University of Coimbra University of Aveiro

Technical session: Pulp II

ABTCP 2008
41º CONGRESSO E EXPOSIÇÃO INTERNACIONAL DE CELULOSE E PAPEL

Comparison of brightening kinetics in the final hydrogen peroxide stage of $DE_{OP}DP$ and OQ(PO)DP bleaching sequences

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Comparação da cinética de branqueamento no estágio final de peróxido de hidrogênio das sequências de branqueamento $DE_{OP}DP$ e OQ(PO)DP

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São Paulo, October 14th, 2008

Overview

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Motivation & Objectives

Introduction: Bleaching Principles

Experimental

Results & Discussion

Conclusions

Acknowledgments

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%

Parthasarathy and Colodette 2007. ICEP, Belo Horizonte;
Carvalho et al. 2008. *Tappi J.* 7(8):8-13;
Loureiro et al. 2008. IPBC, Québec City.

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

DEDD *versus* DEDP

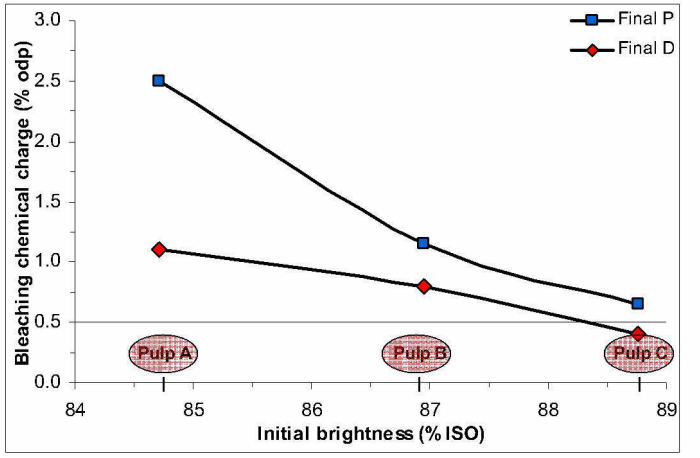


Figure 1. Chemical charges needed to attain 90±0.5% ISO brightness *versus* D_1 pulp brightness.

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

DEDD *versus* DEDP

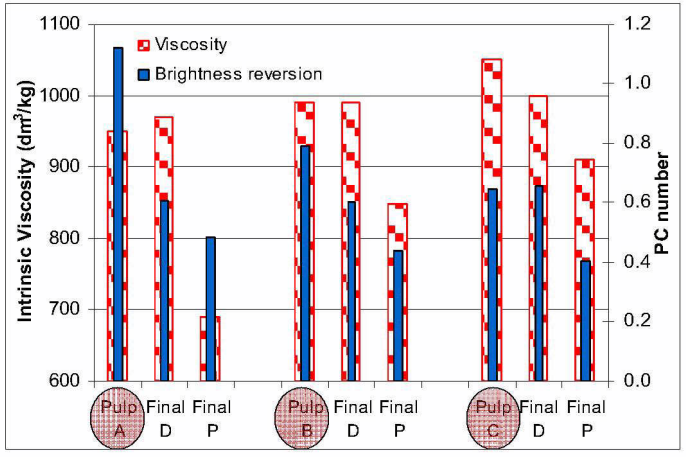


Figure 1. Intrinsic viscosity and brightness reversion (PC number).

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

DEDD *versus* DEDP

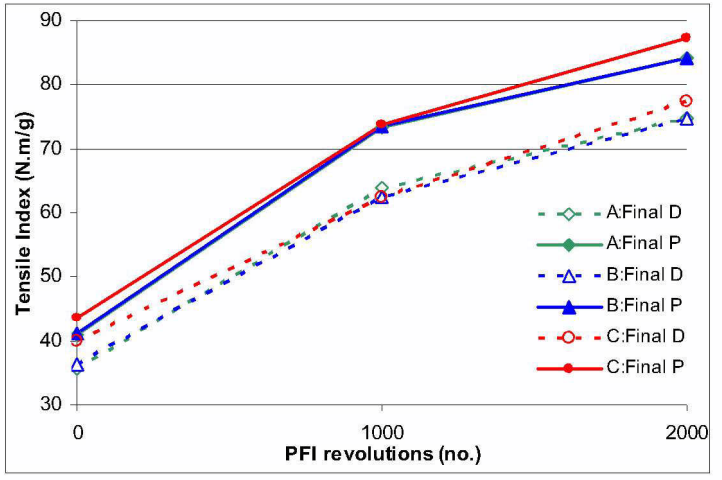


Figure 3. Tensile index *versus* PFI revolutions.

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

DEDD *versus* DEDP

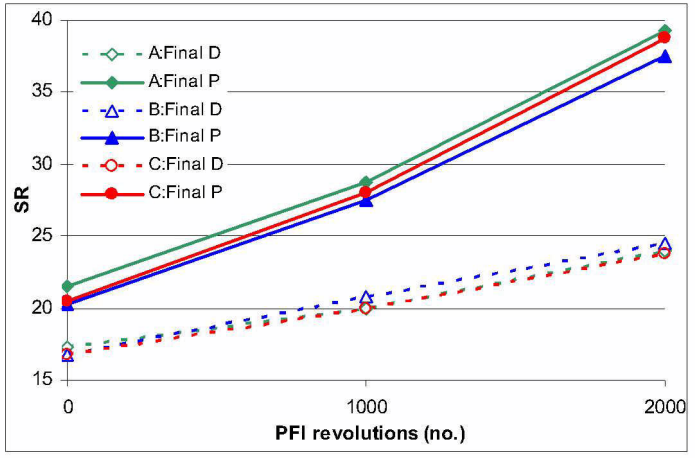


Figure 2. Pulp drainability (Schopper-Riegler method) *versus* PFI revolutions.

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

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:**

    OQ(PO)D *versus* $DE_{OP}D$

  - **Development of mathematical kinetic models – ongoing research**

Process control and optimization

Intro: Bleaching Principles

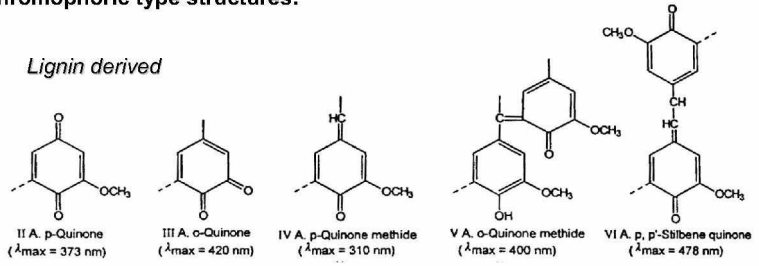
- **Final Hydrogen Peroxide bleaching stage**
  - **Brightening reactions:**

Alkaline conditions: $HOOH + HO^- \leftrightarrow HOO^- + H_2O$

brightening agent

Chromophoric type structures:

Lignin derived



Dence, C.W. 1996 in Dence, C.W. and Reeve D.W. (eds.), Pulp Bleaching – Principles and Practice. TAPPI PRESS, Atlanta.

Intro: Bleaching Principles

- **Final Hydrogen Peroxide bleaching stage**
  - **Decomposition reactions:**

Base-catalyzed: $HOOH + HOO^- \rightarrow HO\cdot + \cdot O_2^- + H_2O$ (pH > 11.6)

Metal-catalyzed: e.g., $HOOH + M \rightarrow M^+ + HO\cdot + HO^-$ M – Transition metal

Transition metals: **Mn**; **Fe**; **Cu**

Many pathways proposed in the literature – complex phenomena!

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

Wuorimaa, A., et al. 2006. *Nord. Pulp Pap. Res. J.* 21(4):435-443.

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" ⇨ role of $Mg(OH)_2$

Important parameter: — > 30 ⇨ ensure effective H_2O_2 bleaching (T ≤ 90ºC)

Devenyns et al. 1994. 3rd EWLP, Stockholm

Experimental

- **Materials**

- Industrial samples of *Eucalyptus globulus* kraft pulps partially bleached with the sequences:

$DE_{OP}D$ and **OQ(PO)D**

- **Methodology**

⇩

Further **washed** in the laboratory

⇩

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

⇩

Chemicals consumption — **Kinetic study** — ness — Pulp intrinsic viscosity

Experimental

- **Bleaching conditions:**

Bleaching variable	Preliminary studies	Kinetic studies
H_2O_2 (% odp)	$DE_{OP}DP$: 1.0 OQ(PO)DP: 0.5	0.5 – 2.0
NaOH (% odp)	0.60	0.6 – 0.9
DTPA (% odp)	0.05-0.20	0.05
EDTA (% odp)	0.05-0.20	---
$MgSO_4$ (% odp)	0.025-0.100	---
Temperature (ºC)	70	70 – 90
Time (min)	30	0 – 180
Consistency (%)	10	10

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

Pulp	ISO brightness (%)	Intrinsic viscosity (dm^3/Kg)
DE$_{OP}$D	87.5	1066
OQ(PO)D	87.4	988

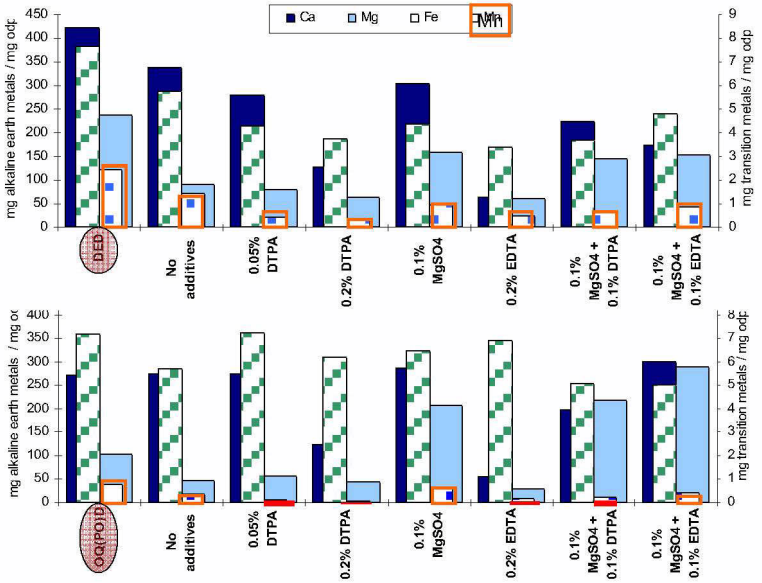
Results & Discussion

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

Stabilizer charge (% odp)			$DE_{OP}DP$ (1.0% odp H_2O_2 charge)			OQ(PO)DP (0.5% odp H_2O_2 charge)		
$MgSO_4$	DTPA	EDTA	H_2O_2 consumed (%)	ISO brightness (%)	Intrinsic viscosity (dm^3/kg)	H_2O_2 consumed (%)	ISO brightness (%)	Intrinsic viscosity (dm^3/kg)
---	---	---	31	90.2	989	57	90.9	912
0.025	---	---	21	89.9	1002	30	90.4	951
0.100	---	---	43	90.0	1041	23	90.5	973
---	0.050	---	9	90.1	1051	19	90.5	961
---	0.200	---	9	89.8	1055	22	90.2	974
0.025	0.050	---	15	89.9	1018	17	90.5	957
0.100	0.100	---	28	89.9	1053	12	90.1	986
---	---	0.050	22	90.0	1000	39	90.5	941
---	---	0.200	15	89.7	1001	14	90.4	963
0.025	---	0.050	14	89.9	1050	20	90.3	975
0.100	---	0.100	19	89.7	1035	20	90.3	982

Results & Discussion

❑ **Metal contents**

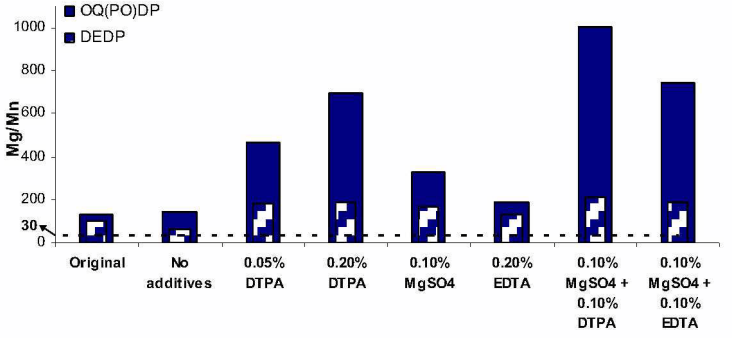


❑ $DE_{OP}D$ pulp has a higher content of **Ca**, **Mg** and **Mn** than OQ(PO)D pulp

❑ DTPA is very efficient in **Mn** removal

❑ **Fe** is not equally removed in both pulps

Results & Discussion



❑ 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

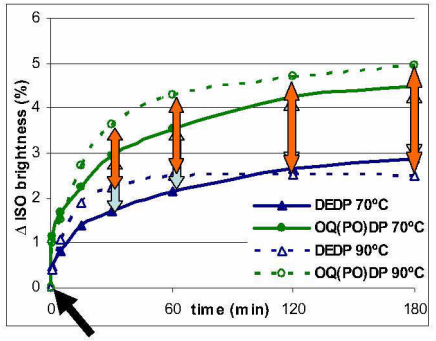


Figure 1. ISO brightness gain kinetics in the final P stage of the sequences $DE_{OP}DP$ and OQ(PO)DP with **0.5% odp H_2O_2** at **70** and **90°C**.

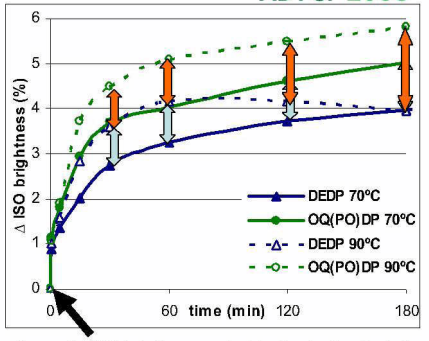


Figure 2. ISO brightness gain kinetics in the final P stage of the sequences $DE_{OP}DP$ and OQ(PO)DP with **2.0% odp H_2O_2** at **70** and **90°C**.

- ❑ OQ(PO)D pulp has faster brightness gain (or evolution)
- ❑ $DE_{OP}D$ pulp brightening at 90 °C is limited by decomposition of H_2O_2 ⇨ **Brightness ceiling**

Results & Discussion

❑ H_2O_2 consumption kinetics

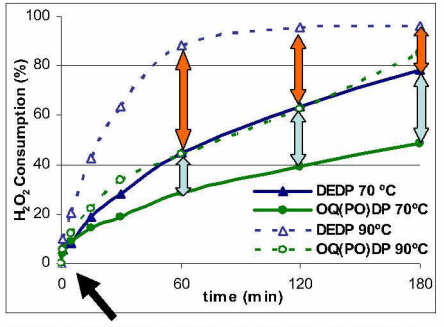


Figure 3. Hydrogen peroxide consumption kinetics in the final P stage of the sequences $DE_{OP}DP$ and OQ(PO)DP with **0.5% odp H_2O_2** at **70** and **90°C**.

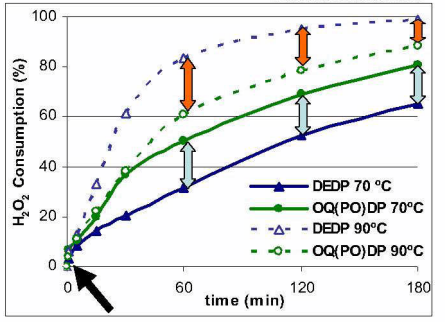


Figure 4. Hydrogen peroxide consumption kinetics in the final P stage of the sequences $DE_{OP}DP$ and OQ(PO)DP with **2.0% odp H_2O_2** at **70** and **90°C**.

- ❑ Higher H_2O_2 consumption with the $DE_{OP}D$ pulp
- ❑ The OQ(PO)D pulp allows higher reaction times at 90°C ⇨ **Continuous brightening**

Results & Discussion

❑ NaOH consumption kinetics

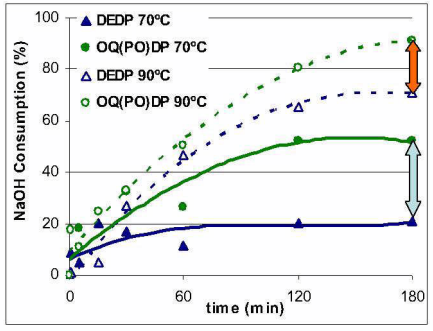


Figure 5. Sodium hydroxide consumption kinetics in the final P stage of the sequences $DE_{OP}DP$ and OQ(PO)DP with **0.5% odp H_2O_2** at **70** and **90°C**.

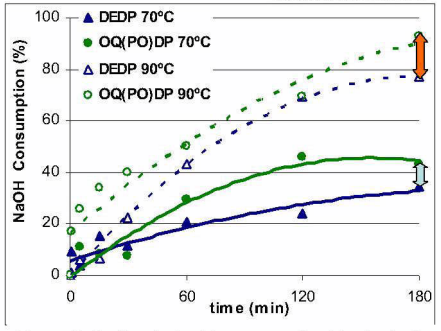


Figure 6. Sodium hydroxide consumption kinetics in the final P stage of the sequences $DE_{OP}DP$ and OQ(PO)DP with **2.0% odp H_2O_2** at **70** and **90°C**.

❑ The OQ(PO)D pulp has higher NaOH consumption

Results & Discussion

❑ Pulp bleachability comparison

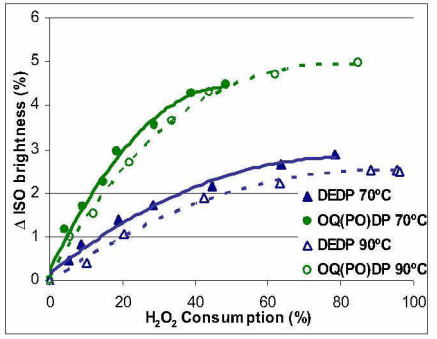


Figure 7. Bleachability of the final P stage for the sequences $DE_{OP}DP$ and OQ(PO)DP with **0.5% odp H_2O_2** at **70** and **90°C**.

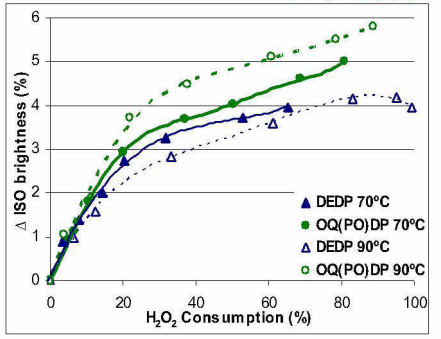


Figure 8. Bleachability of the final P stage for the sequences $DE_{OP}DP$ and OQ(PO)DP with **2.0% odp H_2O_2** at **70** and **90°C**.

❑ OQ(PO)D pulp has higher bleachability than $DE_{OP}D$ pulp!

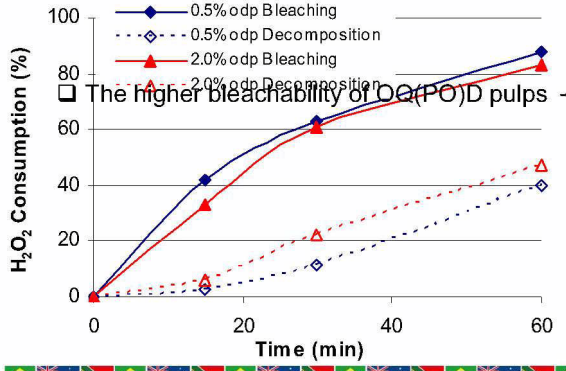
❑ The highest temperature positively affect OQ(PO)D pulp bleachability for the highest charge

Results & Discussion

Why such differences?

❑ $DE_{OP}D$ pulp ⇨
- ➢ Higher H_2O_2 consumption
- ➢ Lower brightness gain

⇨ Decomposition reactions are more significant



❑ The higher bleachability of OQ(PO)D pulps

- ➢ Lower Mn Content
- ➢ Higher Mg/Mn ratio
- ➢ Consumption after 60 min more and amount?

At **90ºC**, the decomposition reached a **half** of the total H_2O_2

⇩

Further study

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.

Rosenau et al. 2007. Holzforschung 61(6):656-661.

⇩

They negatively affect pulp bleachability in ClO_2 based ECF sequences.

Lachenal et al. 2005. IPBC. Stockholm

These structures are produced in D and O stages, but the D_0 stage raises dramatically the amount of quinones.

Zawadzki 1999.PhD Thesis, Atlanta;

Brogdon et al. 2004. *J. Wood Chem. Technol.* 24(3):201-219.

$DE_{OP}D$ vs. **OQ(PO)D**

⇩

Higher amount of quinoid chromophores in the $DE_{OP}D$ pulp is expected

$D_{HT}P$ was the best option on final chromophores destruction and in brightness stability.

Conclusions

- The best stabilizing system in the final P stage was dependent on the pulp history:
  - $DE_{OP}D$ pulp: DTPA
  - OQ(PO)D pulp: DTPA+$MgSO_4$
- 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 $DE_{OP}D$ pulp;
- The efficiency of accelerating brightening reactions by raising the temperature to 90ºC in the final P stage strongly depends on pulp history;
- The decomposition reactions are more significant with the $DE_{OP}D$ pulp - after 60 min at 90ºC, peroxide is almost depleted and no further brightness increase is achieved;
- At 90ºC, with the OQ(PO)D pulp, it is possible to reach a retention time of 180 min with a continuous brightening evolution;
- For the $DE_{OP}D$ pulp longer times than 60 min at 90ºC 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!