The Chemistry of Bleaching and Post-Color Formation in Kraft Pulps

Göran Gellerstedt
Content

- The structure of residual lignin
- The meaning of kappa number
- General aspects on bleaching
- The oxygen stage
- The chlorine dioxide stage
- The peroxide stage
- Post-yellowing of kraft pulps
- Conclusions
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Degree of delignification for different wood species

<table>
<thead>
<tr>
<th>Pulp type</th>
<th>Kappa No</th>
<th>Lignin kappa</th>
<th>Delign. degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine</td>
<td>28.0</td>
<td>24.6</td>
<td>94.0</td>
</tr>
<tr>
<td>Birch</td>
<td>16.5</td>
<td>4.0</td>
<td>98.2</td>
</tr>
<tr>
<td>Eucalyptus gl.</td>
<td>15.9</td>
<td>5.7</td>
<td>97.5</td>
</tr>
</tbody>
</table>
### G-units/S-units in white birch wood

<table>
<thead>
<tr>
<th>Morphological Differentiation</th>
<th>Guaiacyl/Syringyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre, S2-layer</td>
<td>12 : 88</td>
</tr>
<tr>
<td>Vessel, S2-layer</td>
<td>88 : 12</td>
</tr>
<tr>
<td>Ray parenchyma, S-layer</td>
<td>49 : 51</td>
</tr>
<tr>
<td>Middle lamella (fibre-fibre)</td>
<td>91 : 9</td>
</tr>
<tr>
<td>Middle lamella (fibre-vessel)</td>
<td>80 : 20</td>
</tr>
<tr>
<td>Middle lamella (fibre-ray)</td>
<td>100 : 0</td>
</tr>
<tr>
<td>Middle lamella (ray-ray)</td>
<td>88 : 12</td>
</tr>
</tbody>
</table>

Ref. Saka and Goring, 1988

![Lignin structure](image)
Kraft pulping of birch and E. globulus respectively to similar kappa numbers.
Possible reasons for the more rapid delignification in E globulus

• Higher frequency of β-O-4 structures.  
  Probably not
• Less G-units.  
  Yes, probably true
• Different chain lengths in lignin – more phenolic end-groups in eucalypt.  
  Not known but possible
• Different types of LCC.  
  Yes, according to present knowledge
β-O-4 structures in wood and pulp based on thioacidolysis

(Birch and Euc. gl)

Degradation product, μmol/g of lignin

Klason lignin, %: 16.6 0.6 18.3 0.9

3rd ICEP, 2007
\[\beta\text{-ether cleavage in pulping; birch and eucalyptus globulus}\]

\[\beta\text{-aryl ether structures, mmol/kg lignin}\]

Birch:
Gellerstedt et al, ISWPC 1989

Euc. gl.:
Pinto et al, J Wood Chem Technol, 2002
Kinetic data for model compounds

Phenolic units, 130 °C

\[
\text{HO-} \text{O-} \text{OCH}_3 \quad \rightarrow \quad k = 6.6 \times 10^{-3} \text{ min}^{-1}
\]

\[
\text{HO-} \text{O-} \text{OCH}_3 \quad \rightarrow \quad k = 12.1 \times 10^{-3} \text{ min}^{-1}
\]

Non-phenolic units, 140 °C

\[
\text{HO-} \text{O-} \text{OCH}_3 \quad \rightarrow \quad k = 1.5 \times 10^{-3} \text{ min}^{-1}
\]

\[
\text{HO-} \text{O-} \text{OCH}_3 \quad \rightarrow \quad k = 1.2 \times 10^{-3} \text{ min}^{-1}
\]

Ref. Kondo et al 1995
“Peeling” of linear lignin

A low value of $n$ gives a high number of phenolic end-groups and a faster lignin degradation/dissolution

$$\left(\text{HO-S-O-S}\right)_n$$
Distribution of lignin in LCCs from spruce kraft pulp

(Network = GlcMan-L-Xyl)
Chromatographic separation of pulp polymers in unbleached birch pulp

Ref. Karlsson, 1996

Cellulose
Hemicelluloses
Lignin
Distribution of lignin in LCCs from birch and E. globulus kraft pulps

Kappa Number ~16; Lignin-related Kappa = 4.0 and 5.7 respectively
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## Contribution to kappa number in some selected pulps

<table>
<thead>
<tr>
<th>Pulp type/Kappa number</th>
<th>Lignin(^1)</th>
<th>HexA(^1,2)</th>
<th>Non-lignin(^1,3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine kraft</td>
<td>18.6</td>
<td>14.3</td>
<td>1.9</td>
</tr>
<tr>
<td>Pine soda/AQ</td>
<td>18.9</td>
<td>16.8</td>
<td>0.3</td>
</tr>
<tr>
<td>Birch kraft</td>
<td>13.6</td>
<td>6.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Eucalyptus kraft</td>
<td>17.2</td>
<td>9.0</td>
<td>7.4</td>
</tr>
</tbody>
</table>

1) calculated in Kappa number units  
2) HexA = Hexenuronic acid  
3) Non-lignin = non-specified but oxidizable structures
Formation of hexenuronic acid on kraft pulping of E globulus

160 °C, AA=17%, sulf.=28%, L/W=4

Ref: C. Pascoal Neto et al, 1999
Non-lignin structures vs hemicelluloses

Ref: S. Antonsson et al, 2003
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Brightness development as a function of lignin-related kappa number
Successive changes in kappa number for a softwood kraft pulp

Reduction in kappa number, %

-40 -20 0 20 40 60 80 100

Lignin
HexA
"non-lignin"

O DE QP
Successive changes in kappa number for a birch kraft pulp

Reduction in kappa number, %

-120 -60 0 20 40 60 80 100

O Q(OP) Q(PO)

Lignin
HexA
"non-lignin"
Bleachability in P- and D-based bleaching respectively (softwood)

Chemical charge, kg/odt

- **ECF-sequence**
- **TCF-sequence**

Kappa number after the O-stage

Brightness = 43 % ISO

Brightness = 55 % ISO
Consumption of bleaching chemicals (OXE/kappa No) to reach +90% ISO

Bleaching sequence
Pine: OD(OP)(DQ)(PO)
Birch: OD(OP)D
Euc. gl.: OD(OP)DP

Ref: F. Lundkvist, STFI-PF
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The effect of alkali treatment, "leaching", on kraft pulps

Softwood kraft; 80 °C; 120 min; low cons.; lab. experiments

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Kappa No</th>
<th>Reduction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before</td>
<td>after</td>
</tr>
<tr>
<td>Industrial, after O-stage</td>
<td>11.9</td>
<td>9.6</td>
</tr>
<tr>
<td>Laboratory, unbleached</td>
<td>17.7</td>
<td>13.6</td>
</tr>
<tr>
<td>Laboratory, unbleached</td>
<td>38.4</td>
<td>25.4</td>
</tr>
</tbody>
</table>

Industrial eucalypt kraft; lignin extraction with/without oxygen

<table>
<thead>
<tr>
<th>O-stage</th>
<th>NaOH, kg/t</th>
<th>Oxygen, kg/t</th>
<th>Temp., °C</th>
<th>pH</th>
<th>Kappa No, unbl.</th>
<th>Kappa No, O-stage</th>
<th>Red., %</th>
</tr>
</thead>
<tbody>
<tr>
<td>with oxygen</td>
<td>13.5</td>
<td>11</td>
<td>92</td>
<td>11.9</td>
<td>15.5</td>
<td>9.3</td>
<td>40</td>
</tr>
<tr>
<td>without oxygen</td>
<td>10.6</td>
<td>0</td>
<td>87</td>
<td>11.7</td>
<td>15.5</td>
<td>11.7</td>
<td>25</td>
</tr>
</tbody>
</table>
Modes of lignin degradation in the oxygen stage

... to acidic groups

... and formation of methanol

Sidechain elimination

Ring splitting

Demethoxylation
Major carbohydrate reactions in the O-stage resulting in cleavage of cellulose chains

Further degradation

Alkali stable end-group of the HexA-type
Presence of glucuronic acid and glucuronaldehyde groups in kraft pulps

Spruce/pine

Birch

Blue = Glucuronic acid

Red = Sum of glucuronaldehyde and glucuronic acid
Amount of lignin linked to glucan, xylan and glucomannan after the O-stage

Spruce/pine kraft pulp

Lignin in LCC, %

Δ kappa in O-stage

Glucomannan-LCC

Glucan-LCC

Xylan-LCC
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Delignification response on D and D+C bleaching of kraft pulp with/without phenols

Pine kraft pulp

Chlorine number

Kappa no.

- methylated pulp
- reference

(D + C)E

DE

Time, min

0 30 60 90

Ref. U. Germgård, Ph.D. Thesis 1982
The chemistry of chlorine dioxide oxidation of lignin

Ref: Ni et al, 1991
Formation of organic chlorine in a D-sequence (softwood)

Lignin - H \(\xrightarrow{\text{HOCl/Cl}_2}\) Lignin - Cl

![Graph showing AOX, kg/t for D0, E1, D1, E2, D2, and Total]

AOX, kg/t

- D0
- E1
- D1
- E2
- D2
- Total
Chemical changes in an A-stage, pH=3.5

Eucalyptus gr.; unbleached kappa 17.9; HexA = ~60 μmol/g

Ref: Smedmark and Sjödahl, 2000
Efficiency of hexenuronic acid removal from E. globulus pulp in a D-stage

\[ D_0 = \text{pH 3, 60 °C, 45 min; } D_{ht} = \text{pH 3, 90 °C, 240 min} \]

<table>
<thead>
<tr>
<th>Stage</th>
<th>HexA removal, mmol/kg</th>
<th>Visc., mL/g</th>
<th>Brightness, % ISO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>Hydrol.</td>
<td>Ox.</td>
</tr>
<tr>
<td>-</td>
<td>0 (67)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( D_0 )</td>
<td>36</td>
<td>0.4</td>
<td>36</td>
</tr>
<tr>
<td>( D_{ht} )</td>
<td>60</td>
<td>22</td>
<td>38</td>
</tr>
<tr>
<td>( D_0(EO)D_1D_2 )</td>
<td>55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( D_{ht}(EO)D_1D_2 )</td>
<td>66</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) Original value in pulp after the O-stage
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Cleavage of a phenolic ether structure in lignin with peroxide
Alkaline peroxide oxidation of lignin, isolated from a kraft pulp after the O-stage

![Graph showing Peroxide consumption and Color removal vs. Time (min)]
Brightness after O seems to determine the peroxide consumption

(softwood)
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Yellowing - Influence of moisture

Birch kraft; TCF-bleached; Temp: 60 °C

\[ \Delta \text{light absorption coeff.} \]

\[ 92\% \text{ Dry content} \]

\[ 99\% \text{ Dry content} \]

Time, days
Yellowing – Influence of temperature

Birch kraft; TCF-bleached; Dryness: 92%

\[ \Delta \text{ light absorption coeff.} \]

\[ \begin{array}{c}
\text{Time, days} \\
0 & 2 & 4 & 6 & 8 & 10 \\
\end{array} \]

- 80°C
- 60°C
- 40°C

Ref: C. Rööst, Södra
Post-color number for bleached kraft pulps from spruce, birch and eucalypt
Changes in the content of HexA, FA and FFA with ageing time

E. grandis; ECF-bleached

\[ \mu \text{mol/g} \]

<table>
<thead>
<tr>
<th>Time at 70 °C</th>
<th>Original</th>
<th>2 days</th>
<th>5 days</th>
<th>7 days</th>
<th>9 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>HexA remaining</td>
<td>□</td>
<td>□</td>
<td>□</td>
<td>□</td>
<td>□</td>
</tr>
<tr>
<td>FA + FFA</td>
<td>□</td>
<td>□</td>
<td>□</td>
<td>□</td>
<td>□</td>
</tr>
<tr>
<td>Missing HexA</td>
<td>□</td>
<td>□</td>
<td>□</td>
<td>□</td>
<td>□</td>
</tr>
</tbody>
</table>

\[ \text{HexA} \rightarrow \text{FA} + \text{FFA} \]
Correlation between brightness loss and the “missing HexA”
Reaction scheme for the formation of yellowing products in bleached kraft pulp
Brightness of filter paper after ageing in the presence of oxidized sugars

Ageing: 80 °C, 16 h, 80% Rh

<table>
<thead>
<tr>
<th>Added Compound</th>
<th>Brightness, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>86.8</td>
</tr>
<tr>
<td>Cellobiose</td>
<td>83.5</td>
</tr>
<tr>
<td>Glucuronic acid</td>
<td>37.4</td>
</tr>
<tr>
<td>3-keto-methyl-β-glucoside</td>
<td>37.4</td>
</tr>
<tr>
<td>Reductic acid</td>
<td>19.4</td>
</tr>
</tbody>
</table>

Ref: O. Theander 1988
Possible ways of reducing the yellowing tendency

- Prolonged D-stage at high temperature
- A specific A-stage
- Adjustment of temperature prior to baling
- Addition of radical scavanger
Conclusions

- The chemical reactions between pulp and various bleaching agents are well known
- The chemistry behind the high degree of yellowing of certain bleached kraft pulps is known
- The structure of residual fiber lignin after pulping is partially known
- The importance of condensation reactions in pulping is not known
- The changes occurring in pulping and bleaching of the wood polymers on the ultrastructural level are not known

It is surprising that the lignin after pulping (2-3% in hardwoods) is so resistant towards all bleaching agents.