**ORIGINAL ARTICLE**

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# Modeling of sapwood and heartwood delignification kinetics of *Eucalyptus globulus* using consecutive and simultaneous approaches

**Abstract** *Eucalyptus globulus* sapwood and heartwood were delignified at 130°, 150°, or 170°C by kraft pulping. Pulp yields of heartwood were lower than those of sapwood (46.5% vs. 50.4% at 170°C). Delignification was modeled using consecutive and simultaneous kinetic models. The modeling was similar for heartwood and sapwood, and either approach could be used, with both yielding good correlations between experimental and model data. The consecutive model identified two delignification phases with similar reaction rates and activation energies for heartwood and sapwood at 150° and 170°C. At 130°C only one phase was identified. Three reactive types of lignin fractions were identified using the simultaneous model, without differences between heartwood and sapwood. Their reaction rates were 0.152, 0.138, and 0.003 min$^{-1}$ at 170°C, and the activation energies were 132, 119, and 102 kJ.mol$^{-1}$. The presence of heartwood did not influence the kinetic development of delignification. The negative impact of heartwood in pulping is related to the higher content of extractives (9.8% vs. 3.9% in heartwood and sapwood) and to their influence on the process, namely in the heating-to-temperature phase when a substantial mass loss occurs (30% vs. 20% for heartwood and sapwood).

**Key words** Heartwood · *Eucalyptus globulus* · Delignification · Kinetics · Consecutive model · Simultaneous model

## Introduction

The heartwood content of stems is a major pulping quality variable due to the negative impact of the extractives that accumulate in the process.[1] In *Eucalyptus globulus,* an important species for pulp and paper manufacturing, heart-

wood represents a substantial proportion of the stems at harvest age, and has an increased content of extractives that leads to lower pulp yields compared to that for sapwood.[2,3]

In *Eucalyptus globulus,* a few studies have analyzed the chemical composition and pulp yield of sapwood and heartwood,[2,3] but the information on comparative heartwood–sapwood kinetics is very scarce and their delignification modeling has not yet been attempted. Knowledge of delignification kinetics underlies all process improvements. Delignification usually consists of first-order reactions in relation to the concentration of lignin removed[4–6] and may be interpreted as (i) dissolution of a single lignin species whose reaction mechanism changes with time, or (ii) dissolution of various lignin fractions with different reaction rates. This last hypothesis is in agreement with the chemical diversity within the lignin macromolecule and can be modeled using consecutive or simultaneous reaction approaches.

The consecutive model assumes that the different lignin fractions react consecutively and are removed in successive phases with decreasing reaction rates; often three phases can be seen, named the initial, bulk, and residual phases. Consecutive models are the most commonly used models for wood delignification and have been applied to *E. globulus* in kraft pulping[7–10] and in organosolv processes.[6,10–12]

The simultaneous model is less well known. It assumes that the different lignin fractions react simultaneously in parallel reactions with specific reaction velocities, so that in the last period of reaction only the least reactive lignin fraction remains, since the more reactive lignin moieties had been removed in earlier phases. The simultaneous model has been applied to delignification in *Eucalyptus*[6,13,14] and *Arundo donax*.[15] Most kinetic studies have analyzed the effect of temperature,[10,15] of temperature and reactant concentration,[6,7,9,12,16] or of a high liquor-to-wood ratio.[17]

This article compares the delignification kinetics of *E. globulus* heartwood and sapwood during kraft pulping at three temperatures (130°, 150°, and 170°C) using the consecutive and simultaneous modeling approaches. We chose typical process conditions used in the pulp industry for *E. globulus* with regard to pulping liquor concentration and

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wood:liquor ratio, and studied the time–temperature variation of the delignification of heartwood and sapwood. This study is part of a general evaluation of heartwood in *E. globulus* trees used for pulping and a step in assessing the impact of heartwood in the delignification of the assorted wood supplied to pulp mills.

## Material and methods

### Samples

Heartwood and sapwood samples were taken from a 10-cm-thick disc collected at a height of 1.3 m from one *Eucalyptus globulus* Labill. tree, aged 18 years, from a first-rotation plantation at Quinta do Furadouro, Óbidos, Portugal.[2,18] The tree was 27.7 cm in diameter at a height of 1.3 m with a total height of 36.1 m; the area proportion of heartwood at a height of 1.3 m was 69.3%.[2]

The heartwood and sapwood fractions were separated, milled, and sieved. The 40–60 mesh fraction was used for wood chemical characterization and the 20–40 mesh fraction was used for the pulping experiments.

### Pulping

The samples (5 g oven dry wood) were pulped in 100-ml stainless steel rotating autoclaves placed in an oil bath with temperature control. The pulping conditions were: liquor-to-wood ratio (ml/g) 4:1; sulfidity 30% (as $Na_2O$); active alkali 20% (as $Na_2O$); cooking at isothermal conditions of 130°, 150°, or 170°C. The heating time to isothermal temperature was 5 min, and pulping times at the isothermal temperature ranged between 1 and 180 min. After each pulping time, the autoclaves were removed, cooled in ice, and the samples thoroughly washed with de-ionized hot water and then air dried at 55% relative humidity and 25°C (Tappi 402 os-70). Yield determination was calculated after oven drying at 100° ± 2°C. All pulping experiments were replicated and the results accepted for mean calculation when the difference was lower than or equal to 0.5%; otherwise pulping was repeated.

### Chemical analysis

The heartwood and sapwood fractions were chemically characterized. Extractives were determined by successive Soxhlet extraction with dichloromethane, ethanol, and water; the total lignin was determined as Klason lignin (Tappi 222 om-02) and acid-soluble lignin (Tappi UM 250); and the composition of monosaccharides was determined after total hydrolysis as alditol acetates by gas–liquid chromatography (Tappi 249 cm-00).

The delignified samples were washed by extraction in a Soxhlet system with 70:30 ethanol and water (Tappi 204 cm-97), dried, milled and sieved using a 0.12-mm sieve. The total lignin content was determined as described above.

### Delignification modeling

For application of the consecutive model, the delignification was described mathematically as a three-term equation for lignin percentage according to Labidi and Pla[13] and Miranda and Pereira:[10]

$$\frac{L}{L_0} = a_i \exp(-k_i t) + a_b \exp(-k_b t) + a_r \exp(-k_r t) \qquad (1)$$

where $L$ is the lignin present in the delignified sample; $L_0$ is the lignin in wood at time zero; $t$ is the time (min); $k_i$ is the rate constant ($min^{-1}$), with i, b, and r, corresponding to initial, bulk, and residual phases, respectively; $a_i$ is the mass fraction of lignin removed in the initial phase; $a_b$ is the mass fraction of lignin removed in the bulk phase; and $a_r$ is the mass fraction of lignin removed in the residual phase. According to Labidi and Pla,[13] it was assumed that at $t = 0$, $a_i + a_b + a_r = 100$. The kinetic parameters were obtained by minimizing the residual sum-of-squares (SQR) of the fitted modeling curve using single, double, or triple first-order reactions by using the "solver" add-in from Excel for Windows.

The simultaneous model was applied as described by Shatalov and Pereira[15] using a graphical representation of the logarithm of total lignin values (reported to the initial wood material). The least reactive lignin fraction ($L_n$) was identified at the end of the reaction by drawing a straight line passing through the last value and the aligned previous values until obtaining the intercept parameter. The exponential of this intercept value was the percentage of the least reactive lignin present in the initial wood lignin. The corresponding velocity rate constant ($k_n$) was calculated using the following equation:

$$k_n = \ln(L_{n,0} / L_t)/(t_t - t_n) \qquad (2)$$

where $L_{n,0}$ is the least reactive lignin at time 0, $L_t$ the lignin at time $t$, $t_t$ is the end time, and $t_n$ is the start time of removal of the least reactive lignin. Having determined the proportion of the least reactive lignin fraction ($L_n$) and its reaction rate, the amount of this fraction at earlier pulping times can be calculated using:

$$L_{n,t} = L_{n,0} * (\exp(-k_n t)) \qquad (3)$$

The subtraction of these values from the lignin at each point of time gives the values of ($L - L_n$). The logarithm of these values is graphically represented, describing the delignification without the least reactive lignin fraction. The next least reactive lignin fraction ($L_{n-1}$) is identified by passing a straight line through the last values, the intercept parameter is determined, and the exponential gives the amount of this type of lignin fraction. The velocity rate constant of this stage is calculated as before. The analysis ends when the values obtained by subtraction represent a line and not a curve.

The total amount of lignin dissolved from the wood material ($L$) at an instant of pulping time ($t$) can be calculated as the sum of the different lignin types, as exemplified by Eq. 4 with three types of lignin fractions:

$$L = L_{n-2,0} * (1-\exp(-k_{n-2}t)) + L_{n-1,0} * (1-\exp(-k_{n-1}t)) +$$
$$L_{n,0} * (1-\exp(-k_n t)) \tag{4}$$

where $L_{n-2,0}$, $L_{n-1,0}$, and $L_{n,0}$ are the lignin fractions at time 0, ($L_{n-2}$ is the most reactive and $L_n$ is the least reactive) and the $k$ values are the respective reaction rate constants. The SQR values were calculated to validate this kinetic model.

The experimental activation energy was determined using the Arrhenius equation:

$$k_i = A \exp\left(\frac{E_{ai}}{RT}\right) \tag{5}$$

where $k_i$ is the rate constant for phase i and $A$, $E_{ai}$, $R$, and $T$ are the Arrhenius constant, the activation energy (kJ.mol$^{-1}$), the gas constant (8.314 JK$^{-1}$.mol$^{-1}$), and the absolute temperature (K), respectively. A plot of ln ($k_i$) versus $1/T$ gives a straight line with a slope of $E_{ai}/R$, from which $E_{ai}$ can be calculated.

## Results and discussion

### Characterization of wood

The heartwood and sapwood samples had the following composition: 9.8% extractives and 23.5% total lignin in heartwood, and 3.9% extractives and 24.3% total lignin in sapwood. The monosaccharide composition was similar in heartwood and sapwood: the average composition of the neutral sugars was 1.3% arabinose, 15.6% xylose, 2.2% mannose, 2.8% galactose, and 78.1% glucose. The chemical differences between heartwood and sapwood lie, therefore, in the higher content of extractives (2.5 times more) in heartwood, as previously reported for *E. globulus*.[3,19]

### Pulping

The importance of wood particle size on liquor penetration and diffusion reactions during pulping has already been elucidated by several authors. Wong et al.[20] and Bogren et al.[16] used wood meal to avoid impregnation difficulties and to minimize the influence of mass transport on kinetics. Nelson and Gniel[21] observed that wood meal was delignified faster than shavings and had a lower activation energy in the initial phase, and Dang and Nguyen[22] reported that the delignification rate was reduced by increasing the chip thickness. For the current study, we took these results into consideration and used wood meal (20–40 mesh fraction, corresponding to 425–850 μm particle sizes) to circumvent diffusion-related effects.

The total yield and residual lignin results are presented in Table 1. During the heating period (initial 5 min, represented as 0 min in the table) there was already a very significant mass loss corresponding to almost 30% in heartwood and 20% in sapwood. This mass loss did not correspond to lignin removal (e.g., 95% and 91% of the total lignin still remained in the heartwood and sapwood, respectively, on reaching 150°C) and should be to a large extent the result of extractives solubilization, thereby explaining the differences between heartwood and sapwood. In fact it is known that mass loss during heating is mainly due to removal of wood extractives, detachment of acetyl groups linked to xylan chains, peeling reactions, and dissolution of some low molecular weight carbohydrates and lignin.[5,23]

The substantial mass loss during the heating phase evident in the current study has also been reported in other studies of *E. globulus* wood pulping, e.g., 12% mass loss at 80°C[24] and 3%–4% glucose removal and 17%–23% of total xylan in impregnation at 120°C for 45 min.[25] The same occurs for other species, e.g., 20% and higher values for *Pinus silvestris* sapwood, largely due to loss of galactoglucomannan,[26] and 42% in the soda delignification of hemp.[27]

**Table 1.** Yield (% of initial wood) and residual lignin (% of initial lignin in wood) during kraft pulping at 130°, 150°, and 170°C

| | 130°C | | | | 150°C | | | | 170°C | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Yield (%) | | Lignin (%) | | Yield (%) | | Lignin (%) | | Yield (%) | | Lignin (%) | |
| | H | S | H | S | H | S | H | S | H | S | H | S |
| Wood | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 0 | 76.3 | 84.6 | 96.2 | 92.7 | 73.7 | 82.1 | 94.9 | 90.6 | 68.2 | 76.5 | 88.4 | 86.7 |
| 1 | 75.7 | 84.4 | 96.0 | 91.3 | 71.1 | 78.6 | 92.5 | 87.4 | 67.8 | 70.0 | 81.4 | 79.1 |
| 3 | 73.9 | 81.9 | 94.5 | 92.0 | 70.2 | 76.6 | 91.2 | 85.6 | 62.7 | 69.2 | 72.9 | 68.6 |
| 5 | 73.1 | 81.4 | 93.9 | 91.4 | 68.5 | 75.4 | 87.3 | 80.2 | 57.6 | 62.7 | 55.5 | 48.7 |
| 10 | 71.2 | 79.0 | 91.9 | 87.2 | 65.5 | 71.7 | 78.6 | 73.0 | 53.7 | 56.8 | 34.7 | 23.1 |
| 15 | 69.5 | 77.9 | 90.4 | 85.8 | 63.7 | 68.7 | 69.5 | 63.5 | 51.0 | 54.0 | 24.4 | 13.7 |
| 20 | 68.3 | 77.2 | 87.0 | 82.9 | 62.6 | 66.9 | 57.3 | 53.5 | 49.6 | 53.1 | 13.6 | 7.6 |
| 25 | 67.4 | 75.3 | 85.8 | 82.4 | 60.4 | 65.2 | 51.1 | 48.0 | 49.3 | 53.3 | 9.8 | 6.7 |
| 35 | 66.4 | 74.6 | 80.9 | 78.7 | 56.5 | 61.1 | 35.5 | 30.8 | 48.4 | 52.4 | 9.4 | 5.6 |
| 50 | 65.0 | 73.4 | 78.0 | 75.6 | 54.5 | 58.7 | 24.7 | 22.0 | 48.4 | 52.8 | 8.8 | 5.3 |
| 65 | 63.9 | 71.3 | 74.0 | 68.8 | 52.9 | 56.0 | 19.4 | 18.0 | 46.9 | 52.0 | 8.2 | 5.1 |
| 80 | 63.4 | 69.9 | 71.0 | 66.7 | 52.0 | 55.2 | 16.6 | 14.0 | 47.0 | 51.5 | 8.0 | 4.9 |
| 95 | 60.3 | 66.7 | 63.2 | 58.4 | 50.5 | 54.7 | 11.2 | 7.8 | 46.7 | 51.9 | 7.6 | 4.7 |
| 180 | 53.4 | 61.7 | 47.8 | 38.6 | 49.3 | 54.0 | 10.2 | 7.5 | 46.5 | 50.4 | 7.5 | 4.4 |

Time zero corresponds to the end of the heating period
H, heartwood; S, sapwood

Nelson and Gniel[21] found that 2% of the lignin was removed at 40°C from *E. regnans* heartwood.

The influence of temperature was quite clear, with lower yields and increased lignin extraction obtained with the highest temperature (170°C). At all temperatures, sapwood presented higher pulping yields compared to heartwood (8% higher at 130°C, and 4% at 150° and 170°C), as expected due to the higher extractives content in heartwood. The same has also been reported for *E. globulus*, with yields of 47.5%–48.3% for heartwood and 50.0%–54.1% for sapwood,[3] and for *E. nitens*.[28]

Heartwood was also more difficult to delignify than sapwood at all temperatures, as shown by the relative residual lignin contents at the same pulping times. On average, heartwood presented 4% more residual lignin at 130° and 150°C, and 5% more at 170°C during delignification.

### Modeling of delignification kinetics

#### *Consecutive model*

Experimental data of heartwood and sapwood lignin content versus time were plotted with data obtained by the fitting of Eq. 1 (Fig. 1). At 130°C the data roughly corre-sponded to a straight line and were well represented by a single first-order reaction, i.e., only one delignification phase was identified at this temperature, which is in agreement with the data of Chiang et al.[29] This phase was assumed to include the initial and bulk phases of delignification, desig-nated "initial + bulk" (i + b), which were kinetically handled together. One additional reaction phase (the residual phase) was found when the temperature increased to 150° and 170°C, and therefore two first-order reactions were used for the modeling of sapwood and heartwood delignification at these temperatures. These findings are consistent with those of Santos et al.[7] and of Nelson and Gniel,[21] who found for *E. regnans* that the transition from the initial to the bulk phases occurred at 130° and 140°C at 21% lignin removal.

The predicted values represented well the experimental data for heartwood and sapwood ($R^2$ of 0.995 and 0.992). The delignification at 170°C was quite rapid in the first minutes, decreasing after 15 min and slowing afterwards in agreement with the kinetic parameters that are presented in Table 2.

Delignification rates ($k$) of heartwood and sapwood showed very small differences. For example, at 170°C the initial + bulk phase proceeded at rates of 0.1025 and 0.1309 $min^{-1}$, respectively, and the residual phase at 0.0018 and 0.0017 $min^{-1}$. No data were found in the literature com-
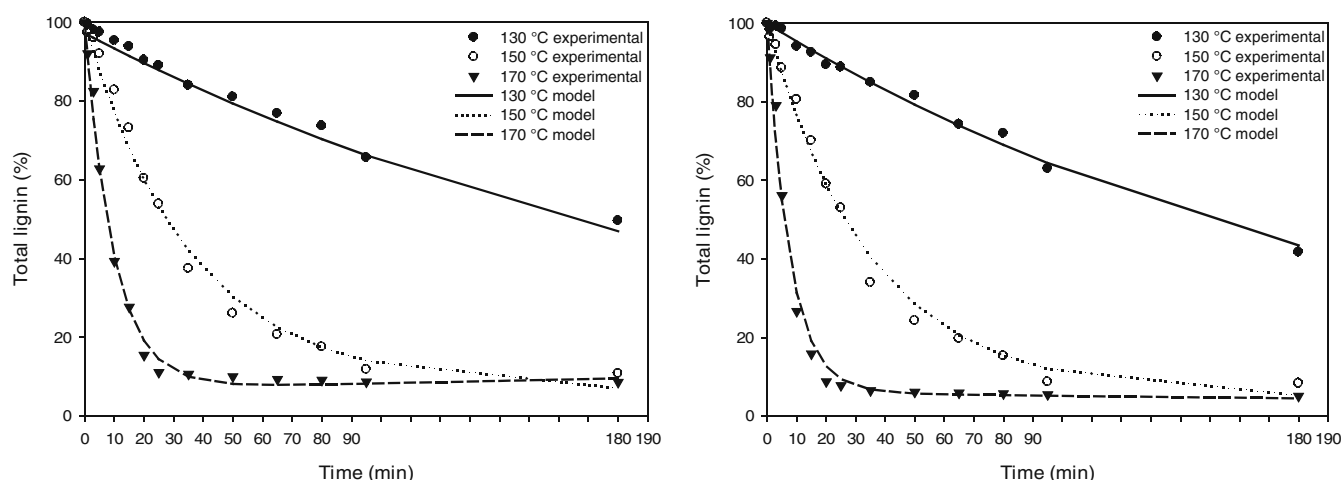


**Fig. 1.** Experimental data of total residual lignin (percentage of initial lignin in wood) in heartwood (*left*) and sapwood (*right*) samples during kraft delignification at 130°, 150°, and 170°C and predictions using the consecutive model

**Table 2.** Kinetic equations obtained with the consecutive model for heartwood and sapwood delignification at three temperatures

| | $T$ (°C) | $L/L_0 = a_{i+b} \exp(-k_{i+b} t) + a_r \exp(-k_r t)$ | SQR | $Ea_{i+b}$ | $Ea_R$ |
|---|---|---|---|---|---|
| Heartwood | 130°C | $L/L_0 = 97.2 \exp(-0.0040 t)$ | 0.0063 | | |
| | 150°C | $L/L_0 = 88.5 \exp(-0.0293 t) + 11.5 \exp(-0.0031 t)$ | 0.0153 | | |
| | 170°C | $L/L_0 = 93.1 \exp(-0.1025 t) + 6.9 \exp(-0.0018 t)$ | 0.0087 | | |
| | Activation energy, $E_a$ (kJ.$mol^{-1}$) | | | 120.4 | 44.3 |
| Sapwood | 130°C | $L/L_0 = 99.9 \exp(-0.0046 t)$ | 0.0026 | | |
| | 150°C | $L/L_0 = 91.4 \exp(-0.0293 t) + 8.6 \exp(-0.0033 t)$ | 0.0115 | | |
| | 170°C | $L/L_0 = 93.9 \exp(-0.1309 t) + 6.1 \exp(-0.0017 t)$ | 0.0154 | | |
| | Activation energy, $Ea$ (kJ.$mol^{-1}$) | | | 124.3 | 49.0 |

Parameters include the lignin fraction removed (%) in each phase ($a_{i+b}$, $a_r$) (where i + b = initial + bulk, r = residual), the respective reaction rates ($k_{i+b}$, $k_r$, $min^{-1}$), and the activation energies ($Ea_{i+b}$, $Ea_R$, kJ.$mol^{-1}$)
SQR, residual sum of squares

paring delignification kinetics of *E. globulus* sapwood and heartwood. For maritime pine delignification at 170°C, no differences were found between sapwood and heartwood, either during the bulk (0.031 vs. 0.027 min⁻¹) or residual phases (both 0.016 min⁻¹).[30]

The existing data for delignification rates of *E. globulus* total wood chips reported by Miranda and Pereira[10] give a comparable value for the residual phase (0.003 min⁻¹) and a lower value for the initial + bulk phase (0.035 min⁻¹). This clearly shows the effect of particle size on the reaction rate, i.e., a rate increase in the current study since wood meal was used.

The activation energies for the heartwood and sapwood delignification reactions were similar. As described by Gierer,[5] the initial phase of delignification is dominated by the cleavage of phenolic $\alpha$-aryl and $\beta$-aryl ether linkages in lignin, followed by the cleavage of $\beta$-aryl ether linkages in nonphenolic units in the bulk phase and by cleavage of C–C bonds in the residual phase, with activation energies of 61, 150, and 120 kJ.mol⁻¹ respectively. The values of 120–124 kJ.mol⁻¹ obtained here for the initial + bulk phase correspond to these reactions, and might suggest that the cleavage of C–C bonds already occurred at this stage, while the effect of diffusion was minimized since diffusion-controlled kinetic processes have lower energy activation values.[31]

Comparison with the few data available on activation energy of delignification shows somewhat higher values than the 84 kJ.mol⁻¹ reported for *E. globulus* wood chips[10] and similar values to the 126 kJ.mol⁻¹ found for *E. diversicolor*.[17] The activation energy for the final residual phase for heartwood and sapwood was lower (44–49 kJ.mol⁻¹) when compared with the 64 kJ.mol⁻¹ for *E. diversicolor*[17] and 75 kJ.mol⁻¹ for *E. globulus*,[10] and might suggest completion of the major bond cleavage in the previous phase.

*Simultaneous model*

The graphic application of the simultaneous model for heartwood and sapwood delignification and the corresponding kinetic parameters are presented in Fig. 2 and Table 3. Three reactive types of lignins with decreasing reaction rates were identified in heartwood and sapwood delignification at 170°C. The two first lignin fractions showed very small differences of reaction rates, whereas the least reactive lignin fraction had a lower reaction rate by about two orders of magnitude ($k_1$ = 0.139, $k_2$ = 0.128, and $k_3$ = 0.002 min⁻¹ for sapwood). At 150°C, the reactivity difference between the two most reactive lignin fractions was more evident ($k_1$ = 0.096 and $k_2$ = 0.028 min⁻¹ for sapwood).
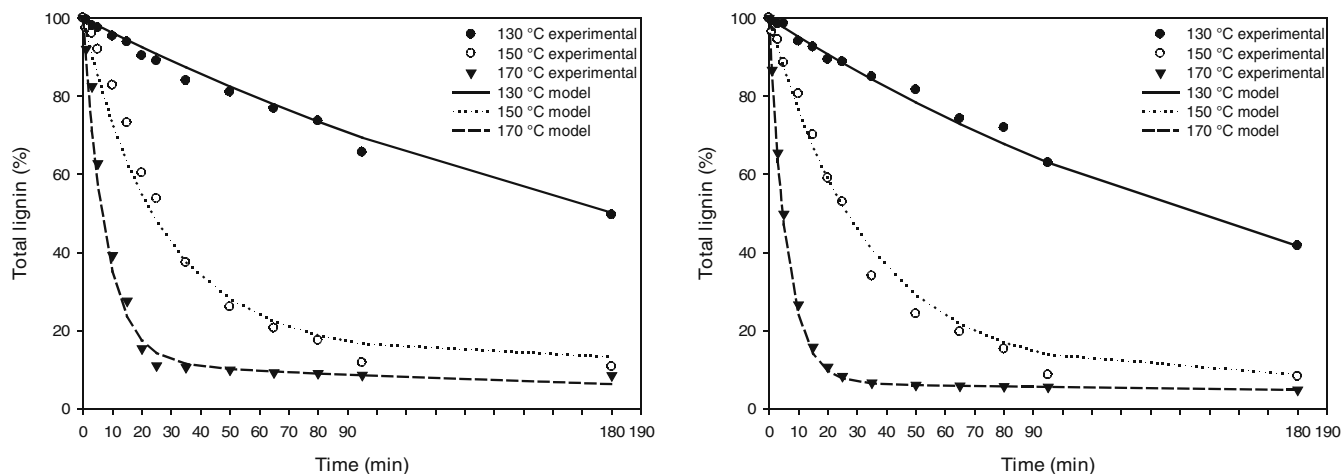


**Fig. 2.** Experimental data of total residual lignin (percentage of initial lignin in wood) in heartwood (*left*) and sapwood (*right*) samples during kraft delignification at 130°, 150°, and 170°C and predictions using the simultaneous model

**Table 3.** Heartwood and sapwood kinetic equations obtained by the simultaneous model

| | $T$ (°C) | $L = L_1 (1\text{-exp} (-k_1 t)) + L_2 (1\text{-exp} (-k_2 t)) + L_3 (1\text{-exp} (-k_3 t))$ | SQR | $Ea_1$ | $Ea_2$ | $Ea_3$ |
|---|---|---|---|---|---|---|
| Heartwood | 130°C | $L = 98.8 (1\text{-exp}(-0.0039\ t))$ | 0.0040 | | | |
| | 150°C | $L = 26.5 (1\text{-exp}(-0.0566\ t)) + 60.5 (1\text{-exp}(-0.0299\ t)) + 13.0 (1\text{-exp}(-0.0010\ t))$ | 0.0383 | | | |
| | 170°C | $L = 33.4 (1\text{-exp}(-0.1388\ t)) + 54.6 (1\text{-exp}(-0.1275\ t)) + 12.0 (1\text{-exp}(-0.0036\ t))$ | 0.0221 | | | |
| | Activation energy, $E_a$ (kJ.mol⁻¹) | | | 133.6 | 113.1 | 96.9 |
| Sapwood | 130°C | $L = 100.0 (1\text{-exp}(-0.0049\ t))$ | 0.0034 | | | |
| | 150°C | $L = 22.5 (1\text{-exp}(-0.0957\ t)) + 68.6 (1\text{-exp}(-0.0282\ t)) + 9.0 (1\text{-exp}(-0.0004\ t))$ | 0.0140 | | | |
| | 170°C | $L = 32.2 (1\text{-exp}(-0.1644\ t)) + 61.3 (1\text{-exp}(-0.1481\ t)) + 6.6 (1\text{-exp}(-0.0017\ t))$ | 0.0249 | | | |
| | Activation energy, $Ea$ (kJ.mol⁻¹) | | | 130.8 | 125.4 | 106.9 |

$L_1$ to $L_3$ are the percentages of lignin removed from the most reactive to the least reactive lignin; $k_1$ to $k_3$ are the respective reaction rates (min⁻¹), and $Ea_1$ to $Ea_3$ are the activation energies (kJ.mol⁻¹)
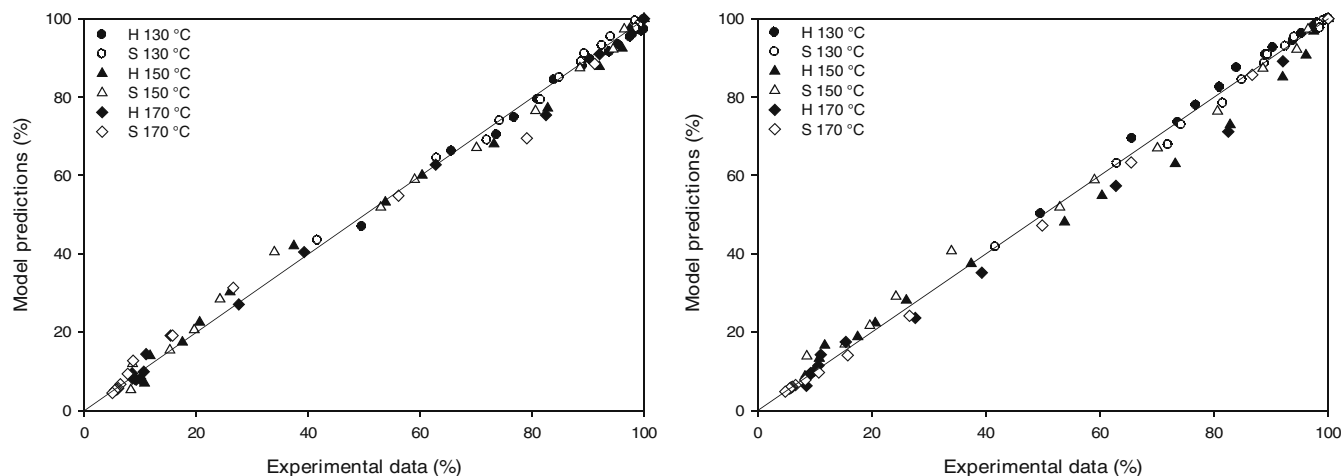
**Fig. 3.** Consecutive (*left*) and simultaneous (*right*) model predicted values versus experimental data of residual lignin (percentage of initial lignin in wood) of heartwood (*H*) and sapwood (*S*) during pulping at 130°, 150°, and 170°C

At 130°C, the different types of lignin could not be identified because the final stage where only the least reactive lignin was present was not attained (longer experimental delignification times would be needed). Therefore, although the several types of lignin were reacting in parallel, their specific reaction rates could not be determined. The composite reaction rate that was calculated is nevertheless mostly determined by the reactive characteristics of the most reactive lignin moiety.

The proportions of the different lignin fractions that were removed were on average 27%, 65%, and 8% from the most to the least reactive fractions, respectively, and were only somewhat influenced by temperature. Shatalov and Pereira[15] also identified three types of lignin fractions during *Arundo donax* organosolv delignification at temperatures of 130°, 140°, and 150°C, corresponding to average values of lignin removed of 62%, 22%, and 16%, respectively, for the most to the least reactive lignin that were independent of temperature. This example clearly shows the difference in lignin chemical composition and in delignification between the annual reed and the eucalypt wood.

The activation energies for the removal of the first two lignins were similar (133 and 113 kJ.mol$^{-1}$ for heartwood, 130 and 125 kJ.mol$^{-1}$ for sapwood) and decreased for the third lignin (96 and 106 kJ.mol$^{-1}$ for heartwood and sapwood respectively). No data were found for comparison, except the results for *Arundo donax*[15] for the three lignins, giving 65, 89, and 96 kJ.mol$^{-1}$ respectively. As regards the reactivity of lignin fractions for heartwood and sapwood, only small differences were found in all cases in relation to reaction rates and the proportion of the different lignin fractions (Table 3).

Overall the model was adequate to explain the experimental results, as demonstrated by the interval of the SQR values (Table 3) for sapwood (0.003–0.025) and heartwood (0.004–0.038).

An assessment of the performance of the consecutive and simultaneous models can be seen in Fig. 3, where the simulated values are plotted versus the respective experi-

mental data. The two models explain very well the lignin reaction kinetics in the range of pulping temperatures tested.

In general very small differences were observed between heartwood and sapwood delignification kinetics, and both share the same modeling approach using either consecutive or simultaneous approaches. Lignin reactivity and the proportion of the different lignin fractions were also similar in heartwood and sapwood, showing an overall chemical homogeneity of lignin within the stem of *E. globulus* trees at the age of harvest. The kinetic development of the process with regards time and temperature may therefore be considered independently of heartwood content in the raw material in relation to delignification. The major fact to be taken into account during eucalypt wood pulping is related to the higher content of extractives in heartwood, leading to consistently lower pulp yields. Attention should be paid to the initial phase of heating to temperature when substantial wood mass loss occurs, especially in heartwood.

## Conclusions

Lignin content, reactivity, and chemical homogeneity regarding delignification under kraft pulping conditions were similar in heartwood and sapwood of *Eucalyptus globulus*, as were their respective kinetics parameters. The modeling of delignification was also similar for heartwood and sapwood, and either the consecutive or simultaneous modeling approaches could be used, with both yielding good correlations between experimental and model data.

The presence of heartwood did not influence the kinetic development of the pulping process as regards delignification. However, heartwood had more extractives compared to sapwood, and lower final yields were obtained in kraft pulping, representing about 4% less pulp yield in heartwood compared to sapwood. The negative impact of heartwood in pulping is, therefore, related to its extractives content and

to the influence of extractives in the process, namely in the initial heating-to-temperature pulping phase.

# References

1. Pereira H, Graça J, Rodrigues JC (2003) Wood chemistry in relation to quality. In: Barnett JR, Jeronimidis G (eds) Wood quality and its biological basis. CRC, Blackwell, Oxford, pp 53–83

2. Miranda I, Gominho J, Lourenço A, Pereira H (2006) The influence of irrigation and fertilization on heartwood and sapwood contents in 18-year-old *Eucalyptus globulus* trees. Can J For Res 36:2675–2683

3. Miranda I, Gominho J, Lourenço A, Pereira H (2007) Heartwood, extractives and pulp yield of three *Eucalyptus globulus* clones grown in two sites. APPITA J 60(6):485–488, 500

4. Kleppe PJ (1970) Kraft pulping. Tappi J 53(1):35–47

5. Gierer J (1980) Chemical aspects of kraft pulping. Wood Sci Technol 14:241–266

6. Oliet M, Rodríguez F, Santos A, Gilarranz MA, Garcia-Ochoa F, Tijero J (2000) Organosolv delignification of *Eucalyptus globulus*: kinetic study of autocatalyzed ethanol pulping. Ind Eng Chem Res 39:34–39

7. Santos A, Rodríguez F, Gilarranz MA, Moreno D, García-Ochoa F (1997) Kinetic modeling of kraft delignification of *Eucalyptus globulus*. Ind Eng Chem Res 36:4114–4125

8. Pérez JM, Gillarranz MA, Rodríguez F, Oliet M, Garcia J (2000) Estudio sobre la cinética de la desalignificación en la fase residual de las cocciones kraft. In: Congreso Iberoamericano de Investigación en Celulosa y Papel (Poster), 19/10, 2000, Misiones, Argentina, http://ciadicyp.unam.edu.ar/trabajos/trabajos/pulpa_y_pulpados/Rodriguez-100-UCMEsp.pdf. Accessed June 2, 2010

9. Gilarranz MA, Santos A, García J, Oliet M, Rodríguez F (2002) Kinetics, catalysis and reaction engineering. Ind Eng Chem Res 41:1955–1959

10. Miranda I, Pereira H (2002) Kinetics of ASAM and kraft pulping of *Eucalyptus* wood (*Eucalyptus globulus*). Holzforschung 56:85–90

11. Pereira H, Oliveira MF, Miranda I (1986) Kinetics of ethanol-water pulping and pulp properties of *Eucalyptus globulus* Labill. APPITA J 39:455–458

12. Gilarranz MA, Rodríguez F, Santos A, Oliet M, Garcia-Ochoa F, Tijero J (1999) Kinetics of *Eucalyptus globulus* delignification in a methanol–water medium. Ind Eng Chem Res 38:3324–3332

13. Labidi PA, Pla F (1992) Délignification en milieu alcalin de bois feullus à l'aide d'un réacteur à lit fixe et à faible temps de passage. Holzforschung 46:155–161

14. Sixta H, Rutkowska EW (2007) Comprehensive kinetic study on kraft pulping of *Eucalyptus globulus*. Part 1. Delignification and degradation of carbohydrates. O Papel 8:54–67

15. Shatalov A, Pereira H (2005) Kinetics of organosolv delignification of fibre crop *Arundo donax* L. Ind Crop Prod 21:203–210

16. Bogren J, Brelid H, Theliander H (2008) Effect of pulping conditions on the rates of formation and degradation of hexenuronic acid in Scots pine. J Pulp Paper Sci 34:23–29

17. Garland CP, James FC, Nelson PJ, Wallis AFA (1987) A study of the delignification of *E. diversicolor* wood during soda pulping. APPITA J 40:116–120

18. Madeira MV, Fabião A, Pereira JS, Araújo MC, Ribeiro C (2002) Changes in carbon stocks in *Eucalyptus globulus* Labill. Plantations induced by different water and nutrients availability. For Ecol Manag 171:75–85

19. Gominho J (2003) Variação do cerne no eucalipto e sua influência na qualidade da madeira para produção de pasta para papel. Dissertação de Doutoramento. Universidade Técnica de Lisboa. Instituto Superior de Agronomia, Lisboa, p 264

20. Wong BM, Deka GC, Roy DN (1995) Bulk delignification kinetics at selected vertical heights within jack pine plus trees. Wood Sci Technol 29:11–18

21. Nelson PJ, Gniel GM (1986) Delignification of *Eucalyptus regnans* wood during soda pulping. APPITA J 39:110–114

22. Dang VQ, Nguyen KL (2008) A universal kinetic model for characterisation of the effect of chip thickness on kraft pulping. Bioresour Technol 99:1486–1490

23. Sjöström E (1981) Wood chemistry. Fundamentals and applications. Academic, London

24. Simão JPF, Egas APV, Baptista CMS, Carvalho MG, Castro JAA (2005) Evolution of methylglucuronic and hexenuronic acid contents of *Eucalyptus globulus* pulp during kraft delignification. Ind Eng Chem Res 44:2990–2996

25. Santiago AS, Neto CP (2008) Impact of kraft process modifications on *Eucalyptus globulus* pulping performance and polysaccharide retention. Ind Eng Chem Res 47:7433–7440

26. Bogren J, Brelid H, Theliander H (2007) Reaction kinetics of softwood kraft delignification – general considerations and experimental data. Nord Pulp Res J 22:177–183

27. De Groot B, Van Dam JEG, Van der Zwan RP, van't Riet K (1994) Simplified kinetic modelling of alkaline delignification of hemp woody core. Holzforschung 48:207–214

28. Mariani S, Torres M, Fernandez A, Morales E (2005) Effects of *Eucalyptus nitens* heartwood in kraft pulping. Tappi J 4(2):8–10

29. Chiang VL, Puumala RJ, Takeuchi H (1988) Comparison of softwood and hardwood kraft pulping. Tappi J 9:173–176

30. Esteves B, Gominho J, Rodrigues JC, Miranda I, Pereira H (2005) Pulping yield and delignification kinetics of heartwood and sapwood of maritime pine. J Wood Chem Technol 25:217–230

31. Schmid R, Sapunov VN (1982) Non-formal kinetics in search for chemical reaction pathways. Monographs in modern chemistry, vol 14. Verlag Chemie, Basel