

Diffusion Dynamics in *Pinus sylvestris* Kraft Impregnation: Effect of Deacetylation and Galactoglucomannan Degradation

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Supporting Information

ABSTRACT: During the impregnation stage of a Kraft cooking, dynamic changes occur in wood properties due to the alkali action. Particularly, its ion transport capacity, the effective capillary cross sectional area (ECCSA), is changed due to chemical reactions and swelling. In this work, the ECCSA in the transverse wood direction has been determined for *Pinus sylvestris* on the basis of the analogy between capillarity and electrical conductivity. Results show that the behavior of ECCSA can be associated with (a) the degree of removal of native acetyl groups and (b) the galactoglucomannan (GGM) losses due to peeling/stopping reactions and alkaline hydrolysis. Kinetic expressions for both reactions were discussed and a correlation between the ECCSA and both acetyl and GGM contents was established.

1. INTRODUCTION

It is accepted that a proper impregnation is essential to achieve an efficient pulping process. For softwoods, it has been shown that incomplete impregnation increases the amount of uncooked rejects and affects pulping yield as well as uniformity, strength, and bleachability of the pulp.^{1–3} A deeper understanding of the alkaline impregnation of wood is necessary to analyze the effects of variables of current and new pulping processes. For detailed modeling and optimization, two different aspects of a given wood must be known: (a) the effective diffusion coefficient for the relevant chemical species and (b) a kinetic expression of the reactions involved. Considering eucalyptus wood, a similar concept was already applied for the Kraft impregnation process, obtaining concentration profiles that were very close to experimental results.^{4,5}

For poplar wood, temperatures up to 90 °C and alkali concentrations up to 0.25 mol/L, it has been shown that the main reaction is the removal of acetyl groups from the hemicelluloses.⁶ The same conclusion was obtained by Inalbon et al.⁷ for eucalyptus wood using temperatures up to 90 °C and alkali concentrations up to 1 mol/L NaOH. The removal of native acetyl groups from hardwood O-acetyl-glucuronoxylans or softwood O-acetyl-galactoglucomannans can have a major effect on both the physical characteristics of the polymer and the structure of the cell wall. For instance, the cell wall accessibility is particularly increased in hardwoods⁸ but also in softwoods.⁹

For *Pinus sylvestris*, temperatures from 80 °C to 130 °C and alkali concentrations ranging 0.31–1.55 mol/L, Paananen et al.¹⁰ showed that carbohydrates degradation is clearly relevant, especially for galactoglucomannans. These polymers suffer significant losses due to the peeling-off reaction in which monomer units are progressively eliminated from the reducing end groups and subsequently transformed into isosaccharinic acids. The stopping reaction of this process takes place when

the reducing end-group is converted into an alkali-stable metasaccharinic acid group. In addition to this, base-catalyzed cleavage of glycosidic bonds is possible at high temperatures. This reaction generates new reducing end groups, which undergo further peeling reactions.

Alkali strongly modifies the ion transport capacity of wood. The effective ion diffusion coefficients ($D_{\text{effective}}^i$) can be expressed in the following way:

$$D_{\text{effective}}^i = D^i \cdot \text{ECCSA} \quad (1)$$

where D^i is the diffusion coefficient of the “ i ” ionic species in the liquid medium, which depends only on temperature, and ECCSA is the area of paths available for diffusion.

ECCSA can be determined as the ratio between the electrical conductivities of the wood and the liquid medium.¹¹

For aspen wood at 25 °C, it was demonstrated that alkalinity induces notable changes in ECCSA in the transverse wood direction.¹¹ For eucalyptus wood at temperatures up to 90 °C, it was shown that these dynamic changes in transverse ECCSA strongly depend on the degree of the deacetylation reaction.¹²

Rigorous modeling of the impregnation phenomenon is useful for the prediction of concentration profiles obtained during impregnation, for each set of process variables. This model analyzes the species concentration distributions along position and time, which are dependent on diffusion speed and reactions rates. The relationship between the extents of reactions and ECCSA is necessary for the resolution of the differential equation system that results from the mass balance.

In the present work, the evolution of ECCSA under different conditions is determined on pine wood. The kinetics of deacetylation and GGM degradation reactions are discussed.

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Finally, the relationship between the extent of these reactions and the ECCSA is analyzed.

2. MATERIALS AND METHODS

2.1. Preparation of Wood Slices. Air-dried *Pinus sylvestris* wood was used for the study. Logs of 18 cm diameter were sawn into disks of about 3.5 cm high and then air-dried. Cubes of 35-mm-side length were sawn from the disks. The cubes were impregnated with distilled water by applying, at least, six vacuum and release cycles of 720 mm Hg and then stored at $-18\text{ }^{\circ}\text{C}$.

Slices of $350\text{ }\mu\text{m}$ thickness were cut from the radial faces of the cubes using a microtome and then stored at $5\text{ }^{\circ}\text{C}$ in their wet state until use.

2.2. Effective Capillarity Determination. ECCSA was determined using the method proposed by Inalbon and Zanuttini.¹² The procedure is based on the analogy between capillarity and electrical conductivities of wood. It involves the measurement of the ratio between the electrical conductivity of the solution-saturated wood slices and the conductivity of the corresponding solution. Radial slices were used to determine the ECCSA in the tangential wood direction.

ECCSA_{inert} is the ECCSA determined in 0.1 N NaCl solution at $20\text{ }^{\circ}\text{C}$. The Cl^- ion was chosen, but really, any inert ion of relatively high mobility could be used.

The inert solution allows the determination on untreated or treated slices. ECCSA of wood under the action of alkali (ECCSA_A), that is, under alkali or alkaline sulfide treatment, was determined for different conditions ranging 0.01–1 mol NaOH/L, 0–25% sulfidity, and $20\text{--}90\text{ }^{\circ}\text{C}$ (see Supporting Information Table S1).

Both ECCSA_A and ECCSA_{inert} were determined for each slice using the procedure proposed by Inalbon et al.¹³

2.2.1. Effects of Variables on ECCSA_A. Slices were placed into a basket of stainless steel mesh with internal compartments. The basket allowed the slices and solution to be in contact and also maintained slices separated from each other. Baskets with slices were placed in a thermostatted solution, the concentration of which can be regarded as constant during the treatment due to the high liquor-to-wood ratio (2000 g solution to 1 g wood). As the treatment time was reached, the baskets with slices were transferred to cold distilled water and washed. The conditions of the different experiments were $50\text{--}130\text{ }^{\circ}\text{C}$, $5\text{--}40\text{ min}$, and $0.01\text{--}1.55\text{ mol/L NaOH}$ (see Supporting Information Table S2 for more detail).

Then, slices were immersed in 0.1N NaCl solution for at least 8 h. Finally, ECCSA_{inert} was determined in this solution.

Each treatment was done on five slices. The ECCSA_A value of each slice under treatment solution was calculated using the ECCSA_{inert}/ECCSA_A relationship.

2.3. Acetyl Group Determination. After ECCSA determination, each slice was washed in distilled water and air-dried. The acetyl content of slices after treatments at selected conditions was determined by gas chromatography using a modification of a published method,¹⁴ as proposed by Inalbon et al.⁷ Butyric acid instead of propionic acid was used as the internal standard. Samples (100–150 mg) were treated at $150\text{ }^{\circ}\text{C}$ for 50 min in closed glass ampules with 1.25 mL of a liquor containing oxalic acid (63 g oxalic acid dihydrate/L) and 1.8 mL butyric acid/L. Acetyl content is reported as % $\text{CH}_3\text{CO/g o.d. wood}$.

2.4. Carbohydrate Analysis. For neutral sugars analysis, air-dried slices were cut into 1 mm^2 pieces and samples of 350

$\pm 20\text{ mg}$ were first acetone-extracted with Soxhlet based on SCAN 49:03. After that, the wood was subjected to acid hydrolysis as explained on the NREL method¹⁵ and the resulting sugars were determined with pulsed amperometric detection (anion exchange chromatography, Dionex HPAEC). The polysaccharide composition was calculated from the extractive content, Klason lignin, and the monosaccharide composition in the hydrolyzed sample using the method proposed by Janson.¹⁶ Klason lignin, extractives, and carbohydrates content, except for galactoglucomannans, are not reported in this work. Results are expressed as GGM weight fraction referred to the original content in wood.

3. RESULTS AND DISCUSSION

3.1. ECCSA_A Estimation from the ECCSA_{inert}. Figure 1 shows the ECCSA_A values directly determined at the end of the

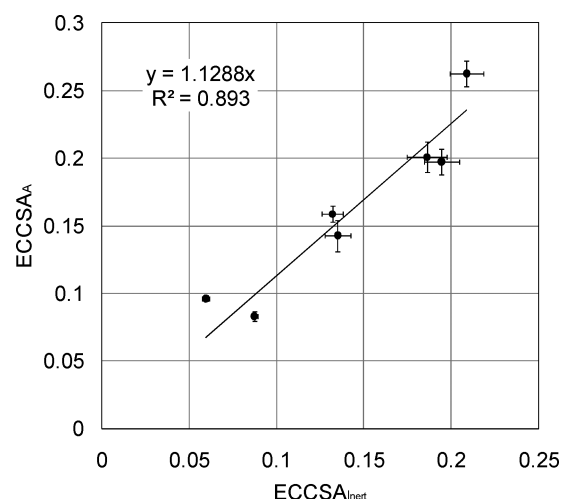


Figure 1. Effective capillarity under alkali (ECCSA_A) versus ECCSA_{inert}, showing linear regression.

treatments under the conditions mentioned in section 2.2 (Supporting Information Table S1) against the corresponding ECCSA values obtained afterward in NaCl at $20\text{ }^{\circ}\text{C}$ (ECCSA_{inert}).

As previously obtained for eucalyptus wood,¹³ a linear relationship can be established irrespective of the treatment conditions. The obtained correlation equation is shown in the plot. This relationship permits a relevant simplification for the determination of ECCSA_A because it allows treating a set of slices simultaneously and then calculating the individual ECCSA_A of each slice from the corresponding ECCSA_{inert}. This method is faster and more reliable, and more data can be obtained counteracting the effect of wood heterogeneity.

The plot also shows that most of the alkaline treatment effect (the increase in ECCSA_A) remains when the alkali is removed. This means that the effects of chemical reactions on the ion transport capacity are irreversible.

The ECCSA_A values discussed below in this paper were determined following this procedure.

3.2. ECCSA Evolution during Alkaline Treatment. ECCSA_A values determined on slices treated with Na_2S and NaOH solution under some of the treatment conditions are shown in Figure 2. As reported in previous papers for eucalyptus wood, ECCSA_A is gradually increased by higher OH^- concentration and/or higher temperature.

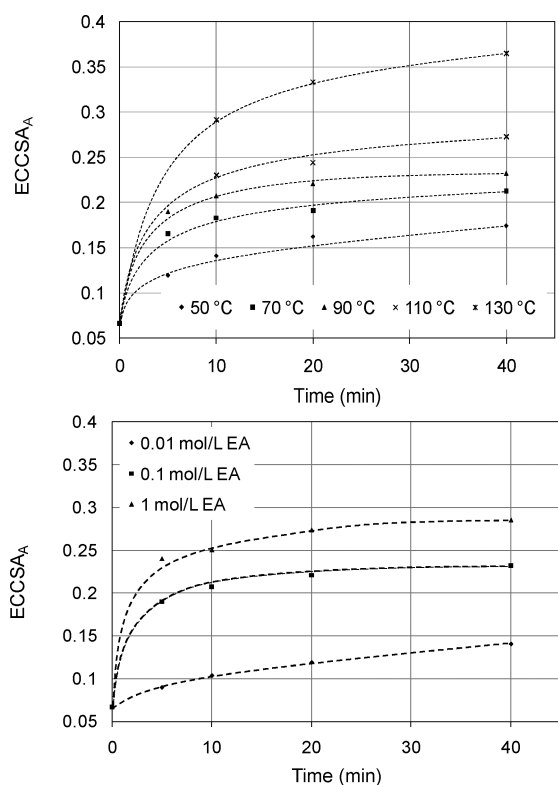


Figure 2. Evolution of $ECCSA_A$ for selected conditions; first: 0.1 mol·L⁻¹; second: 90 °C.

3.3. Relationship between ECCSA and Reactions.

3.3.1. Deacetylation Reaction. The acetyl content determined on slices was used to estimate the kinetic parameters of the expression previously proposed by Zanuttini et al.⁶ for eucalyptus wood:

$$R_{\text{acetyl}} = \frac{-\partial C_{\text{acetyl}}}{\partial t} = k \cdot (C_{\text{acetyl}})^n \cdot (C_{\text{OH}})^m \quad (2)$$

$$k = A \cdot \exp\left(\frac{-E}{RT}\right) \quad (3)$$

where R_{acetyl} is the acetyl reaction rate (%·min⁻¹); k is the specific rate constant of deacetylation ((%)¹⁻ⁿ·L^m·mol^{-m}·min⁻¹); C_{acetyl} is the acetyl concentration on o.d. wood (%); C_{OH} is the effective alkali concentration (mol·L⁻¹); R is the ideal gas constant (8 314 J·(mol·K)⁻¹); T is the absolute temperature (K); t is the time (min); E is the activation energy (J·mol⁻¹); n is the acetyl reaction order; m is the alkali reaction order; and A is the pre-exponential factor ((%)¹⁻ⁿ·L^m·mol^{-m}·min⁻¹).

Table 1 shows the parameters that were obtained after fitting all data. The R^2 parameter is acceptable. The values of A , E/R , n , and m are similar to those reported for eucalyptus.⁷

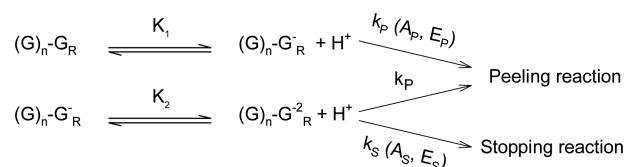
3.3.2. GGM Degradation. GGM degradation was studied following the model proposed by Paananen et al.¹⁰ This model accounts for peeling/stopping reactions (Scheme 1) and alkaline hydrolysis (Scheme 2):

In Schemes 1 and 2, $(G)_n$ -G_R, $(G)_n$ -G_R⁻, and $(G)_n$ -G_R⁻² are GGM with neutral, mono, or dianionic reducing end-group; GH and G⁻ are neutral GGM and GGM after the deprotonation reaction; k_p , k_s , and k_H are rate constants for peeling, stopping, and alkaline hydrolysis reactions; A_p , A_s , and A_H are pre-exponential factors for peeling, stopping, and

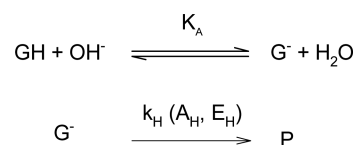
Table 1. Fitted Parameters for the Kinetic Expression

parameters	
C_{acetyl}^0 (%)	1.45
A ((%) ¹⁻ⁿ ·L ^m ·mol ^{-m} ·min ⁻¹)	1.12×10^7
E/R (K)	4495.3
n	2.40
m	1.54
R^2_{adjusted} (%)	97.8

Scheme 1. Scheme of the Peeling/Stopping Reactions (Considered As First Order)



Scheme 2. Simplified Scheme of the Base-Catalyzed Cleavage of Glycosidic Bonds



alkaline hydrolysis reactions; E_p , E_s , and E_H are activation energies for peeling, stopping, and alkaline hydrolysis reactions; and K_1 , K_2 , and K_A are ionization equilibrium constants.

Paananen et al.⁸ fitted this model on experimental data (GGM mass fraction) obtained at 80–130 °C and alkali effective ranging 0.31–1.55 mol OH⁻/L.

In the present study, the temperature range was 50–130 °C and the concentration range was 0.1–1.55 mol OH⁻/L (conditions indicated in Supporting Information Table S3). Fitting the combined data to the model by a nonlinear regression yields the values of the parameters and the R^2 values shown in Table 2. They are similar to those found by Paananen et al.¹⁰

Table 2. New Parameter Set for the GGM Degradation Model Proposed by Paananen et al.^{10 a}

parameter	unit	value
K_1		1.57×10^{-13}
K_2		2.95×10^{-15}
K_A		4.86×10^{-14}
A_p	min ⁻¹	1.67×10^{15}
A_s	min ⁻¹	1.13×10^{14}
A_H	min ⁻¹	1.20×10^{12}
$E_{A,p}$	kJ·mol ⁻¹	116.7
$E_{A,s}$	kJ·mol ⁻¹	114.0
$E_{A,H}$	kJ·mol ⁻¹	99.1

^a $R^2 = 0.983$.

Figure 3 shows the results for 0.1 mol/L and 90, 110, and 130 °C, where model fitting (lines) are displayed. The model prediction is excellent at 130 °C and acceptable for 110 and 90 °C.

3.3.3. Expression of the ECCSA_A Dependence on Variables. The dependence of ECCSA_A on temperature, time, and

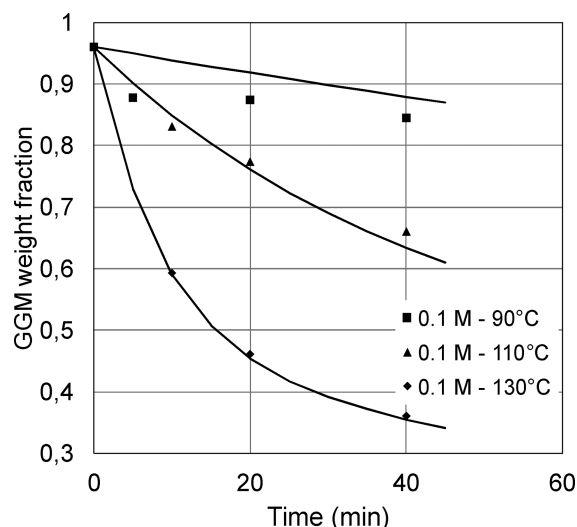


Figure 3. GGM weight fractions (based on untreated wood) versus time. Points are experimental values and lines are model predictions.

hydroxide concentration is complex and difficult to mathematically express.

Nevertheless, ECCSA can be better related to the degrees of reaction. Figure 4 shows the ECCSA_A as a function of acetyl

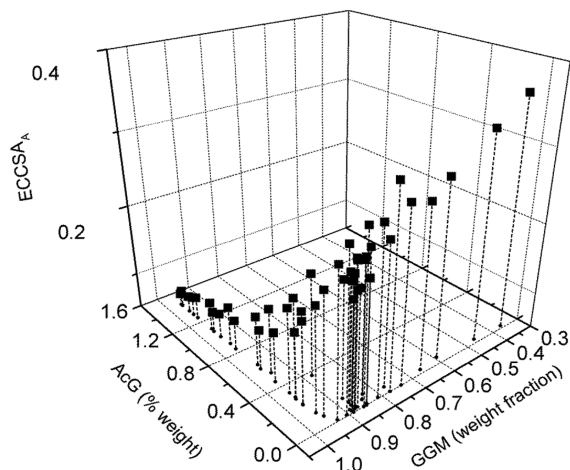


Figure 4. ECCSA_A versus acetyl and GGM contents.

and GGM contents. It can be observed that it is possible to distinguish three different regions. One corresponds to moderate conditions for which the GGM content is approximately constant (GGM ~ 0.96). In this case, the ECCSA_A increase can be related, in great part, to the deacetylation reaction. Another region corresponds to intense conditions and/or long time treatment for which deacetylation is complete and ECCSA changes can be related mainly to GGM degradation. Finally, there is an intermediate region, for which both reactions (deacetylation and GGM losses) are relevant for ECCSA_A.

This situation is different from that one found by Inalbon¹³ for eucalyptus wood where ECCSA changes were related only to the deacetylation degree. The acetyl group content of native pine wood (1.45% in weight) is almost half that of eucalyptus. The lower acetyl content, lower stability of the hemicelluloses, and more intense conditions make both reactions relevant for the level of ion-transport capacity of the wood.

An expression for ECCSA_A as a function of acetyl and GGM contents and temperature can be obtained with an acceptable fitting for tangential ionic diffusion:

$$\text{ECCSA}_A = C + f_1(\text{AcG}, T) + f_2(\text{GGM}, T)$$

$$\begin{aligned} \text{ECCSA}_A = & 0.573 + [0.224 \cdot \text{AcG} - 0.0013 \cdot \text{AcG} \cdot T \\ & + 0.0002 \cdot (\text{AcG}^2) \cdot T] + [-0.867 \cdot \text{GGM}^2 \\ & - 0.0018 \cdot \text{GGM} \cdot T + 0.0033 \cdot (\text{GGM}^2) \cdot T] \end{aligned}$$

$$R^2_{\text{adjusted}} = 98.0\%$$

(4)

Equation 4 is a simple expression that includes the effects of all variables (temperature, time, and hydroxide concentration) using temperature and two dependent variables (degree of the reactions). The kinetic expressions of both variables are known.

In a rigorous modeling of impregnation, a one-dimensional differential mass balance for each species is

$$\begin{aligned} \frac{\partial C_i}{\partial t} + \frac{\partial}{\partial x} \left(-\text{ECCSA}_A \cdot D^i \cdot \frac{\partial C_i}{\partial x} - \frac{z_i \cdot F \cdot \text{ECCSA}_A \cdot D^i \cdot C_i}{R \cdot T} \right. \\ \left. \cdot \frac{\partial \phi}{\partial x} \right) = R_i \end{aligned} \quad (5)$$

Therefore, eq 4 is very useful for the resolution of the equation system.

4. CONCLUSIONS

As previously shown for eucalyptus wood, the effective capillary cross sectional area under alkali action (ECCSA_A) can be estimated from the ECCSA measured after the treatment in sodium chloride solution at room temperature (ECCSA_{inert}). This method is easy to perform and allows obtaining reliable results in a relatively short time.

The ECCSA variation could be expressed as a function of temperature, deacetylation degree, and GGM degradation degree. For mild treatment conditions, deacetylation is the main reaction to which the ECCSA_A increase can be related. For more intense conditions, when deacetylation is complete, the degree of GGM degradation is determinant for ECCSA_A.

The nonlinear relationship found between ECCSA_A, GGM content, and deacetylation degree is very useful for a differential mass balance, which is necessary for a rigorous modeling of the industrial impregnation operation.

■ ASSOCIATED CONTENT

Supporting Information

Table S1: Treatment conditions for ECCSA_A/ECCSA_{inert} determinations. Table S2: Variables considered for the experimental analysis of tangential ECCSA_A. Table S3: Conditions for which sugar analysis was performed. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

A = pre-exponential factor $((\%)^{1-n} \cdot L^m \cdot \text{mol}^{-m} \cdot \text{min}^{-1})$
 AcG = acetyl groups
 A_p, A_s, A_H = pre-exponential factors for peeling, stopping, and alkaline hydrolysis reactions
 C_{Acetyl} = acetyl concentration on o.d. wood (%)
 C_{OH} = effective alkali concentration ($\text{mol} \cdot \text{L}^{-1}$)
 D^i = diffusion coefficient in the liquid medium ($\text{cm}^2 \cdot \text{min}^{-1}$)
 $D^i_{\text{effective}}$ = effective diffusion coefficient in wood ($\text{cm}^2 \cdot \text{min}^{-1}$)
 E = activation energy for deacetylation reaction ($\text{J} \cdot \text{mol}^{-1}$)
 EA = effective alkali ($\text{mol} \cdot \text{L}^{-1}$)
 ECCSA = effective capillary cross sectional area (dimensionless)
 ECCSA_A = ECCSA in alkali (dimensionless)
 $\text{ECCSA}_{\text{inert}}$ = ECCSA in inert solution (dimensionless)
 E_p, E_s, E_H = activation energies for peeling, stopping and alkaline hydrolysis reactions ($\text{J} \cdot \text{mol}^{-1}$)
 F = Faraday’s constant = $96487 \text{ (J} \cdot \text{mol}^{-1} \cdot \text{V}^{-1})$
 GGM = galactoglucomannan
 GH, G^- = neutral GGM and GGM after the deprotonation reaction
 $(\text{G})_n\text{-G}_R, (\text{G})_n\text{-G}_R^-, (\text{G})_n\text{-G}_R^+ = \text{GGM with neutral, mono, or dianionic reducing end-group}$
 k = specific rate constant of deacetylation $((\%)^{1-n} \cdot L^m \cdot \text{mol}^{-m} \cdot \text{min}^{-1})$
 K_1, K_2, K_A = ionization equilibrium constants
 k_p, k_s, k_H = rate constants for peeling, stopping, and alkaline hydrolysis reactions
 m = alkali reaction order
 n = acetyl reaction order
 o.d. = oven-dried
 OH^- = hydroxyl ion
 R = ideal gas constant ($8,314 \text{ J} \cdot (\text{mol} \cdot \text{K})^{-1}$)
 R_{acetyl} = acetyl reaction rate ($\% \cdot \text{min}^{-1}$)
 R_i = “ i ” species reaction rate ($\text{mol} \cdot (\text{L} \cdot \text{min})^{-1}$)
 R^2 = coefficient of determination
 T = absolute temperature (K)
 t = time (min)
 x = position (cm)
 z_i = ion valence
 ϕ = electric potential (V)

■ REFERENCES

- (1) Gullichsen, J.; Kolehmainen, H.; Sundqvist, H. On the nonuniformity of the kraft cook. *Pap. Puu* **1992**, *74* (6), 486–490.
- (2) Gullichsen, J.; Hyvärinen, R.; Sundqvist, H. On the nonuniformity of the kraft cook. Part 2. *Pap. Puu* **1995**, *77* (5), 331.
- (3) Malkov, S.; Tikka, P.; Gullichsen, J. Towards complete impregnation of wood chips with aqueous solutions. Part 4. Effects of front-end modifications in displacement batch kraft pulping. *Pap. Puu* **2002**, *84* (8), 526–530.

(4) Inalbon, M. C.; Mussati, M. C.; Zanuttini, M. A. Experimental and theoretical analysis of the alkali impregnation of eucalyptus wood. *Ind. Eng. Chem. Res.* **2009**, *48* (10), 4791–4795.

(5) Inalbon, M. C.; Mussati, M. C.; Mocchiutti, P.; Zanuttini, M. A. Modeling of alkali impregnation of eucalyptus wood. *Ind. Eng. Chem. Res.* **2011**, *50* (5), 2898–2904.

(6) Zanuttini, M.; Marzocchi, V. Kinetics of alkaline deacetylation of poplar wood. *Holzforchung* **1997**, *51* (3), 251–256.

(7) Inalbon, M. C.; Mocchiutti, P.; Zanuttini, M. The deacetylation reaction in eucalyptus wood. Kinetics and effects on the effective diffusion. *Bioresour. Technol.* **2009**, *100* (7), 2254–2258.

(8) Sumi, Y.; Hale, R. D.; Meyer, J. A.; Leopold, A. B.; Ranby, B. G. Accessibility of wood and wood carbohydrates measured with tritiated water. *Tappi J.* **1964**, *47* (10), 621–624.

(9) Sjöström, E.; Haglund, P. Studies on factors affecting the determination of carboxyl groups in cellulose. *Sven. Papperstidn.* **1961**, *64* (11), 438–446.

(10) Paananen, M.; Tamminen, T.; Nieminen, K.; Sixta, H. Galactoglucomannan stabilization during the initial kraft cooking of Scots pine. *Holzforchung* **2010**, *64* (6), 683–692.

(11) Stone, J. E. The effective capillary cross-sectional area of wood as a function of pH. *Tappi J.* **1957**, *40* (7), 539–543.

(12) Inalbon, M. C.; Zanuttini, M. A. Dynamics of the effective capillary during the alkaline impregnation of eucalyptus wood. *Holzforchung* **2008**, *62* (4), 397–401.

(13) Inalbon, M. C.; Montagna, P.; Galván, M. V.; Demonte, L.; Zanuttini, M. Wood capillarity and deacetylation during eucalyptus alkaline impregnation. Sulphidity effects and comparison between transverse directions. *Holzforchung* **2013**, *67* (1), 41–46.

(14) Solár, R.; Kacik, F.; Melcer, Y. Simple semi-micromethod for the determination of O-acetyl groups in wood and related materials. *Nord. Pulp Pap. Res. J.* **1997**, *2* (4), 139–141.

(15) Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, B.; Templeton, D.; Crocker, D. *Determination of Structural Carbohydrates and Lignin in Biomass*, NREL Report TP-510-42618; NREL: Golden, CO, 2008.

(16) Janson, J. Calculation of polysaccharide composition of wood and pulp. *Pap. Puu* **1970**, *52* (5), 323–329.