MODELING of the ALKALINE IMPREGNATION of EUCALYPTUS CHIPS. REACTIONS and ION TRANSPORT

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KRAFT PROCESS

STEAMING

IMPREGNATION
(105 – 120 °C)

COOKING
(165 °C)
Degree of impregnation

A proper impregnation leads to a more homogeneous 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
Partially impregnated chip

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

Radial

Tangential

Transverse wood directions
Steaming stage and pressurized impregnation: consequences

If wood has an acceptable permeability:
Steaming rapidly displaces the air from the chip.

A good steaming + pressurized impregnation → High liquid uptake
(Malkov et al. 2001).

Under these conditions, for eucalyptus wood, we have shown that:
- Wood results almost saturated with liquid
- No evidence of alkali inside wood was found
  (Inalbon y col. 2005).
Liquor penetration and reaction

Spent liquor penetration

Chip

Liquor penetration and reaction
Assumption

Impregnation (in thickness direction) is considered:

- Isothermal process

- A diffusion process in wood saturated with liquid (penetration has finished)
Chemical reactions

- a) Deacetylation.
- b) Acid groups neutralization or hydrolysis of their esters.
- c) Peeling.

The deacetylation is the main reaction:

- It accounts for most of the alkali consumption (Zanuttini et al, 2003).
- It can be taken as indicative of the wood swelling produced by the alkali treatment (Zanuttini et al, 1999).
Chemical reactions consequences

- Alkali consumption (5 – 6 % on wood)
- Chemical species
  - Mobile ions:  
    a) Sodium (+)
    b) Hydroxide (-)
    c) Acetate (-)
  
  - Fixed:  
    a) Acetyl groups
    b) Non ionic acid groups
    c) Ionized acid groups (-)
For the modeling we need:

- Kinetics of reactions
- Diffusion properties of each ion
Kinetics of reactions

a) Deacetylation

For the eucalyptus wood under study we made an experimental kinetic analysis:

Slices of wood (350 μm) were treated under different alkali concentrations and at 20°, 45° and 90 °C.
Deacetylation kinetics

- Obtained expression:

\[
R_{Acetyls} = k \left( C_{Acetyls} \right)^{2.09} \left( C_{OH^-} \right)^{1.53}
\]

- \( k \) : Specific rate constant
- \( C_{Acetyls} \) : Acetyl concentration
- \( C_{OH^-} \) : Hydroxil concentration

The \( k \)-constant follows the Arrhenius law:

\[
k(T) = A \exp \left( - \frac{E}{RT} \right)
\]

- \( A \) : Arrhenius constant
- \( E / R \) : Relative activation energy
- \( T \) : Temperature (°K)
Acid groups reactions

- Acid groups neutralization
- Ester hydrolysis

These reactions represent an additional alkali consumption (1 % NaOH on wood)

Assumption:
We consider them as coupled to deacetylation reaction (they have the same reaction rate)
Ion diffusion coefficients

- The concept of effective capillary (Stone 1957) allows considering for each ion:

\[ D_i = EC \cdot D_i^0 \]

\( D_i^0 \) can be interpolated in temperature using the Nernst-Einstein equation (\( u_i \) : ion mobility): 

\[ D_i^0 = u_i \cdot R \cdot T \]
Effective capillarity

Method:
- Slices of wood (400 µm)
- A low mass and thermal diffusion restriction

- The evolution of electrical conductivity through slices, was followed using laboratory conductivimeter
EC determination

Slices were placed between electrodes of the conductivimeter cell

The slice was considered as a series electrical circuit with the solution
Effective Capillarity vs. pH

- 20°C-60 min

Graph showing the relationship between effective capillarity and pH, with a sudden increase at pH values above 12.
Effective Capillarity vs. pH

- 20°C-60 min
- 45°C-60 min

Temperature (T) and pH are plotted on the graph, showing the effective capillary changes with pH at different temperatures.
Effective Capillarity vs. pH

- 20°C-60 min
- 45°C-60 min
- 90°C-60 min

pH Range: 7 to 14

Effective capillary vs. pH graph showing different temperatures and time periods.
Effective Capillarity vs. pH

- 20°C-60 min
- 45°C-60 min
- 90°C-60 min
- Stone, 25°C, 24 hs

pH range: 7 to 14

Effective capillary range: 0 to 0.45
Effective Capillarity vs. Acetyl content

Acetyl content (%) vs. Effective capillary

20°C

pH 12
Effective Capillary vs. Acetyl content

Acetyl content (%)

Effective capillary

20°C

pH 12

pH 13
Effective Capillary vs. Acetyl content
An empiric equation of Capillarity as a function of acetyl content and temperature was used for modeling:

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

\( Ac \): Acetyl content  \( T \): Temperature
Modeling

For each chemical species we consider:

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

Where:

\( c_i \): Molar concentration of \( i \) specie

\( t \): Time

\( x \): Position from the external interphase

\( D_i \): Diffusion coefficient of \( i \)
Differentialequationssystem

\[ z_i : \text{Charge number of } \text{“i”} \]
\[ F : \text{Faraday constant} \]
\[ \Phi : \text{Electric potential} \]
\[ R_i : \text{Reaction rate} \]

**Differential equations system**

It involves 9 differential equations and 9 variables in space and time:

- ✓ 6 chemical species concentrations
- ✓ Deacetylation rate
- ✓ Effective Capillary
- ✓ Electrical potential
Results

Co = 0.5 M; T = 110ºC; 15 minutes

Concentration (mol/l)

Position (cm)

Na+
Results

Co = 0.5 M; T = 110ºC; 15 minutes

Concentration (mol/l)

Position (cm)

Na⁺

OH⁻

Concentration (mol/l)

Position (cm)

0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18 0.20 0.22

0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0

0.0 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18 0.20 0.22

OH⁻  Na⁺
Results

Co = 0.5 M; T = 110°C; 15 minutes

Concentration (mol/l)

Position (cm)

Na⁺

OH⁻

Acetyl
Results

Co = 0.5 M; T=110ºC; 15 minutes

Concentration (mol/l)

Position (cm)

Acetate

Acetyls

Na⁺

OH⁻
Results

Co = 0.5 M; T = 110ºC; 15 minutes

Concentration (mol/l)

Position (cm)

Acetate

AG

Na⁺

OH⁻

Acetyls
Results

Co = 0.5 M; T = 110°C; 15 minutes

Concentration (mol/l)

Position (cm)

AG
Acetate
Acetyls
nrAG
Model vs. Experimental Data

0.25N ; 105ºC; 5 minutes

Content (% on wood)

Position (microns)
Model vs. Experimental Data

0.25N ; 105ºC; 5 minutes

Content (% on wood)

Position (microns)

Acetyls

Acetyls exp
Model vs. Experimental Data

0.25N ; 105ºC; 5 minutes

Content (% on wood)
Content (% on wood)

Position (microns)
Position (microns)

0 500 1000 1500 2000
0 500 1000 1500 2000

- acetyls
- acetyls exp
- Na+ exp
Model vs. Experimental Data

0.25N; 105ºC; 5 minutes

Content (% on wood)

Position (microns)

- acetyl exp
- Na+ exp

0,25N; 105ºC; 5 minutes
Model vs. Experimental Data

0.25N; 105°C; 5 minutes

Content (% on wood) vs. Position (microns)

- Acetyls
- Na+
- OH- exp
- Na+ exp
Model vs. Experimental Data

0.25N; 105ºC; 5 minutes

Content (% on wood)

Position (microns)

- acetyl groups
- OH- groups
- Na+ groups

Experimental data points:
- Acetyl groups
- OH- groups
- Na+ groups
$C_0: 0.25 \text{ N; } 110^\circ \text{C}$

Acetyl Groups

1 min

Acetyl Groups

OH$^-$

Position (cm)

Concentration (mol/l)

Acetyls (1min)  OH- (1min)
$C_0$: 0.25 N; 110° C
C₀: 0.25 N; 110°C

10 min

Concentration (mol/l)

Position (cm)

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

The graph shows the concentration of Acetyl groups and OH- over position (cm) after 15 minutes. The concentration of Acetyl groups increases while the concentration of OH- decreases significantly.
$C_0: 0.25 \text{ N; } 110^\circ \text{C}$

**Graph:**
- Y-axis: Concentration (mol/l)
- X-axis: Position (cm)
- Line colors:
  - Pink: Acetyl (20 min)
  - Blue: OH- (20 min)

**Legend:**
- Acetyl: Pink line
- OH-: Blue line

**Note:** The graph shows the concentration change over position at 20 minutes under specific conditions.
$C_0: 0.25 \text{ N}; 110^\circ \text{C}$
$C_0$: 0.25 N; 110°C

30 min

Position (cm)

Concentration (mol/l)

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

35 min

Position (cm)

Concentration (mol/l)

Acetys (35min)  OH- (35min)
$C_0: 0.25 \text{ N; } 110^\circ \text{C}$

**Graph:**
- **Y-axis:** Concentration (mol/l)
- **X-axis:** Position (cm)
- **40 min**
- **Lines:**
  - Pink: Acetyl (40 min)
  - Blue: OH- (40 min)
$C_0$: 0.25 N; 110$^\circ$C

50 min

Position (cm)

Concentration (mol/l)

Acetyl (50min)  OH- (50min)
$C_0: 0.25 \text{ N; 110}^\circ \text{C}$

- **Concentration (mol/l)**
  - 0.00 to 0.50

- **Position (cm)**
  - 0.00 to 0.22

- **Graph**
  - Blue line: OH- (70 min)
  - Pink line: Acetyl (70 min)

- **70 min**
C₀: 0.25 N; 110°C

90 min

Position (cm)

Concentration (mol/l)

Acetyl (90min)  OH⁻ (90min)
Application

For a given wood and set of conditions:

- A sequence like this can give a criterion to take a decision regarding the extent of impregnation stage
Front Position vs. Time

![Graph showing the relationship between position (cm) and time (minutes) for two different conditions: 105°C-0.25N (black line) and 105°C-0.5N (blue line). The graph illustrates the increase in position over time for each condition.]
Front Position vs. Time

![Graph showing front position vs. time for different temperatures and forces.](image-url)
Speed of impregnation

• Model shows that a change in alkali concentration from 0.25 M to 1.0 M speeds up impregnation more than an increase in temperature from 105 to 120 °C
Concluding Remarks (1)

This model allows the analysis of the effects of impregnation variables such as:
- external alkali concentration
- temperature
- time
- chip thickness.

For a specific wood:
- effective capillary
- kinetic parameters

Should be experimentally verified before the application of the model.
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 outer zone.

- The alkali profile differs from Sodium concentration profile; the latter goes in the front of the former.
Concluding Remarks (3)

Besides the variables here analyzed, the model allows considering:

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

b) Chip thickness distribution

c) Changes in external alkali concentration including different alkali profiling scenarios
Deacetylation in biofuel production
Capillarity

1) to determine
2) to promote it by deacetylation

Are useful to analyze the effects of pre-treatments for fermentation processes
Deacetylation and Capillarity

Wood → Pretreatment → Biological treatment → Fermentation → Capillarity
• Thanks for your attention!