min at 90°C are not advisable while for the OQ(PO)D pulp wider time and temperature ranges are possible.

Acknowledgments

- RAIZ – Instituto de Investigação da Floresta e do Papel, for the laboratorial assistance
- Grupo Portucel Soporcel and Celbi mill for supplying the pulps
- Fundação para a Ciência e Tecnologia for the PhD scholarship granted to Pedro Loureiro
Thank you for your attention!

Obrigado pela vossa atenção!