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The deacetylation reaction in Eucalyptus wood: Kinetics and effects on the effective diffusion

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ABSTRACT

The removal of native acetyl groups from hardwood O-acetyl-glucuronoxylan has a strong effect on physical characteristics, accessibility and structure of this polymer. The removal also has effects on the swelling and ion transport capacity of the cell wall of hardwoods. In this work, a kinetic expression for Eucalyptus wood deacetylation is determined. Two liquid mediums are considered: a simple alkaline one and another with a higher sodium concentration. The kinetic expression is a power law for the acetyl content and the concentrations in the liquid medium dependence, and is an Arrhenius type expression for temperature dependence. The kinetic expression can be useful to predict the physical properties of wood since the analysis of deacetylation effects on effective capillarity (ECCSA) shows that the acetyl content is a determining factor of wood ionic transport capacity.

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1. Introduction

The hemicellulose component of Eucalyptus wood is acetylated, as many hemicelluloses of different plant tissues are. The removal of native acetyl groups from hardwood O-acetyl-glucuronoxylan 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 notably increased in softwoods (Sjöstrom and Haglund, 1961) as well as in hardwoods (Sumi et al., 1964).

The enzymatic removal of the acetyls from dissolved glucomannans substantially reduces their solubility, and thus, they can be sorbed onto cellulose fiber (Laffend and Swenson, 1968; Holmbom et al., 1991). This sorption can help improve the bonding capacity of fibers (Laffend and Swenson, 1968), and in addition, it can increase the production yield in a mechanical pulping process (Thornton et al., 1994). Detailed analyses of the enzymatic deacetylation of dissolved hemicellulose have been performed for mannans (Poutanen et al., 1980) and xylans (Tenkanen et al., 1993).

Deacetylation is the main reaction that takes place during the first stage of any alkaline pulping process. For hardwoods, this reaction is responsible for a considerable part of alkali consumption (Zanuttini et al., 2003).

The reaction, together with alkali swelling, leads to a complex pattern of the alkaline impregnation process. Instead of following an unsteady-state Fickean diffusion, wood behaves like a glassy polymeric solid. An advancing boundary zone separates an intact inner part of the particle from a swollen outer shell (Zanuttini et al., 2000). In wood almost saturated by liquid, the existence of an advancing boundary suggests that the process of diffusion with chemical reaction and swelling can be, in great part, described by a classical model used to analyze heterogeneous reacting systems, the shrinking core model. The acetyl concentration profile that is established in the interior of the wood always approaches a step-form pattern. On the contrary, the alkali concentration profile depends on the conditions of temperature and external alkali concentration (Inalbon et al., 2007), with the result that changes in the relative relevance of chemical reaction and diffusion restrictions take place.

A comprehensive analysis of the alkali impregnation process requires a differential mass balance that considers reactions and diffusion of reagents and products. For this, knowledge of two aspects is necessary: (a) a kinetic expression of involved reactions, which considers the ionic strength in the medium and (b) the effective diffusion coefficient for the relevant chemical species.

In this paper, a kinetic expression of Eucalyptus wood deacetylation is found for a temperature from 20 to 90 °C and for an alkali concentration from 0.01 to 0.1 N NaOH. Regarding ion concentration, two situations are considered: first, simple alkaline conditions and then a higher sodium concentration. After that, the impact of the deacetylation degree on the ion transport capacity of wood determined by the relative electrical conductivity of the wood (ECCSA) is analyzed.

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Nomenclature

C_{Acetyl}	acetyl concentration on o.d. wood (%)	T	absolute temperature (K)
C_{NaOH}	alkali concentration (mol/l)	t	time (min)
C_{Na}	sodium concentration (mol/l)	E_1 and E_2	activation energy (mol/l atm)
R	gas constant (1.987 cal/mol K)		

2. Methods

2.1. Materials

In order to minimize the resistance to heat and mass transfer, thin wood slices were used. They were obtained from green, freshly felled wood (*Eucalyptus grandis*) with an average density of 0.37 g/cm^3. Logs from 6-year old trees were supplied by INTA – Concordia, Argentina. They were sawn into disks of about 3.5 cm high and then stored in polyethylene bags at −10 °C.

From the sapwood of disks and using a carpentry saw, cubes with 35-mm side length were obtained, presenting cube faces with tangential, transverse and almost radial cuts (Fig. 1).

From these blocks, radial 350-μm thick slices were obtained using a microtome. The slices were then cut into four parts with a scissor. These pieces were assorted, and eight of them were randomly chosen for each experience. To avoid wood drying, all the stages were carefully performed. The average moisture content of the original wood was 1.17 g water/g wood.

Slices were impregnated with distilled water using at least six cycles of 720-mmHg vacuum and release. Slices lost their buoyancy after the first 4–5 cycles. For preservation, they were immersed in a 0.55-ppm $CuSO_4 \cdot 5H_2O$ solution for 20 min, and then kept in closed bags at low temperature and were used within 48 h. Before treatment, the slices were washed in distilled water.

2.2. Alkali treatment

For each condition, 24 slices were treated in 1.0 l of thermostated solution under mild agitation. Slices were wrapped with a rigid plastic mesh in order to preserve their integrity. The vessel was closed, and the system was continuously purged with nitrogen. The alkali concentration did not change during treatment due to the high liquor-to-wood ratio (1 l–0.2 g wood). After the established period of time, a group of eight slices was withdrawn from the solution. Slices were immediately washed in distilled water up to the elimination of ions as indicated by conductivity measurements. They were then air dried at 23 °C and at 50% RH. Alkali treatments were done in duplicate.

2.3. Acetyl group content determination

Acetyls were determined on air-dried slices by gas chromatography using a modification of a published method (Solár et al., 1997). Butyric acid instead of propionic acid was used as an internal standard. Samples (100–150 mg) were treated at 150 °C for 50 min in closed glass ampoules with a 1.25 ml of a liquor containing oxalic acid (63-g oxalic acid dihydrate/l) and 1.8 ml butyric acid/l. Specific hydrolysis tests showed that there were no differences in the acetic acid concentration obtained when the treatment temperature varied from 145 to 152 °C. The hydrolysis liquor was directly analyzed by gas chromatography. Acetyl content is reported as percent g CH_3CO/g o.d. wood.

2.4. Conditions for alkali treatments

In the first series of experiments, three levels were considered for the following factors: alkali concentration, temperature and time. Concentration and time levels were adopted in geometric progression. Table 1 shows the set of conditions applied. The 27 experimental results were obtained in duplicate.

In order to assess the effect of a higher sodium concentration, the second series of experiments was performed. Here, sodium chloride was added to reach a 0.2 N total Na concentration. Conditions are listed in Table 2. A total of 42 experimental results obtained in duplicate were considered for the kinetic analysis.

2.5. ECCSA determination

The effective capillary cross-sectional area (ECCSA) was determined by making use of the analogy between diffusion and electrical conductivity. The concept was initially applied by Stone (1957) to follow the effects of the alkali on a hardwood. Here, the ECCSA was determined as the ratio of the electrical conductivity of 350 μm-thick wood slice, previously fully impregnated, to the

Table 1
Conditions of the first series of experiments.

Factor	Levels
NaOH concentration (N)	0.01–0.032–0.1
Temperature (°C)	20–45–90
Time (min)	5–15–45

Table 2
Conditions used in the second series of experiments. Corresponding alkali concentrations of the first series are included.

Factor	NaOH concentration (N)	Na^+ concentration (N)	Temperature (°C)	Time (min)
Levels	0.01	0.2–0.01[a]	20–90	5–15–45
	0.032	0.2–0.032[a]	20–45–90	5–15–45
	0.1	0.2–0.1[a]	20–90	5–15–45

[a] Experiments done in the first series.

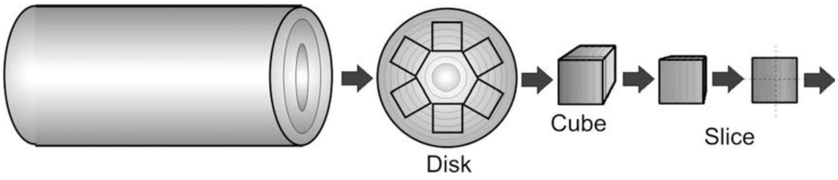

Fig. 1. Procedure followed to obtain the slices used in the kinetic analysis.

conductivity of the solution. A laboratory conductivity cell was used with a specially designed PTFE frame, which keeps the slice flat and equidistant from the electrodes leaving in each face of it an area of 25 × 25 mm in contact with the solution. The specific conductivity of the wood was calculated by considering slice thickness and electrical resistance in a series circuit with the electrical resistance of the solution that exists between the electrodes. This experimental device was described elsewhere (Inalbon, 2008; Inalbon and Zanuttini, 2008). The method makes possible the determination of the slice conductivity and its change over time while wood undergoes the alkali action.

The change in ECCSA of wood when it is alkali treated at different solution pHs at 45 °C was determined as a function of time.

3. Results

3.1. Kinetics under the alkali ionic strength

In the first series of experiments, three temperatures and alkali concentration levels were considered (Table 1). Each data value was obtained as the average of two replicates.

Fig. 2 shows the acetyl content (%) as a function of the time of treatment at 90 °C. Results corresponding to the three levels of alkali are displayed.

It can be observed that the reaction is relatively fast and that a clear effect of the alkali concentration exists. At 90 °C, the reaction is completed in <1 h if the highest alkali concentration is applied.

To analyze the results taking into account all the factors simultaneously (temperature, concentration and time), the general form of the kinetic expression found by Zanuttini and Marzocchi (1997) was considered here. The expression which was derived for the deacetylation of milled poplar wood is as follows:

$$R_{(1)\mathrm{Acetyl}} = \frac{-\partial C_{\mathrm{Acetyl}}}{\partial t} = k_1 \cdot (C_{\mathrm{Acetyl}})^{n_1} \cdot (C_{\mathrm{NaOH}})^{m_1} \quad (1)$$

$$k_1 = A_1 \cdot \exp\left(\frac{-E_1}{RT}\right) \quad (2)$$

where $R_{(1)\mathrm{Acetyl}}$ is the deacetylation rate (%/min), n_1 is the acetyl reaction order, m_1 is the alkali reaction order, k_1 is the specific rate constant of deacetylation $((\%)^{1-n} \cdot \mathrm{l}^m/\mathrm{mol}^m \cdot \mathrm{min})$ and A_1 is the pre-exponential factor $((\%)^{1-n} \cdot \mathrm{l}^m/\mathrm{mol}^m \cdot \mathrm{min})$.

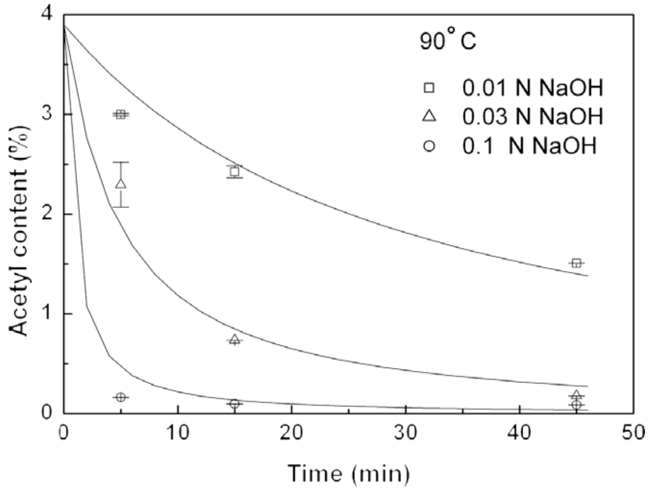

Fig. 2. Removal of acetyl groups under alkali treatment at 0.01, 0.03 and 0.1 N NaOH concentration and at 90 °C. The average value and range (% o.d. wood) of two replicates are shown as a function of time (open points), the curves correspond to the derived kinetic model (expression (3)).

Table 3
Fitting the experimental results of the first series of experiments to expression (3). In this series, sodium and hydroxide concentrations are the same.

Parameter	Estimated value	Standard error
n_1	1.794	0.186
m_1	1.505	0.0531
A_1	5.761 E6	3.1 E−8
$-E_1/R$	−4.742 E3	6.81 E−4

R^2 = 0.973; $R^2_{\text{adjusted to d.f.}} = 0.969$.
Standard error of estimation = 0.23% on o.d. wood.
Chi-square goodness of fitting = 16.04; p = 0.14.

Integrating expression (1)

$$C_{\mathrm{Acetyl}} = \left[(C_{\mathrm{Acetyl}})^{(1-n_1)} - A_1 \cdot (1-n_1) \cdot \exp\left(-\frac{E_1}{RT}\right) \cdot C^{m_1}_{\mathrm{NaOH}} \cdot t \right]^{\frac{1}{(1-n_1)}} \quad (3)$$

Fitting the data points to Eq. (3) by nonlinear least squares yields the values of the parameters listed in Table 3. Rate constants, R^2 values, standard errors and goodness of fit are included.

Fig. 3 shows all the data observed as a function of the predicted values. Errors of the prediction can be considered to be randomly distributed.

Tests for normality for studentized residuals (not shown here) give p values greater than 0.1, therefore the idea that the residual comes from a normal distribution with at least 90% confidence cannot be rejected.

Statistical parameters listed in Table 3 and the analysis of errors indicate that the fit achieved by the model is acceptable. This can also be observed for the results obtained at 90 °C, shown in Fig. 2, where the drawn curves correspond to the model.

3.2. Alkaline kinetics at higher ionic strength

In the second series of experiments, when necessary, sodium chloride was added to the liquor to reach a total 0.2 N Na concentration. The conditions are listed in Table 2.

Fig. 4 shows the acetyl group content (%) as a function of the time of the alkaline treatment at 90 °C for the three levels of alkali concentration applied. Results corresponding to a lower ionic strength, already shown in Fig. 2, are included.

Fig. 4 indicates that a clear effect of the sodium concentration exists. Significant differences due to the sodium concentration

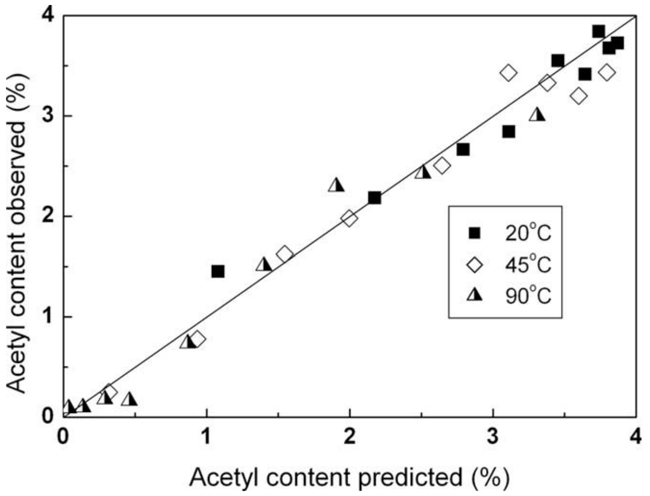

Fig. 3. Experimental results obtained at 20, 45 and 90 °C, as a function of the values predicted by kinetic expression (3).

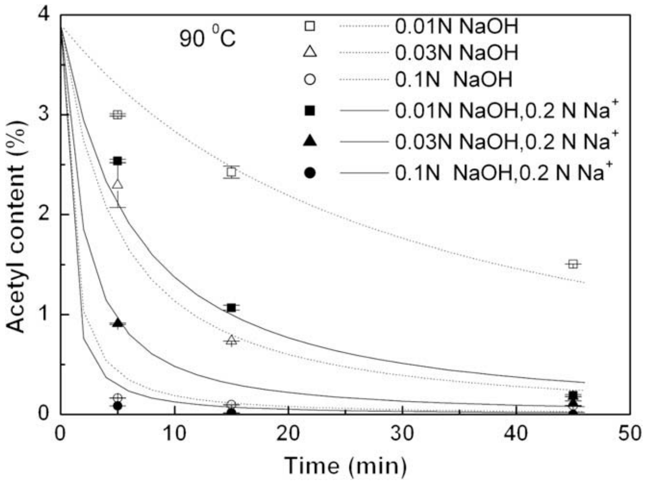

Fig. 4. Removal of acetyl groups under alkali treatment at 0.01, 0.03 and 0.1 N NaOH concentration and at 90 °C. Acetyl content results (%) after treatment with a liquor containing a total sodium concentration of 0.2 N (open points in the plot) and results corresponding to the simple alkaline treatment are shown (black points). Average value and range of two replicates are indicated. The curves correspond to the derived kinetic model (expression (8)).

were verified by a statistical hypothesis test (not shown here). The reaction rate is higher at higher ionic strength.

A proper kinetic expression should consider the effect of the ionic strength (I, mol/l), which can be expressed as

$$I = \frac{1}{2}\sum_{\mathrm{i}} z_{\mathrm{i}}^2 c_{\mathrm{i}} \tag{4}$$

where z_{i} is the ion electric charge and c_{i} is the ion concentration (mol/l).

As the only cation existing in the medium is sodium, the ionic strength is

$$I = \frac{2}{2} C_{\mathrm{Na}^+} = C_{\mathrm{Na}^+} \tag{5}$$

This means that the concentration of sodium is equal to the ionic strength in the solution.

A kinetic expression for the deacetylation reaction rate ($R_{(2)\mathrm{Acetyl}}$, %/min) that considers the effect of added NaCl is as follows:

$$R_{(2)\mathrm{Acetyl}} = \frac{-\partial C_{\mathrm{Acetyl}}}{\partial t} = k_2 \cdot (C_{\mathrm{Acetyl}})^{n_2} \cdot (C_{\mathrm{OH}})^{m_2} \cdot (C_{\mathrm{Na}})^{p} \tag{6}$$

$$k_2 = A_2 \cdot \exp\left(\frac{-E_2}{RT}\right) \tag{7}$$

where k_2 is the specific rate constant of deacetylation $((\%)^{1-n} \cdot \mathrm{l}^{(m+p)}/\mathrm{mol}^{(m+p)} \cdot \mathrm{min})$, n_2 is the acetyl reaction order, m_2 is the hydroxyl reaction order, p is the sodium reaction order and A_2 is the pre-exponential factor $((\%)^{1-n} \cdot \mathrm{l}^{(m+p)}/\mathrm{mol}^{(m+p)} \cdot \mathrm{min})$.

Integrating expression (7)

$$C_{\mathrm{Acetyl}} = \left[(C_{\mathrm{Acetyl}})^{(1-n_2)} - A_2 \cdot (1-n_2) \cdot \exp\left(-\frac{E_2}{RT}\right) \cdot t \cdot (C_{\mathrm{OH}})^{m_2} \cdot (C_{\mathrm{Na}})^{p}\right]^{\frac{1}{(1-n_2)}} \tag{8}$$

Table 4 shows the values and standard errors of the parameters of this kinetic expression as obtained by nonlinear regression.

Fig. 5 shows the acetyl content values obtained experimentally against the values predicted by the model. It can be observed that fitting errors are randomly distributed.

Tests for normality for studentized residuals (not shown here) give p values greater than 0.1, therefore the idea that the residual comes from a normal distribution with at least 90% confidence cannot be rejected.

Table 4
Fitting the experimental results of the second series of experiments to expression (8).

Parameter	Estimated value	Standard error
n_2	1.735	0.123
m_2	1.004	0.043
p	0.491	0.047
A_2	9.778 E6	1.8 E−8
$-E_2/R$	−4.913 E3	0.00074

$R^2 = 0.977$; $R^2_{\text{adjusted to d.f.}} = 0.974$.
Standard error of estimation = 0.21% on o.d. wood.
Chi-square goodness of fitting = 13.0.
$p = 0.52$ ($p > 0.10$).

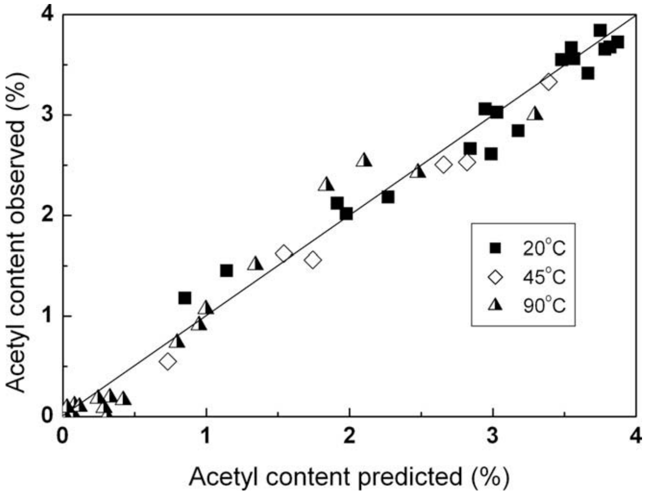

Fig. 5. Experimental results obtained at 20, 45 and 90 °C, as a function of the values predicted by kinetic expression (8).

Table 5
Summary of the kinetic parameters.

Parameter	Chemical species considered	
	NaOH	OH^- and Na^+
n	1.794	1.735
m	1.505	1.004
p	0	4.913 E−1
A	5.762 E6	9.779 E6
$-E/R$	−4.742 E3	−4.913 E3

Statistical parameters listed in Table 4 and error analysis indicate that the fit of the model is acceptable. For the 90 °C treatment, the good fit can be observed in Fig. 4 where the drawn curves correspond to the model prediction.

Fig. 6 shows a response surface obtained with the model expression for a 0.05 N total sodium concentration.

The expression found agrees with the one described above for a simple alkaline treatment. Table 5 allows a comparison between the coefficients obtained in each case.

The value of reaction order m_1, obtained for expression (3), is similar to the sum of the m_2 and p values found for expression (8) that considers a higher sodium concentration. This kinetic expression is more general, and when there are no other ions besides sodium hydroxide, it is equal to expression (3).

3.3. Effect of the deacetylation on the ECCSA

Fig. 7 shows the ECCSA obtained at 45 °C as a function of the acetyl content for three alkali concentration levels. This content

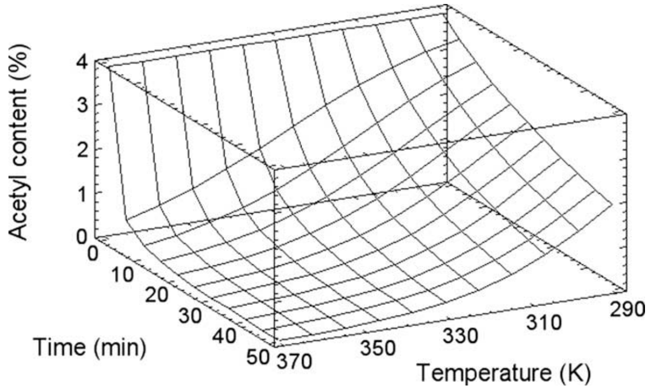

Fig. 6. Acetyl content as a function of temperature and time for 0.05 N NaOH.

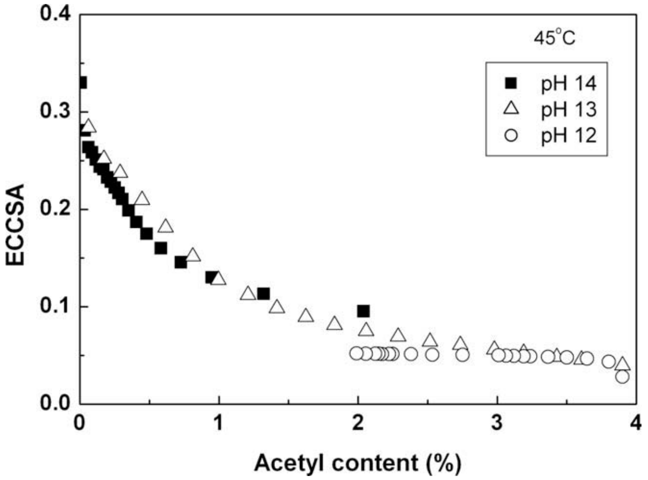

Fig. 7. ECCSA as a function of the calculated acetyl content, at 45 °C and at different pHs.

was calculated using the kinetic expression (8). The plot indicates that the degree of deacetylation is a determining factor of ECCSA. It cannot be said that alkali concentration has no influence on it. Alkali has an indirect action through the deacetylation reaction.

The strong relationship shown here, between the reaction degree and changes in ion transport capacity of the wood, indicates that they can be simultaneously considered in a mathematical model of an alkaline diffusion process.

4. Conclusions

The reaction of deacetylation in Eucalyptus wood is fast. At 90 °C, the removal is almost completed in a few minutes. A clear effect of the alkali concentration exists. On the other hand, the ionic strength also has a positive effect on the rate of reaction.

Kinetics of deacetylation under conditions where NaOH is the only source of solution and also under conditions of greater ionic strength can be modeled by a relatively simple power law expression for the ion content and concentration dependence, and by an Arrhenius type expression for the reaction rate temperature dependence.

For impregnation or washing of lignocellulosic material, the speed of ion diffusion is strongly affected by the deacetylation degree.

The acetyl content is a determining factor of the ionic transport capacity of wood, as can be observed from its influence on the ECCSA. The strong relationship shown here indicates that reaction and changes in ion transport capacity of wood can be simultaneously considered in a differential mass balance applied to alkaline diffusion.

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