Modelling of *Eucalyptus Globulus* Kraft Pulping

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Outline

- Objective and review of existing cooking models
- Structure of selected kinetic model for
  - Delignification / cellulose degradation
  - Depolymerization
  - HexA formation
- Validation of the model
- Structural characterization of lignin during kraft pulping using a new method for lignin isolation
- Summary
Objective, Background

- *Eucalyptus globulus* Labill, one of the most interesting species among the > 600 species comprising the genus *Eucalyptus*\(^*\) represents the fiber source with the highest pulp yield and quality in both PP and DP.

- Major wood source for the production of market hardwood bleached kraft pulp in Europe (Spain, Portugal). Growing interest to grow *E. globulus* in plantations in Australia and South America.

- However, little information is available about delignification kinetics of the *Eucalyptus* species in general and of *E. globulus* in particular.

- It is the objective to develop a comprehensive kinetic model to predict delignification, carbohydrate degradation, depolymerization (viscosity loss) and HexA formation and degradation.
Literature Review on Modeling of *E. globulus* Kraft pulping
Three Phase Model\(^1\)

Concept of Consecutive Reactions

- **Initial delignification:** Lignin > 0.82\(L_0\)
  \[
  - \frac{dL}{dt} = 252 \cdot \exp\left(-\frac{37700}{R \cdot T}\right) \cdot \sqrt{T} \cdot L
  \]
  \[
  \frac{d[OH^-]}{d[L]} = 2.7
  \]

- **Bulk delignification:** 0.05\(L_0\) < Lignin < 0.82\(L_0\)
  \[
  - \frac{dL}{dt} = 3.13 \cdot 10^{11} \cdot \exp\left(-\frac{106000}{R \cdot T}\right) \cdot [OH^-]^{0.15} [SH^-]^{0.16} \cdot L
  \]
  \[
  \frac{d[OH^-]}{d[L]} = 0.92
  \]

- **Residual delignification:** Lignin < 0.05 (0.03 – 0.065) \(L_0\)
  \[
  - \frac{dL}{dt} = 1.13 \cdot 10^8 \cdot \exp\left(-\frac{86000}{R \cdot T}\right) \cdot [OH^-]^{0.59} \cdot L
  \]
  \[
  \frac{d[OH^-]}{d[L]} = 0.55
  \]

Transition from the bulk to the residual phase is dependend on \([OH^-]\) and \(T\):
\[
\Delta L/L_0 = 0.022[OH^-] + 6.9 \times 10^{-4}T + 0.82
\]
Min = 0.93 (0.7 \(OH^-/150^\circ C\)), Max = 0.97 (1.6M \(OH^-/180^\circ C\))

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Prediction of Step Changes: $[\text{OH}^-] = 0.1 \text{ M} \oplus 1.0 \text{ M}$

$T = 160 \degree \text{C}$
Experimental
**Wood Source**

*E. globulus*, M'Bopicua, Uruguay (ENCE)

<table>
<thead>
<tr>
<th>Parameter, % od</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Klason Lignin</td>
<td>KL 22,1</td>
</tr>
<tr>
<td>Acid Soluble Lignin</td>
<td>AL 4,6</td>
</tr>
<tr>
<td>Cellulose</td>
<td>C 47,3</td>
</tr>
<tr>
<td>4-O-methylglucuronoxylan</td>
<td>X 21,8</td>
</tr>
<tr>
<td>Glucomannan</td>
<td>GM 2,2</td>
</tr>
<tr>
<td>Resins, Ash</td>
<td>2,0</td>
</tr>
<tr>
<td>Total</td>
<td>100,0</td>
</tr>
</tbody>
</table>

### Reaction conditions

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Impregnation</th>
<th>Reaction Kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L1</td>
<td>L2</td>
</tr>
<tr>
<td>[OH⁻]</td>
<td>mol/L</td>
<td>0,37</td>
</tr>
<tr>
<td>[SH⁻]</td>
<td>mol/L</td>
<td>0,16</td>
</tr>
<tr>
<td>[Na⁺]</td>
<td>mol/L</td>
<td>1,5</td>
</tr>
<tr>
<td>L/S</td>
<td>kg/kg</td>
<td>10</td>
</tr>
<tr>
<td>Temperature (T)</td>
<td>°C</td>
<td>100</td>
</tr>
<tr>
<td>Time (max at T)</td>
<td>min</td>
<td>60</td>
</tr>
</tbody>
</table>
Structure of Selected Kinetic Model
Model Structure: Delignification, Carbohydrate Degradation

- General rate expression / general solution of first-order equations:

\[
\frac{dW_{i,j}}{dt} = -k_{W_{i,j}} \cdot W_{i,j}
\]

\[
W_{i,tot} = \sum_{j=2}^{3} W_{i,j}^0 \cdot \text{Exp}(-k_{W_{i,j}} \cdot t)
\]

- Dependency of rate expressions on the reaction conditions:

\[
k_{W_{i,j}} = A_{W_{i,j}} \cdot \text{Exp}\left[ \frac{EA_{W_{i,j}}}{R} \cdot \left( \frac{1}{443} - \frac{1}{T} \right) \right] \cdot \left[\text{[OH}^{-}]^{a} \cdot \text{[HS}^{-}]^{b} \cdot \text{[Na}^{+}]^{c} + k_r \right]
\]
Concept of Interchanging Species\\(^2\)

\(W_2\) and \(W_3\) interchange reversibly: \(W_2 = W_3 = W^* = f(\text{conditions})\)

\[L^* = 0.001487 \cdot \left( [OH^-] + 0.025 \right)^{-0.625} \cdot \left( [HS^-] + 0.045 \right)^{-0.308} \cdot \left( [Na^+] + 5.0 \right)^{4.106}\]

\[CH^* = 55.44 + 68.45 \cdot [OH^-] - 0.48 \cdot T \cdot [OH^-]\]
Kinetics of Cellulose Chain Scissions

\[
\left( \frac{1}{DP_{n,t}} - \frac{1}{DP_{n,0}} \right) = A \cdot \exp\left( - \frac{E_{A_c}}{R} \frac{1}{T} \right) \cdot [OH^{-}]^d \cdot [Na^+]^e \cdot t
\]

- **Kinetic Constants**

<table>
<thead>
<tr>
<th>Model parameter</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP_{n,0}</td>
<td>4900</td>
</tr>
<tr>
<td>ln A</td>
<td>(1/M*min) 36.48</td>
</tr>
<tr>
<td>E_{A_c}</td>
<td>kJ/mol 180.30</td>
</tr>
<tr>
<td>d</td>
<td>1.08</td>
</tr>
<tr>
<td>e</td>
<td>0.74</td>
</tr>
</tbody>
</table>

- An increase in ionic strength relates to an increase in cellulose degradation.
Diffusivity of Alkali, Chemical Consumption

- Gustafson\(^3\) corrected diffusivity based on McKibbins\(^4\) with respect to pH and lignin content with the ECCSA data published by Hartler;

\[
D = 0.057 \cdot \sqrt{T} \cdot \exp\left(-\frac{2452.4}{T}\right) \cdot \left(0.00364 \cdot \kappa \# + 0.13 \cdot \left[OH^-\right]^{0.55} + 0.58\right)
\]

- Consumption of active cooking chemicals (in the range of the data reported by Christensen\(^5\) et al.):

<table>
<thead>
<tr>
<th>Component</th>
<th>EA-consumption</th>
<th>HS-consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td>0.20</td>
<td>0.04</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>0.45</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Course of [OH$^-$] during Batch Cooking

E. globulus Kraft

- Chip thickness: 4.0 mm
- Moisture content: 35%
- Chip density: 0.50 kg/L
- L/S: 4:1
- [$OH^-$]$_{t=t_0}$: 1.6 M
- [$HS^-]_{t=t_0}$: 0.245
- Temperature (at): 160 °C
- time_to: 90 min
- time_at: 112 min
- H-Factor: 800

Calculated:
- Free-[OH$^-$]
- Bound-[OH$^-$]
- Chip centre-[OH$^-$]

Experimental:

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Change of HexA is controlled by MeGlcA and HexA concentration (no dissolution considered)

\[
\frac{d[\text{HexA}]}{dt} = k_1 \cdot [\text{MeGlcA}] - k_2 \cdot [\text{HexA}]
\]

Solution of the differential equation describing a consecutive reaction

\[
[\text{HexA}] = \frac{k_1 \cdot [\text{MeGlcA}]_0}{(k_2 - k_1)} \cdot (\text{Exp}(-k_1 t) - \text{Exp}(-k_2 t))
\]

[MeGlcA]_0 = 166 mmoL/kg wood
[HexA]_0 = 0 mmoL/kg wood

---

Effect of Temperature on HexA profile

Model describes sufficiently well the pattern of a simple successive first-order reaction. Activation energies quite comparable to those reported by Danielsson et al.
Validation of the Kinetic Model
Prediction of Step Changes at L/S = 40:1

Immediate change from 0.1 M [OH\(^-\)] to 1.0 M [OH\(^-\)]

Agreement between calculated and measured kappa numbers satisfactory
Prediction of Kappa and Viscosity at L/S = 3:1

Pilot Plant trials with *E. globulus*

*H-Factor: 300, 450, 600, 800*

- $[\text{OH}^-]_0$: 1.60 M
- $[\text{HS}^-]_0$: 0.25 M
- $[\text{Na}^+]$: 2.00 M
- $T$: 160 °C

Good fit between measured and calculated pulp properties.

Surprisingly, prediction of viscosity more precisely as compared to the kappa number.
Structural Characterization of Lignin during Kraft Pulping using a New Method for Lignin Isolation

Isolation of **Dissolved Wood Lignin (DWL)**

Lignocellulose Preparation

- drying
- milling in cutting mill (40 mesh)
- extraction in aceton:water=9:1
- drying at 0.003 mbar

Dissolution

- ball milling under N2, 48 h
- dissolution in 30 mL 2 vol DMSO + 1 vol NMI per g substrate

Lignin/Carbohydrate Separation

- precipitation in 600 mL 9 vol dioxane + 1 vol water
- centrifugation at 5000 rpm to separate cellulose
- destillation of solvent, recovery of raw lignin

Lignin Purification

- dissolution of raw lignin in 75%HOAc
- centrifugation, filtration, precipitation in water
- centrifugation at 13000 rpm
- drying of purified lignin

Removal of Extractives

- DCM- and acetone extractions in ASE

Removal of Metal Ions

- lignin dissolution in 5 vol acetone + 1 vol water
- addition of washed ion exchanger Amberlite IR748C, shaking overnight
- filtration
- washing, freeze-drying

Lignin Acetylation

- acetylation according to S.Y. Lin and C.W. Dence in acetic anhydride/pyridine

Characterization of Lignin Samples

<table>
<thead>
<tr>
<th>Origin</th>
<th>DWL</th>
<th>Yield</th>
<th>kappa number</th>
<th>K Lignin</th>
<th>AS Lignin</th>
<th>Xylan</th>
</tr>
</thead>
<tbody>
<tr>
<td>wood</td>
<td>1</td>
<td>100</td>
<td>141</td>
<td>141</td>
<td>22,4</td>
<td>4,0</td>
</tr>
<tr>
<td>precook11</td>
<td>2</td>
<td>90</td>
<td>101</td>
<td>91</td>
<td>19,5</td>
<td>4,3</td>
</tr>
<tr>
<td>CBC266</td>
<td>3</td>
<td>65</td>
<td>73</td>
<td>48</td>
<td>5,9</td>
<td>3,4</td>
</tr>
<tr>
<td>CBC256</td>
<td>4</td>
<td>54</td>
<td>34</td>
<td>19</td>
<td>1,5</td>
<td>0,8</td>
</tr>
<tr>
<td>CBC211</td>
<td>5</td>
<td>51</td>
<td>14</td>
<td>7</td>
<td>1,1</td>
<td>0,6</td>
</tr>
</tbody>
</table>

$k_{1} = 141$
$k_{2} = 91$
$k_{3} = 48$
$k_{4} = 19$
$k_{5} = 7$

DWL appears to be a facile new method for lignin isolation, applicable also for the isolation of residual lignin of low-kappa number pulps.
### HSQC spectrum of *E. globulus* kraft pulp, κ# = 91

#### Assignment 13C 1H Int (OMe) change rel. to native

<table>
<thead>
<tr>
<th>Assignment</th>
<th>13C</th>
<th>1H</th>
<th>Int (OMe)</th>
<th>change rel. to native</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-O-4: α</td>
<td>73.9</td>
<td>6.1</td>
<td>0.4</td>
<td>12%</td>
</tr>
<tr>
<td>β-O-4: α S2 + β-1?</td>
<td>75.0</td>
<td>6.1</td>
<td>0.4</td>
<td>46%</td>
</tr>
<tr>
<td>β-O-4: α S3</td>
<td>74.8</td>
<td>5.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Σβ-O-4: α</td>
<td>--</td>
<td>--</td>
<td>0.8</td>
<td>40%</td>
</tr>
<tr>
<td>β-O-4: β</td>
<td>80.7</td>
<td>4.4</td>
<td>12.4</td>
<td>47%</td>
</tr>
<tr>
<td>s-2,6</td>
<td>103.9</td>
<td>6.6</td>
<td>15.4</td>
<td>58%</td>
</tr>
<tr>
<td>s-2,6-α carbonyl</td>
<td>105.8</td>
<td>7.1</td>
<td>2.4</td>
<td>1%</td>
</tr>
<tr>
<td>g-2</td>
<td>111.0</td>
<td>6.9</td>
<td>2.5</td>
<td>0%</td>
</tr>
<tr>
<td>g-6</td>
<td>119.3</td>
<td>6.9</td>
<td>2.4</td>
<td>17%</td>
</tr>
<tr>
<td>g-5</td>
<td>122.3</td>
<td>6.9</td>
<td>1.4</td>
<td>-10%</td>
</tr>
<tr>
<td>β-β: β</td>
<td>54.1</td>
<td>3.0</td>
<td>0.4</td>
<td>14%</td>
</tr>
<tr>
<td>β-β: α</td>
<td>85.5</td>
<td>4.7</td>
<td>1.6</td>
<td>33%</td>
</tr>
<tr>
<td>β-β: γ</td>
<td>71.7</td>
<td>3.9</td>
<td>1.2</td>
<td>12%</td>
</tr>
<tr>
<td>β-β: γ</td>
<td>71.7</td>
<td>4.3</td>
<td>1.0</td>
<td>24%</td>
</tr>
<tr>
<td>β-5: α</td>
<td>88.0</td>
<td>5.4</td>
<td>0.5</td>
<td>-25%</td>
</tr>
<tr>
<td>β-5: β</td>
<td>50.2</td>
<td>3.8</td>
<td>0.5</td>
<td>-13%</td>
</tr>
</tbody>
</table>

**Note:** The acetylated DWL spectra show changes relative to the native wood, indicating modifications during the kraft pulp production process.
Quantitative $^{13}$C NMR

aliph.OAc
phen.OAc
kappa 48
kappa 91
native

ArC-O ArC-C ArC-H
Structural Changes of *E. globulus* Lignin during Kraft Pulping

After initial delignification, kappa number 91 odw

- preferential dissolution of G type units, DWL enriched in S type units
- increase in β-O-4-units
- moderate increase in β–β-structures
- no change in the amount of quarternary carbons in aromatic nuclei, ArC-C
- decrease in β-5: (α-O-4)

During bulk delignification, kappa number 48 odw

- decrease in S type units, predominantly s-2,6.
- decrease in β-O-4-units
- moderate decrease in β–β-structures
- slight increase in the amount of ArC-C
- no significant changes in the amount of aliphatic and aromatic OH
Conclusions

- Comprehensive kinetic model, based on the concept of Andersson et al., adequately describes delignification, carbohydrate degradation, HexA formation and degradation and cellulose chain scissions.

- Distribution model introduced by Andersson et al. suitable for offline studies and industrial kraft cooks.

- New Method for Lignin Isolation: The combination of total dissolution of lignocellulosic substrates with elements from the classical MWL preparation appears to be a facile new method for lignin isolation and presumably also for carbohydrate isolation.
Acknowledgment

- Wood *Kplus* and Lenzing AG provided financial support

- Co-workers of Pulp R&D department of Lenzing AG
**HexA vs. Kappa number**

**Influence of [OH⁻]**
- [OH⁻], Mol/L: 0.10 (black), 0.52 (blue), 1.23 (red)

**Influence of T**
- Temperature, °C: 140 (black), 150 (blue), 170 (red)

**Influence of [SH⁻]**
- [SH⁻], Mol/L: 0.17 (black), 0.28 (blue), 0.64 (red)

**Influence of [Na⁺]**
- [Na⁺], mol/L: 0.8 (black), 1.5 (blue), 2.5 (red)