DINAMICS OF IMPREGNATION IN EUCALIPTUS KRAFT PULPING.

Inalbon, M. C., Bernal, J. I., Mussati, M. C., Citroni, M. A., Zanuttini, M. A.

ITC-FIQ-UNL and INGAR

Santa Fe, ARGENTINA
Degree of impregnation

A proper impregnation leads to a more uniform pulp.

A narrower kappa number distribution of the individual fibers can be obtained (Malkov et al. 2003).
Incomplete impregnation leads to:

- **Uncooked rejects** (Gullichsen 1995).
- **Pulping yield** (Gullichsen et al. 1992, 1995).
- **Pulp strength** (Gullichsen 1995).
- **Pulp bleachability** (Malkov 2002).
Wood direction of interest

- The critical dimension for alkali impregnation is the chip thickness
Wood direction of interest

• The critical dimension for alkali impregnation is the chip thickness
Wood direction of interest

- The critical dimension for alkali impregnation is the chip thickness
Partially impregnated chip

- 9% NaOH/wood
- 95 °C
- 30 min
Chip thickness: critical dimension

Radial

Tangential

transverse wood directions
In the last ICEP we present a model with the following characteristic.

**Unidireccional**

**Chemical reactions:**
- a) Deacetylation (is the main one)
- b) Acid groups neutralization or hydrolysis of their esters.

**Chemical species**
- Mobile ions: a) Sodium
  - b) Hydroxide
  - c) Acetate
- Fixed: a) Acetyl group
  - b) Non ionic acid groups
  - c) Ionized acid groups

**Diffusion affected by de Effective capillary (Tangential)**

Inalbon, M.C. Doctoral Thesis UNL 2008
Modeling

For each chemical species we consider:

\[
\frac{\partial c_i}{\partial t} = - \frac{\partial}{\partial x} \left( - D_i \frac{\partial c_i}{\partial x} \right) + \frac{z_i F D_i c_i}{RT} \frac{\partial \Phi}{\partial x} + R_i
\]

Where:

- \( c_i \): Molar concentration of "i" specie
- \( t \): Time
- \( x \): Position from the external interphase
- \( D_i \): Diffusion coefficient of "i"
- \( z_i \): Charge number of "i"
- \( F \): Faraday constant
- \( \Phi \): Electric potential
- \( R_i \): Reaction rate
$C_0: 0.25 \text{ N}; 110^\circ \text{C}$

**Graph:**
- **Y-axis:** Concentration (mol/l)
- **X-axis:** Position (cm)
- **Lines:**
  - Pink: Acetyl (1min)
  - Blue: OH- (1min)
- **Note:** 1 min mark on the graph.
$C_0: 0.25 \text{ N; 110}^\circ \text{C}$

![Graph showing concentration over position](image)

- **Acetyl** (5min)
- **OH-** (5min)

5 min
C₀: 0.25 N; 110°C

![Graph showing concentration vs. position](image)

- **Position (cm)**
  - 0.00 to 0.22
- **Concentration (mol/l)**
  - 0.0 to 0.5

- **10 min**
- **Acetyl (10min)**
- **OH- (10min)**
$C_0: 0.25 \text{ N; } 110^\circ \text{C}$

15 min

- Concentration (mol/l)
  - Acetyl (15 min)
  - OH- (15 min)

Position (cm)
$C_0: 0.25 \text{ N; } 110^\circ \text{C}$

Graph showing concentration (mol/l) versus position (cm) with the text "20 min" at the center.

- Pink line: Acetyls (20min)
- Blue line: $\text{OH}^-$ (20min)
$C_0: 0.25 \text{ N; } 110^\circ\text{C}$

25 min

Position (cm)

Concentration (mol/l)

- Acetlys (25min)
- OH- (25min)
C₀: 0.25 N; 110°C

30 min

Concentration (mol/l)

Position (cm)

Acetyl (30min) OH- (30min)
C₀: 0.25 N; 110°C

35 min

Concentration (mol/l)

Position (cm)

Acyls (35 min)  OH- (35 min)
C₀: 0.25 N; 110°C

Graph showing the concentration (mol/l) over position (cm) for Acetyl (40 min) and OH- (40 min).
$C_0: 0.25 \text{ N; } 110^\circ\text{C}$

![Graph showing concentration vs. position](image)

- **50 min**

- **Concentration (mol/l)**
  - Y-axis: 0.00 to 0.50
  - Values: 0.00, 0.10, 0.20, 0.30, 0.40, 0.50

- **Position (cm)**
  - X-axis: 0.00 to 0.22
  - Values: 0.00, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14, 0.16, 0.18, 0.20, 0.22

- **Graph lines**
  - Pink: Acyls (50min)
  - Blue: OH- (50min)
C₀: 0.25 N; 110°C

70 min

Concentration (mol/l)

Position (cm)

Acetyls (70min)  OH- (70min)
Advances:

• Effective Capillary: **Radial** and **Tangential**

• Deactylation kinetics (**ion strength effect**)

• Donnan effect on concentrations of ions in the wood

• Sulfidity effect (**25% and 35%**)

• Extended experimental profiles corroboration
The concept of effective capillary (Stone 1957) allows considering for each ion:

$$D_i = EC \cdot D_i^0$$

- Diffusion coefficient in wood
- Effective Capillary (the same for all ions)
- Ion diffusion coefficient in the liquid medium
- Slices of wood (400 µm)
- a low mass and thermal diffusion restriction

The evolution of electrical conductivity through slices, was measured when slice undergoes the alkali action.
**Determination**

The slice was considered as a electrical series circuit with the solution

---

**Arrangement used for conductivity determination**

(Inalbon M.C.; Zanuttini, M. Holzforschung 2008, 62 (4))
An empiric equation of Capillary as a function of acetyl content and temperature was obtained:

\[ EC = f(Ac, T) \]

\( Ac \) : Acetyl content  \( T \) : Temperature
Effective Capillary Radial and Tangential

- pH12, 20°C, radial
- pH12, 20°C, tangential
Effective Capillary
Radial and Tangential

Acetyls (%) vs. Effective Capillary

- pH13, 45°C, radial
- pH13, 45°C, tangential
- pH12, 20°C, radial
- pH12, 20°C, tangential
Kinetics of reactions

Deacetylation

- 350 µm thickness slices treated under different conditions of alkali concentration at 20º, 45º and 90 ºC.
- Total ion strength effect was considered

Inalbon, M.C., Mocchiutti, P., Zanuttini, M. 2009. Bioresourse Technology 100 (7), 2254-2258
Deacetylation kinetics

\[ R_{\text{Acetyl}} = A \cdot \exp\left(\frac{-E}{RT}\right) \cdot (C_{\text{Acetyl}})^n \cdot (C_{\text{OH}})^m \cdot (C_{\text{Na}})^p \]

\( A \) : Arrhenius constant
\( E / R \) : Relative activation energy
\( T \) : Temperature (°K)
\( C_{\text{Acetyl}} \) : Acetyl concentration
\( C_{\text{OH}} \) : Hydroxyl concentration
\( C_{\text{Na}} \) : Sodium concentration
\( n, m, p \) : Reaction orders
Acid groups reactions

- Acid groups neutralization
- Esters hydrolysis

These reactions represent an additional alkali consumption (21 % more than deacetylation).

\[
\frac{\text{Reacting acid groups}}{\text{AcetylS}} = \frac{0.198 \text{ eq/Kg}}{0.907 \text{ eq/Kg}} = 0.21
\]

We consider them as coupled to deacetylation reaction (they have the same reaction rate).

\[
R_{NaOH} = 1.21 \cdot R_{Acetilo}
\]
Donnan effect

Relationship between concentrations:

- liquor
- wood side of the interphase

Donnan: “The ion activity is the same in both phases”

\[ \lambda = \frac{Na_i^+}{Na_e^+} = \frac{OH_e^-}{OH_i^-} = \frac{SH_e^-}{SH_i^-} \]

i: internal  E: external

Internal and external electroneutrality:

\[ Na_e^+ = OH_e^- + SH_e^- \quad Na_i^+ = OH_i^- + SH_i^- + GA_i^- \]
Example of the concentrations distribution between the liquor and internal side of the liquor-wood interface according to Donnan effect.

<table>
<thead>
<tr>
<th></th>
<th>External solution (liquor) (mol/L)</th>
<th>Internal side of the interphase (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>0.285</td>
<td>0.373</td>
</tr>
<tr>
<td>OH⁻</td>
<td>0.25</td>
<td>0.19</td>
</tr>
<tr>
<td>SH⁻</td>
<td>0.035</td>
<td>0.027</td>
</tr>
<tr>
<td>GA⁻</td>
<td>--</td>
<td>0.156</td>
</tr>
</tbody>
</table>
Experimental profiles

- Eucalyptus grandis (6 year old) cubes of 3 cm
- Pre steaming
- Impregnation at 0.6 Mpa

<table>
<thead>
<tr>
<th>NaOH (g/L)</th>
<th>Sulfidity (%)</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ; 20</td>
<td>25 ; 35</td>
<td>110</td>
<td>15 ; 30</td>
</tr>
</tbody>
</table>
On 200 µm slices determination of:

- Liquid content (by weight)
- Hydroxyls content (titration-SCAN N 2:63)
- Sulfhydrate content (titration-SCAN N 2:63)
- Acetyls content (FTIR)
- Sodium content (atomic absorption spectroscopy)
Differential equations system

It involves 10 differential equations and 10 variables in space and time:

- 7 chemical species concentrations
- Deacetylation rate
- Effective Capillarity
- Electrical potential

Numerically solved by gPROMS.
Results
Model vs. Experimental Data

Exp Acetyls

$110^\circ$C, 30 min
EA: 9.6 g/L
sulfidity 25%
Results
Model vs. Experimental Data

110°C, 30 min
EA: 9.6 g/L
sulfidity 25%
Results
Model vs. Experimental Data

Concentration (mol/L)

Position (mm)

110°C, 30 min
EA: 9.6 g/L
sulfidity 25%
Results
Model vs. Experimental Data

Concentration (mol/L)

position (mm)

110°C, 30 min
EA: 9.6 g/L
sulfidity 25%

Acetyls
Acetyls Exp
OH
OH Exp

Results
Model vs. Experimental Data

110°C, 30 min
EA: 9.6 g/L
sulfidity 25%
Results

Model vs. Experimental Data

110°C, 30 min
EA: 9.6 g/L
sulfdity 25%
Results
Model vs. Experimental Data

Concentration (mol/L)

position (mm)

110°C, 30 min
EA: 9.6 g/L
sulfidity 25%
Results
Model vs. Experimental Data

![Graph showing concentration profiles of Acetyl, Na, OH, and SH with experimental data points.](image)

- **Acetys**
- **Acetys Exp**
- **Na**
- **Na exp**
- **OH**
- **OH Exp**
- **SH exp**

**110°C, 30 min**
EA: 9.6 g/L
sulfidity 25%
Results

Model vs. Experimental Data

- Acetylts
- Acetylts Exp
- Na
- Na exp
- OH
- OH Exp
- SH
- SH exp

110°C, 30 min
EA: 9.6 g/L
sulfidity 25%
**Results**

**Model vs. Experimental Data**

**Acetylts:**
Reduction to 50% of the original content of acetylts in wood

**Hydroxyl:**
Start the increases of hydroxyl from null concentration
Results

EA: 10 g / L - sulfidity 25 %
110 °C - 30 min

Concentrations (mol/L)

Position (mm)
Results

EA: 10 g / L - sulfidity 25 %
110 °C - 30 min

Results
Results

EA: 10 g / L  -  sulfidity 25 %
110 °C        -  30 min

Concentrations (mol/L)

Position (mm)
Results

EA: 10 g / L - sulfidity 25 %
110 °C - 30 min

Concentrations (mol/L)

Position (mm)
Results

EA: 10 g / L - sulfidity 25 %
110 °C - 30 min

Concentrations (mol/L)

Position (mm)

Na
OH
Acetate
Acetyl
SH
Results

EA: 10 g / L - sulfidity 25 %
110 °C - 30 min

Concentrations (mol/L)

Position (mm)

Na

Acetyl

OH

Acetate

GA

SH
**Results**

EA: 10 g / L - sulfidity 25 %
110 °C - 30 min

![Graph showing the concentrations of various components over position (mm).]
Results

Position of the impregnation front predicted by the model (start the increases in hydroxyl from null concentration) 5, 15, 30 min

AE: 10 g/L; S: 25%
AE: 10 g/L; S: 35%
AE: 14 g/L; S: 25%
AE: 14 g/L; S: 35%
AE: 20 g/L; S: 25%
AE: 20 g/L; S: 35%
Results

Position of the impregnation front predicted by the model (start the increases in hydroxyl from null concentration) 5, 15, 30 min
Results
Position of the impregnation front predicted by the model (start the increases in hydroxyl from null concentration) 5, 15, 30 min
Results

Chemical consumption of the “impregnation reactions” and “total alkali taken by wood”
Results

Chemical consumption of the “impregnation reactions” and “total alkali taken by wood”
Results

Chemical consumption of the “impregnation reactions” and “total alkali taken by wood”
Results

Chemical consumption of the “impregnation reactions” and “total alkali taken by wood”
Applications

Chip thickness distribution can be considered
Applications

Different alkali profiling scenarios

Co-current

Countercurrent
EA: 20 g NaOH/L, Sulfidity: 25%

110 °C
EA: 20 g NaOH/L, Sulfidity: 25%

110 °C
EA: 20 g NaOH/L, Sulfidity: 25%  
110 °C
EA: 20 g NaOH/L, Sulfidity: 25%

110 °C

Concentration (mol/L)

Position (mm)

OH
Acetyls

10 min
EA: 20 g NaOH/L, Sulfidity: 25%

110 ºC

15 min
EA: 20 g NaOH/L, Sulfidity: 25%

110 °C

Concentration (mol/L)

Position (mm)

20 min

OH

Acetyls
EA: 20 g NaOH/L, Sulfidity: 25%

110 ºC

Concentration (mol/L)

Position (mm)

25 min
EA: 20 g NaOH/L, Sulfidity: 25%

110 °C

30 min
EA: 20 g NaOH/L, Sulfidity: 25%
110 °C

35 min
EA: 20 g NaOH/L, Sulfidity: 25%
110 °C

40 min
Application

- A sequence like this can give a criterion to take a decision regarding the extent of impregnation stage
This model allows the analysis of the effects of impregnation variables such as:
• external alkali concentration,
• temperature,
• time
• chip thickness
• sulfidity

For a specific wood:
The experimental determination of the effective capillary and the kinetic parameters are necessary to make predictions.
Concluding Remarks (2)

• Phenomenon: A reaction front is established which moves to the interior of the wood and separates an intact inner zone from a reacted and swollen outer zone.

• Sodium profile goes faster than the alkali concentration profile.
Concluding Remarks (3)

the model allows considering:

• a) Additional ions such as sulfide; hydrosulfide, carbonate and others.

• b) Chip thickness distribution

• b) Changes in external alkali concentration including different alkali profiling scenarios.
Acknowledgments:

- Universidad Nacional del Litoral
- CONICET
- ANPCyP

Thank you for your attention