The importance of wood density and chemistry on eucalyptus clone selection

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MARKET PULP DEMAND BY GRADE

- Bleached Softwood
- Bleached Hardwood
- Eucalyptus

Hardwood surpasses Softwood

Source: Cenibra/HW
Bleached HWD Fiber Production Cost Composition in 2006

Outline

• Kraft Pulp Production
  – Wood density
  – Wood extractives content
  – Wood lignin content
    • Lignin syringyl/guaiacyl ratio
  – Wood Cellulose content
  – Wood hemicelluloses/uronic acid contents

• Pulp Refinability

• Pulp Drainability
Kraft Pulp Production
Wood Quality Traits

- Wood density
- Wood Contents of:
  - Cellulose
  - Extractives
  - Lignin
    - Lignin S/G
  - Hemicelluloses
  - Uronic Acids

- PULPING YIELD
- SWC

SWC = Specific Wood Consumption = $m^3$ wood/odt pulp
Wood Quality Traits

Wood density

Wood Contents of:
- Cellulose
- Extractives
- Lignin
  - Lignin S/G
- Hemicelluloses
- Uronic Acids

- PULPING YIELD
- SWC
7-8 yr old eucalyptus samples cooked to kappa 17-18

Source: Colodette et al. (7)
7-8 yr old eucalyptus samples cooked to kappa 17-18

Source: Colodette et al. (7)
Chilean *Eucalyptus globulus* cooked to kappa 15-16

Effect of wood density and pulping yield on SWC for *Eucalyptus grandis* and *Eucalyptus urophylla* cooked to kappa 17-18

<table>
<thead>
<tr>
<th>Trait</th>
<th><em>Eucalyptus grandis</em></th>
<th><em>Eucalyptus urophylla</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood density, kg/m³</td>
<td>389</td>
<td>544</td>
</tr>
<tr>
<td>Pulping yield, %</td>
<td>55.9</td>
<td>51.7</td>
</tr>
<tr>
<td>SWC, m³/odt pulp</td>
<td>4.60</td>
<td>3.56</td>
</tr>
</tbody>
</table>

Source: Colodette et al. [7]
Higher densities are desirable to minimize SWC.

No clear correlation with pulping yield for Brazilian grown eucalyptus.

Overall, one should strive for high wood densities.
Wood Quality Traits

- Wood density
- Wood Contents of:
  - Cellulose
  - Extractives
  - Lignin
    - Lignin S/G
  - Hemicelluloses
  - Uronic Acids

- PULPING YIELD
- SWC
Effect of wood cellulose content on pulping yield at kappa 18±0.5 for twelve 7-9 year old *Eucalyptus* clones

\[ y = 1.246x - 7.862 \]
\[ R^2 = 0.587 \]

Conclusions: Cellulose

- Maintaining other traits constant, cellulose content should correlate very positively with pulping yield;
- Brazilian grown eucalyptus contain unusually high cellulose contents as compared to northern HWDs.
Wood Quality Traits

Wood density

Wood Contents of:
- Cellulose
- Extractives
- Lignin
  - Lignin S/G
- Hemicelluloses
- Uronic Acids

- PULPING YIELD
- SWC
Effect of wood ethanol/toluene and DCM extractive contents on pulping yield at kappa 18±0.5 for ten seven-year old *Eucalyptus*

\[
y = -0.246x + 16.04 \\
R^2 = 0.664
\]

\[
y = -0.014x + 1.018 \\
R^2 = 0.059
\]

Source: Gomide & Colodette (9)
## Effect of age on eucalyptus wood extractive content and pulping yield at kappa 17-21.5 (Uruguayan Plantations)

<table>
<thead>
<tr>
<th>Species</th>
<th>E. grandis</th>
<th>E. saligna</th>
<th>E. benthamii</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Age, yr</strong></td>
<td>4</td>
<td>9</td>
<td>4 9</td>
</tr>
<tr>
<td><strong>Extractives, %</strong></td>
<td>0.8 2.9</td>
<td>0.9 3.2</td>
<td>1.0 4.3</td>
</tr>
<tr>
<td><strong>Density, kg/m³</strong></td>
<td>445 498</td>
<td>460 509</td>
<td>450 479</td>
</tr>
<tr>
<td><strong>Kappa No.</strong></td>
<td>19.7 17.2</td>
<td>21.5 18.5</td>
<td>19.9 17.1</td>
</tr>
<tr>
<td><strong>Effective Alkali, %</strong></td>
<td>16.5 17.0</td>
<td>15.7 17.9</td>
<td>16.3 18.0</td>
</tr>
<tr>
<td><strong>Pulping Yield, %</strong></td>
<td>48.5 47.9</td>
<td>48.5 46.4</td>
<td>47.8 46.6</td>
</tr>
</tbody>
</table>

*Source: Backman et al. (11)*
Eucalyptus low molecular weight (apolar = lipophyllic) extractives that cause pitch problems

Swan, B.; Akerblom, I.S. Svensk Papperstidn. 70(7), 239-244, 1967.
Conclusions: Extractives

- Extractives negatively affect pulping yield;
- Brazilian grown eucalyptus contains low extractives because of young harvesting age, but content increases fast with aging (premature formation of heartwood);
- *Eucalyptus globulus* develops heartwood at a later age and extractives are less of a problem;
- *Eucalyptus lipophyllic* extractive fraction causes severe pitch problems (steryl esters).
Wood Quality Traits

- Wood density
- Wood Contents of:
  - Cellulose
  - Extractives
  - Lignin
    - Lignin S/G
    - Hemicelluloses
    - Uronic Acids

- PULPING YIELD
- SWC
Effect of lignin content on pulping yield and effective alkali demand to kappa 18±0.5 for ten seven-year old samples

Source: Gomide & Colodette (8)
Relationship between pulping yield and effective alkali demand at kappa 17±0.5 for seventy-five eucalyptus wood samples (5-8.6 yr old)

\[ y = -0.14x^2 + 3.33x + 36.16 \]

\[ R^2 = 0.71 \]

Source: Costa, 2009 (with permission)
Main sustructures of *Eucalyptus globulus* lignin (RMN $^{13}\text{C}$, $^{1}\text{H}$, $^{13}\text{C}-^{1}\text{H}$)

- $\beta$-$\text{O}$-$4$: 56%
- $\alpha$-$\text{O}$-$4$: 23%
- $\beta$-$\beta$ + $\gamma$-$\text{O}$-$\alpha$: 10%

Conclusions: Lignin

- Lignin correlates significantly and negatively with pulping yield

- Lignin correlates significantly and positively with effective alkali demand

- Overall, one should strive for low lignin contents, if fiber line yield is main priority
Wood Quality Traits

- Wood density
- Wood Contents of:
  - Cellulose
  - Extractives
  - Lignin
    - Lignin S/G
  - Hemicelluloses
  - Uronic Acids

- PULPING YIELD
- SWC
Molar Proportion of *Eucalyptus globulus* basic structural Units

- **H**: 2-3% (p-Hidroxyphenilpropane)
- **G**: 12-18% (Guaiacylpropane)
- **S**: 80-86% (Syringylpropane)

Effect of lignin S/G ratio on pulping yield at kappa 17 for twenty-four three-year old *Eucalyptus urograndis* wood samples.

\[ y = 4.358x + 39.45 \]

\[ R^2 = 0.615 \]

*Source: Gomes, Colodette & Gomide (10).*
Relationship between wood lignin content and syringyl/guaiacyl ratio for 100 samples of three-year old *Eucalyptus urograndis*

Source: Colodette et al. (20).

From Genolyptus Project
Conclusions: Lignin S/G

- Lignin S/G correlates positively with pulping yield
- Lignin S/G ratio correlates negatively with wood lignin content
- Overall, one should strive for high lignin S/G
Wood Quality Traits

- Wood density
- Wood Contents of:
  - Cellulose
  - Extractives
  - Lignin
    - Lignin S/G
  - Hemicelluloses (xylans)
  - Uronic Acids

- PULPING YIELD
- SWC
## Total Hemicellulose Content in Eucalyptus (7 yr old trees)

<table>
<thead>
<tr>
<th>Clone</th>
<th>Brazilian Elite Clones</th>
<th>Eucalyptus globulus - Aust</th>
<th>Eucalyptus nitens - Aust</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.7</td>
<td>29.1</td>
<td>30.8</td>
</tr>
<tr>
<td>2</td>
<td>23.1</td>
<td>28.7</td>
<td>32.6</td>
</tr>
<tr>
<td>3</td>
<td>21.9</td>
<td>27.7</td>
<td>32.4</td>
</tr>
<tr>
<td>4</td>
<td>22.6</td>
<td>28.2</td>
<td>32.0</td>
</tr>
<tr>
<td>5</td>
<td>23.9</td>
<td>28.4</td>
<td>31.2</td>
</tr>
<tr>
<td>6</td>
<td>22.1</td>
<td>27.9</td>
<td>33.1</td>
</tr>
<tr>
<td>7</td>
<td>21.3</td>
<td>27.1</td>
<td>32.2</td>
</tr>
<tr>
<td>8</td>
<td>22.9</td>
<td>26.8</td>
<td>29.5</td>
</tr>
<tr>
<td>9</td>
<td>24.7</td>
<td>27.3</td>
<td>33.1</td>
</tr>
<tr>
<td>10</td>
<td>24.8</td>
<td>23.3</td>
<td>28.7</td>
</tr>
</tbody>
</table>

*Source: Gomide & Colodette, 2005; Wallis, 1996.*
### Effect of Wood Age on Xylan content

<table>
<thead>
<tr>
<th>Species</th>
<th>Age 4 yrs</th>
<th>Age 9 yrs</th>
<th>Xylan Loss with 5yrs Aging, %</th>
<th>Xylan Loss/yr, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>E. grandis</td>
<td>16,2</td>
<td>13,6</td>
<td>16,0</td>
<td>3,2</td>
</tr>
<tr>
<td>E. saligna</td>
<td>17,7</td>
<td>14,1</td>
<td>20,3</td>
<td>4,1</td>
</tr>
<tr>
<td>E. dinnii</td>
<td>18,8</td>
<td>15,8</td>
<td>16,0</td>
<td>3,2</td>
</tr>
<tr>
<td>E. maidenii</td>
<td>19,6</td>
<td>17,9</td>
<td>8,7</td>
<td>1,7</td>
</tr>
<tr>
<td>E. benthamii</td>
<td>16,1</td>
<td>13</td>
<td>19,3</td>
<td>3,9</td>
</tr>
</tbody>
</table>

*Source: Backman et al. (11)*
Distribution of eucalyptus wood O-acetyl-4-O-methylglucuronoxylans xylans after kraft pulping to kappa 17, expressed in % of wood original value

<table>
<thead>
<tr>
<th>Wood Species</th>
<th>Xylans, % of original wood</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pulp</td>
</tr>
<tr>
<td><strong>E. dunni</strong></td>
<td>51.3</td>
</tr>
<tr>
<td><strong>E. globulus</strong></td>
<td>54.1</td>
</tr>
<tr>
<td><strong>E. grandis</strong></td>
<td>57.3</td>
</tr>
<tr>
<td><strong>E. nitens</strong></td>
<td>52.6</td>
</tr>
<tr>
<td><strong>E. urograndis</strong></td>
<td>49.7</td>
</tr>
<tr>
<td><strong>E. urophylla</strong></td>
<td>58.7</td>
</tr>
</tbody>
</table>

*Source: Magaton & Colodette (5).*
Effect of wood O-acetyl-4-O-methyl-glicuronoxylans content on pulping yield at kappa 18±0.5 for ten seven-year old clones

Source: Gomide & Colodette (8).
Effect of wood xylan content on kraft pulp xylan content for various eucalyptus species at kappa 17

![Graph showing the relationship between xylan content in wood and xylan content in pulp. The graph includes data points for different eucalyptus species: E. nitens, E. globulus, E. urograndis, E. dunnii, and E. urophylla. The equation of the trend line is y = 1.027x + 1.786 with R² = 0.912.]

Source: Magaton & Colodette (5).

Considering the xylan backbone only.
Effect of active alkali dose on xylan degradation across pulping to kappa 17 for various eucalyptus species

Considering the xylan backbone only

\[ y = 2.712x - 13.27 \]
\[ R^2 = 0.796 \]

Source: Magaton & Colodette (5).
### Molar Ratio 4-O-MeGUA / 10 xyloses, in xylans from various eucalyptus species, measured by methanolysis – GC/MS and $^1$H NMR

<table>
<thead>
<tr>
<th>Wood Species</th>
<th>4-O-MeGUA / 10 xyloses</th>
<th>Methanolysis – GC/MS</th>
<th>$^1$H NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>E. dunni</em></td>
<td>1.5</td>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td><em>E. globulus</em></td>
<td>1.7</td>
<td></td>
<td>2.6</td>
</tr>
<tr>
<td><em>E. grandis</em></td>
<td>2.2</td>
<td></td>
<td>2.8</td>
</tr>
<tr>
<td><em>E. nitens</em></td>
<td>1.4</td>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td><em>E. urograndis</em></td>
<td>1.3</td>
<td></td>
<td>1.9</td>
</tr>
<tr>
<td><em>E. urophylla</em></td>
<td>2.0</td>
<td></td>
<td>2.6</td>
</tr>
</tbody>
</table>

Source: Magaton & Colodette (5).
Molar Ratio between $O_2$ Substituted 4-O-MeGUA / Total 4-O-MeGUA, in xylans from various eucalyptus species, measured by $^1$H NMR

<table>
<thead>
<tr>
<th>Wood Sample</th>
<th>4-O-MeGUA/ 10 xyloses (mol/mol)</th>
<th>$O_2$ Substituted 4-O-MeGUA/ 10 xyloses (mol/mol)</th>
<th>$O_2$ Substituted 4-O-MeGUA / Total 4-O-MeGUA, %</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>E. dunni</em></td>
<td>2.1</td>
<td>0.40</td>
<td>19</td>
</tr>
<tr>
<td><em>E. globulus</em></td>
<td>2.6</td>
<td>0.44</td>
<td>17</td>
</tr>
<tr>
<td><em>E. grandis</em></td>
<td>2.8</td>
<td>0.64</td>
<td>23</td>
</tr>
<tr>
<td><em>E. nitens</em></td>
<td>2.1</td>
<td>0.19</td>
<td>9</td>
</tr>
<tr>
<td><em>E. urograndis</em></td>
<td>1.9</td>
<td>0.19</td>
<td>10</td>
</tr>
<tr>
<td><em>E. urophylla</em></td>
<td>2.6</td>
<td>0.68</td>
<td>26</td>
</tr>
</tbody>
</table>

Source: Magaton & Colodette (5).
Eucalyptus xylans possess galactose/glucose side chains, unusually high uronic acid contents, and are reasonably stable towards kraft pulping.
Effect of 4-O-MeGUA content on xylan degradation across pulping to kappa 17 for various eucalyptus species

Source: Magaton & Colodette (5).

Considering the xylan backbone only

$y = -11.45x + 65.57$

$R^2 = 0.771$
Effect of wood total uronic acid content on pulping yield at kappa 17 for twenty four three-year old *Eucalyptus urograndis* wood samples

Source: Gomes & Colodette (10).
Eucalyptus has twice as much uronic acids compared to northern HWD

4-O-Me-glucuronic Acid

Hexenuronic Acid

Pulping

NaOH  MeOH
Effect of uronic acid content on HexAs generation/degradation across pulping to kappa 17 for various eucalyptus species

Source: Magaton & Colodette (5).
MW (kDa) of xylans in the wood and in the corresponding kraft pulp: harvesting age eucalyptus clones of various origins cooked to kappa number 17 [5]

<table>
<thead>
<tr>
<th>Species</th>
<th>Wood</th>
<th>Kraft Pulp</th>
<th>Black Liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td>E. dunni</td>
<td>36.7</td>
<td>19.4</td>
<td>13.4</td>
</tr>
<tr>
<td>E. globulus</td>
<td>33.0</td>
<td>19.6</td>
<td>14.3</td>
</tr>
<tr>
<td>E. grandis</td>
<td>37.9</td>
<td>20.9</td>
<td>14.7</td>
</tr>
<tr>
<td>E. nitens</td>
<td>33.2</td>
<td>19.8</td>
<td>13.8</td>
</tr>
<tr>
<td>E. urograndis</td>
<td>34.9</td>
<td>19.9</td>
<td>14.3</td>
</tr>
<tr>
<td>E. urophylla</td>
<td>39.4</td>
<td>21.1</td>
<td>18.1</td>
</tr>
</tbody>
</table>
Effect of pulp delignification degree (Kappa No.) on pulp xylan molecular weight (kDa) : harvesting age eucalyptus clones of various origins cooked to kappa number 15-22

Source: Magaton & Colodette (5).

Higher MW xylans are more desirable to improve pulp properties.
Conclusions: Xylans/ Uronic Acids

- Brazilian grown eucalyptus have low xylan content, but they are rich in uronic acid (2-2.5/10 xyloses) and reasonably stable towards kraft pulping as compared to northern HWDs.

- Xylan MW in the wood is in the range of 30 kDa and decreases to about half of that value after pulping to kappa 17. Pulp xylan MW increases with increasing kappa no.

- High xylans in the wood means high xylans in the pulp, but xylans are very sensitive to EA dosed during pulping.

- Overall, one should strive for high xylans and uronic acids in the wood, but cook the wood properly (gently).
Pulp Refinability and Drainability
World Paper Production

- Euca Pulp: 32%
- Container Board: 15%
- Printing & Writing: 13%
- Card Board: 8%
- Newsprint: 15%
- Tissue: 32%

Foelkel, 2006
Effect of wood density on energy demand at 70 N.m/g tensile index. Eight seven year old *Eucalyptus* wood samples cooked to kappa 17

$y = 0.0668x^2 - 57.55x + 12913$

$R^2 = 0.7703$

Source: Costa, 2009.
Effect of pulp xylan content on energy demand at 70 N.m/g tensile index. Twenty four three-year old *Eucalyptus urograndis* wood samples cooked to kappa 17 and ECF bleached to 90% ISO brightness.

Source: Gomes & Colodette (10).
Effect of pulp xylan content on energy demand at 60 N.m/g tensile index. Two seven-year old *Eucalyptus urograndis* wood samples cooked to kappa 17 and ECF bleached to 90% ISO brightness under unusual conditions.

Source: Pedrazzi & Colodette 2009
“At 60 N.m/g tensile, an increase in pulp xylan content from 13% to 17% decreased energy demand by 40%, which signifies about 10% energy savings per one percent xylan increase”
Effect of wood density on bleached pulp fiber coarseness and refinability to 30 °SR. Eight harvesting age eucalyptus wood samples cooked to kappa 17-18 and ECF bleached to 90% ISO brightness

Source: Colodette et al. (7).
Effect of wood fiber coarseness on capilarity Klemm (unrefined pulp). Eight harvesting age eucalyptus wood samples cooked to kappa 17-18 and ECF bleached to 90% ISO brightness.

\[ y = 2.485x - 5.291 \]
\[ R^2 = 0.706 \]

Source: Colodette et al. (7).
Effect of wood fiber coarseness on WRV (unrefined pulp). Eight harvesting age eucalyptus wood samples cooked to kappa 17-18 and ECF bleached to 90% ISO brightness

Source: Colodette et al. (7).
Effect of wood density on Bulk at 70 N.m/g tensile index. Eight seven year old *Eucalyptus urograndis* wood samples cooked to kappa 17

\[ y = -8E-06x^2 + 0.0095x - 1.3271 \]

\[ R^2 = 0.8225 \]

*Source: Costa, 2009 (with permission).*
Conclusions: Refinability / Drainability

- Refinability improves with increasing pulp xylan content and decreasing fiber coarseness (wood density), with the opposite being observed for drainability.

- Increasing pulp xylan content is desirable, but decreasing fiber coarseness is questionable since it means use of lower density woods and poorer drainability in the paper machine (hampers throughput).

- At the end of the day one wants high refinability and drainability which calls for coarse and xylan rich fibers.
What Shall We Do?

Thanks!!!