ADVANCES IN EUCALYPTUS PULP BLEACHING TECHNOLOGY
Advances in eucalyptus pulp bleaching technology

- Advances in Eucalyptus pulp bleaching technology
- Introduction
- Bleaching process development
- Recent topics in pulp bleaching technology
  - Oxygen delignification
  - Pulp washing
  - Hexenuronic acid removal
- Modern bleaching sequences
- Pulp quality
- Power, steam, effluent
- Recent mill results
- Future topics and conclusion
Introduction

- Use of eucalyptus pulp has increased rapidly
- Production capacity increase in the southern hemisphere
  Fast-wood plantations
  Uniform quality
- Mill capacities growing
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WORLD Consumption of Bleached Eucalyptus Chemical Pulp

Market
Integrated

Million ton Consumption

Source: JP World Fiber Outlook 2006 + cop

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Development of pulp mill capacity

Year

Capacity, ADT/D

0 1000 2000 3000 4000
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Specific Investment Requirements
Investment costs for new capacity continue to grow but so does the size. New hardwood pulp mill projects have a capacity as high as one million tons. Investment cost/ton continues to drop, but increasingly slowly.

Source: JP World Fiber Outlook 2006
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Bleaching process development

- From elemental chlorine to chlorine dioxide
- Less bleaching stages
- Oxygen delignification
- Oxygen and peroxide reinforced pulp bleaching
- Medium consistency pumping
- Equipment technique
  - High shear mixing
  - Pulp washers
- ECF, Light-ECF, TCF bleaching
  - New bleaching chemicals
  - Ozone, Paa, PMo
- Reduced effluent discharges
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**Graphs:**
- **Water consumption in bleaching m³/admt**
  - Data points show a decrease over time.

- **Total active chlorine consumption, kg/admt**
  - Data points show a decrease over time.

- **AOX in bleach effluent, kg/admt**
  - Data points show a decrease over time.

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Bleaching process development

- O/O-A/D-E_{OP}
- O/O-A/D-E_{OP}-D-P
- O/O-D_{Hot}E_{OP}-D_{ND}
- O/O-A/D-E_{OP}-D_{ND}
- O/O-D-E_{OP}-D_{ND}
- O/O-D-E_{OP}-D(-D)
- O/O-D-E_{O}-D-D
- O-C/D-E_{O}-D-D
- O-C/D-E-D-E-D
- C/D-E-H
- C-E-H-D-E-D
- C-E-H-H


TCF

1995

O/O-Q-Z-Q-Z-P
O/O-Q-Z-Q-P
O/O-A-Z-P-Z-P
O/O-Z/Q-P-Z/Q-P
O/O-Q-P-Q-P
O/O-Q-P_{AA}-Q-P

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Bleaching process development

Year


Drum Displacer (DD) bleaching
Wash Press bleaching
Displacement bleaching
Diffuser bleaching
Ozone bleaching
Oxygen delignification
Medium consistency technology
Medium consistency pump & equipment
Drum washer bleach plant
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Bleaching process development
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Bleaching process development

Diffuser bleaching
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Bleaching process development
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Bleaching process development

Medium consistency pump
- capacity >4000 admt/d
- head up to 200 m
- consistency 10…12%

High density stock pump
- capacity <1500 admt/d
- head up to 100 m
- consistency 10…15%
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Bleaching process development

Chemical mixer
- capacity <1500 adm/d
- consistency 10...13%

Medium consistency chemical mixer
- capacity >4000 adm/d
- consistency 10...13%

Rotor

Chemical

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Topics in pulp bleaching technology

- Oxygen delignification
- Removal of Hexenuronic acid
- Bleaching sequences
- Pulp washing
- Pulp quality
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Oxygen delignification

Single-stage system

Two-stage system

Process parameters
  Temperature profile
  Chemical profile
  Pressure profile
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Single-stage oxygen delignification

Two-stage oxygen delignification
Two-stage versus single-stage oxygen delignification

✓ Enables better process parameter controls
  ✓ retention time, pressure, chemical, temperature

✓ Enables better potential for kappa reduction, selectivity, brightness
  ✓ 1-2 units higher kappa reduction
  ✓ 5 - 10 units higher brightness

✓ Pulp washing before oxygen delignification in a key role
  ✓ there is peroxide formation in oxygen reactions and black liquor catalyzes the degradation of peroxide
  ✓ COD carryover less than 90 kg/adt
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Removal of hexenuronic acid
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HexA contents in different pulps

✓ Scandinavian softwood pulps 20 – 30 mmol/kg
✓ Scandinavian birch pulp 40 – 60 mmol/kg
✓ Eucalyptus pulp 45 – 85 mmol/kg
✓ Acacia and mixed hardwood pulps 35 – 50 mmol/kg

10 – 12 mmol HexA /kg corresponds to 1 kappa unit
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Relation between HexA and residual lignin of the hardwood and softwood pulp kappa number

Softwood

Hardwood

In eucalyptus pulp 30…50% of kappa can originate from HexA

HexA “False” lignin

Residual lignin

Residual lignin

HexA “False” lignin

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- HexA consumes bleaching chemicals ($O_3$, $ClO_2$, and $P_{AA}$)
- HexA does not react with $O_2$ and $H_2O_2$
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Oxygen Delignification, Hardwood

- Delignification degree 60…65 %
- Kappa reduction 40…50 %
### A-Stage - typical process conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>HexA content</td>
<td>40-80 mmol/kg HW, 20-30 mmol/kg SW</td>
</tr>
<tr>
<td>pH</td>
<td>3 – 3,5</td>
</tr>
<tr>
<td>pulp consistency</td>
<td>medium; 10-12%</td>
</tr>
<tr>
<td>COD carryover</td>
<td>*10-15 kg/adt</td>
</tr>
<tr>
<td>temperature</td>
<td>90 - 100°C</td>
</tr>
<tr>
<td>time</td>
<td>2 - 4 h</td>
</tr>
</tbody>
</table>

$$\Rightarrow$$ 60-80% HexA decrease

3 - 5 kappa units, hardwood

1 - 3 kappa units, softwood
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A-stage alternatives

A-stage in storage tower

A-stage in separate up-flow tower

Post Oxygen Washers

Low pressure steam
Condensate

A-stage 85 °C
pH 3.5

H₂SO₄
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Development of HexA as a function of time (pH = 3.5)

Development of HexA as a function of time (pH = 3.0)

/1/, /2/ Vuorinen, T., Buchert, J., Teleman, A., Tenkanen, M. & Fagerström, P
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South-American euca, HexA content 54 mmol/kg

A-stage kappa vs. time, 90 °C pH 3.4

- 10.1
- 7.6
- 6.5
- 5.4
- 4.2

Time, min

Kappa number
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Competing removal of HexA and lignin

Relative lignin content (%)

Relative HexA content (%)

0 20 40 60 80 100

Paa-stage
Z-stage
D-stage

1/ Vuorinen, T., Buchert, J., Teleman, A., Tenkanen, M. & Fagerström, P
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Reaction of 2-furoic acid with ClO$_2$ and HOCl/Cl$_2$
($T=90^\circ C$, $pH=2$)

Toikka, K et al
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Combining Hexa removal to bleaching
Modern bleaching sequences
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A / D₀ʷ

D_{Hot}ʷ

A / Zʷ

Aʷ − Zʷ

Z / Dʷ

Aʷ − Z / Dʷ
Effect of interstage washing on the performance of the selective hydrolysis of HexA in chlorine dioxide bleaching of birch kraft pulp

<table>
<thead>
<tr>
<th></th>
<th>A-D-E-D</th>
<th>A/D-E-D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kappa A-D-E</td>
<td>Bright. ISO%</td>
</tr>
<tr>
<td>Pulp 1</td>
<td>2.4</td>
<td>86.1</td>
</tr>
<tr>
<td>Pulp 2</td>
<td>2.7</td>
<td>84.5</td>
</tr>
<tr>
<td>Pulp 3</td>
<td>2.0</td>
<td>88.6</td>
</tr>
</tbody>
</table>

/1/ Vuorinen, T., Buchert, J., Teleman, A., Tenkanen, M. & Fagerström, P

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### Advances in eucalyptus pulp bleaching technology

Effect of interstage washing on the performance of the selective hydrolysis of HexA in ozone bleaching of birch kraft pulp

<table>
<thead>
<tr>
<th></th>
<th>Kappa number</th>
<th>Brightness ISO%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-A</td>
<td>4.1</td>
<td>53.6</td>
</tr>
<tr>
<td>O-A-Z</td>
<td>1.8</td>
<td>72.1</td>
</tr>
<tr>
<td>O-A/Z</td>
<td>3.7</td>
<td>56.2</td>
</tr>
</tbody>
</table>
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A stage combined with $D_0$ stage

HW, Kappa 11.5, 33.2 kg/bdmt (act Cl), $T=63^\circ C$, residuals kg/admt
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Relative benefits (+/-) of different bleaching sequences with respect to each other

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Capital cost</th>
<th>Chemical cost</th>
<th>Brightness flexibility</th>
<th>Brightness reversion</th>
<th>Effluent</th>
</tr>
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<tbody>
<tr>
<td>Z/D-Eop-D-P</td>
<td>- - -</td>
<td>+ +</td>
<td>+ + +</td>
<td>+ + +</td>
<td>+ + +</td>
</tr>
<tr>
<td>A-Z/D-Eop-D</td>
<td>- - -</td>
<td>+ + +</td>
<td>+ + +</td>
<td>+ +</td>
<td>+ + +</td>
</tr>
<tr>
<td>A/D-Eop-D-P</td>
<td>-</td>
<td>+ + +</td>
<td>+ + +</td>
<td>+ + +</td>
<td>+ +</td>
</tr>
<tr>
<td>A/D-Eop-Dn-D</td>
<td>- -</td>
<td>+ +</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>A/D-Eop-DnD</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A/D-Eop-D</td>
<td>+</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
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<td>Z/D-Eop-DnD</td>
<td>0</td>
<td>-</td>
<td>+</td>
<td>+</td>
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</tr>
<tr>
<td>A/D-Eop-D/P</td>
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<td>0</td>
<td>0</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Z/D-Eop-D/P</td>
<td>+</td>
<td>0</td>
<td>0</td>
<td>+</td>
<td>+ +</td>
</tr>
</tbody>
</table>
Effect of pulp washing

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Advances in eucalyptus pulp bleaching technology

Effect of post O$_2$ carryover and D$_{100}$ recycle to D$_{100}$ stage on D$_{100}$-E$_{op}$ kappa number and brightness. The letters PO stand for post oxygen.

Effect of post O$_2$ carryover and D$_{100}$ recycle to D$_{100}$ stage on D$_{100}$ E$_{op}$ kappa number and brightness

Pulp: Southern Pine, PO kappa 18
D$_{100}$ recycle 8.5 kg/t COD, PO carryover 10 kg/t COD, 18.5 kg/t COD total
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Effect of COD originating from different sources on brightness decrease and kappa increase after the E-stage

- COD caused by lignin from cooking
- COD caused by lignin from oxygen delignification
- COD caused by lignin from D0-stage

/5/ Viirimaa, M., Dahl, O., Niinimäki, J., Ala-Kaila, K. and Perämäki, P

ISO-Brightness (%) decrease after E-stage

ISO-brightness (%) decrease

kgCOD/bdt into the D-stage

0 1 2 3 4 5 6 7 8 9 10

0 0.5 1 1.5 2 2.5 3 3.5

kgCOD/bdt into the D-stage

0 1 2 3 4 5 6 7 8 9 10

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1

COD caused by lignin from cooking
COD caused by lignin from oxygen delignification
COD caused by lignin from D0-stage
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Laboratory bleaching trial dilution with clean water and circulating filtrate in D₀-stage. Bleaching sequence D₀-EP-D₁-D₂. SWSA, kappa 13.1. ClO₂ charge in D₀ 3.8% and in D₁ 1.5%.

Increase in the chemical consumption, when diluting with filtrates

Brightness, % ISO

Total ClO₂ charge, kg act.Cl/bdt

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/6/ Alastalo, J., Vehmaa, J., Pikka, O
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3-stage bleach plant with fractional and non-fractional washing at normal and reduced effluent discharge

Total COD in pulp kg/adt

<table>
<thead>
<tr>
<th></th>
<th>A/D₀</th>
<th>Eop</th>
<th>D₁</th>
<th>DM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bleach Plant Effluent 15 m³/adt</td>
<td>5</td>
<td>8.9</td>
<td>5</td>
<td>1.9</td>
</tr>
<tr>
<td>Bleach Plant Effluent 10.8 m³/adt</td>
<td>5</td>
<td>22.8</td>
<td>14.5</td>
<td>3.6</td>
</tr>
<tr>
<td>Segregated washing</td>
<td>17.9</td>
<td>16.6</td>
<td>11.5</td>
<td>5.4</td>
</tr>
<tr>
<td>Non-segregated washing</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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Pulp quality
Fiber deformation/Fiber damage

Caused by chemical and mechanical treatment

- at high alkali concentration
- at high temperature
- brown stock/oxygen delignification areas most critical
Fiber curl                     Fiber kink                 Microcompression

Dislocation                     Fiber Twist                  Fiber wall collapse

/11/ Rauvanto, I., Henricson, K.,
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The effect of HexA in brightness reversion in laboratory-bleached eucalyptus pulps

Delta Brightness, %

HexA, meq/kg

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Correlation between PC and carbonyl content after 48 h of ageing at 80°C and 65% relative humidity

PC, 48h ageing

oxidized kraft pulp
oxidized kraft pulp (xylan reduced)

/7/ Adorjan, I., Zhou, Z., Jääskeläinen, A.-S., Potthast, A., Vuorinen, T.,
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OX in pulp in different bleaching sequences

OX ppm

DEDD, DEDD, A/DEDD, A/DEDD, A/DEDP

Sequence

/8/ Martikka, M

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A modern effluent treatment system

Reductions:
- COD: 70-75%
- AOX: 50-60%
- BOD5: 95%
- Color: 60-70%
Recent mill results
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Veracel Fiberline 3000 ADMT/D

Cooking with Lo-Solids
Brownstock washing
Oxygen Delignification
Knotting & Screening

Bleaching

Pulp brightness 92% ISO
Active chlorine 23 kg/ADT
Peroxide 5 kg/ADT

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2405 ADMT/D
Eucalyptus
92 ISO
27.5 kg act Cl/adt
3.7 kg H₂O₂/adt
Viscosity >1000SCAN
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Eucalyptus Fiberline, 800,000 ADMT/a

Cooking with Lo-Solids®

Brownstock Washing

Oxygen Delignification

Knotting & Screening

Blow Tank 6000 m³

2 x DD4580.2MC

O₂

55 min

2x DD4580.2LC

Condensate/Hot Water

Brownstock Hi-D Tank 6000 m³

Bleaching

A

120 min

Dₘ

15 min

E₂o₃

60 min

Dₚ

120 min

Dₘ

2.5 min

Dₜ

120 min

To Hot Water Tank

Warm Water

White water

Hot water

Bleached HD Tanks 2 x 6000 m³

Pulp brightness 92% ISO

Active chlorine 27.5 kg/ADT

Peroxide 3.7 kg/ADT

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Development of Chemical Pulp Mill during 10-15 years

Driving forces: Efficiency - Quality - Environmental safety/Energy - Raw materials

Single line capacity doubled, MC-technology in wider use

Improved control of chip raw material and pulp quality

Improved cooking:
- LoSolids, EAPC, ITC, Supebatch

1990

Modern mill:
1000-1300 tpd
C/DEDED
Effluent 50-70 m³/t
AOX 1,5-3,0 kg/t

Modern mill:
1600-2000 tpd
DEoDD or ZPZP
Effluent 10-20 m³/t
AOX < 0.5 kg/t
Surplus electricity +

1995

Modern mill:
2500-3000 tpd
A/DEopD(PO) or (ZD)EopDPO
Effluent 10-15 m³/t
AOX 0.1-0.2 kg/t
Surplus electricity ++
Advanced controls

2000

Modern mill:
3000-4000 tpd
A/DEopD(PO) or (ZD)EopDPO or Shorter sequence
Bleach filtrate treatment
Chemical balance control
Effluent <10-15 m³/t or less
AOX < 0.1 kg/t
Surplus electricity +++
Advanced controls
Simulation
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Conclusion

Double-stage oxygen delignification creates the basis for low chemical bleaching

Low carryover to bleaching and a low carryover amount in each bleach stage is very important

ECF bleaching is a dominant bleach concept. Several variations of bleach sequences are possible

HexA removal is an established stage in the bleaching sequence. A four-stage sequence A/D-Eop-D-P is recommended for 92+ISO brightness

Brightness reversion is improved through the removal of HexA. Reduction of act. chlorine usage and a final P-stage improve brightness stability
Conclusion …

OX in pulp is reduced by lower act. chlorine usage and a final P-stage

Electricity and steam consumption in a modern bleach plant is 70-80 kWh/adt and 359-450 kg/adt respectively

Effluent flow from ECF bleaching is 10-15 m$^3$/adt. AOX, COD and BOD5 discharges are very low after a modern effluent treatment system

Chemical consumption of 23 kg act. Cl/adt and 5 kg/adt peroxide in four-stage bleaching to 92.5 ISO in mill conditions has been achieved
Thank you for your attention