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A systematic approach for determination of optimal conditions for Lo-Solids^{TM} kraft pulping of *Eucalyptus nitens*

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Abstract

Kraft pulping of thin chips of *Eucalyptus nitens* was performed in laboratory flow-through reactors under isothermal condition. The effects of process variables on the dissolutions of the lignocellulosic components, i.e. lignin, pentosans and cellulose, of the chips were studied. It was found that at a target kappa number, higher pulp yields could be obtained by pulping at a temperature below 150 °C and with an effective alkali concentration below 0.5 M. The effects of all process conditions were combined using the Nuclei Growth kinetic models.

Keywords: Cellulose; Delignification; *Eucalyptus nitens*; Flow-through reactor; High-yield; Kraft pulping kinetics; Pentosans

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1. Introduction

Kraft pulping is the dominant process for the production of chemical pulps. The objective of kraft pulping is to liberate the wood structure into fibres for papermaking. In doing this, the lignin macromolecules, which act as the binding substance of the lignocellulosic matrix, need to be broken down into smaller molecular fragments enough to diffuse out to the aqueous pulping liquor.

Kraft pulping process is complex, involving many chemical reactions between the cooking chemicals, comprising of mainly sodium hydroxide and sodium sulphide, and components of wood. Chemical reactions take place to degrade lignin and extractives as well as carbohydrates. These reactions consume alkali, resulting in a concentration gradient within the wood chips providing the driving force for continuous diffusion of cooking chemicals from the bulk liquor to the reaction sites. The degraded products are dissolved and diffuse out of the fibre wall. In a typical kraft cook more than 90% of lignin is removed compared with about 30% of carbohydrate loss. The final yield is normally within 45–65% depending on the extent of the cook.

The delignification reactions are primarily hydrolysis reactions. The delignification includes cleavage reactions of α- and β-aryl ether bonds in phenolic units of lignin as well as cleavage of β-aryl ether bonds in non-phenolic units [1]. These reactions liberate phenolic and glycolic groups from the lignin structure and form soluble, low-molecular-weight fragments. Other major reactions are extended cleavage reactions of α-aryl ether bonds, reaction of the hydrogen sulphide ions with the methyl groups and cleavage of carbon–carbon bonds in propane units.

Many models have been established to approximate the kinetics of these complex reactions. Several empirical and semi-empirical kinetic models are available in the literature [2–5]. Most of the models simplified the complex heterogeneous delignification kinetics by using underlying theory such as Fick's law for diffusion, which is applicable to homogeneous reaction systems. Most of these models divided the delignification process into three distinct phases (initial, bulk and residual) based on the decelerating trend of the process kinetics. Other approaches treated the lignin as composed of several fractions dissolving at different rates and used two or three simultaneous rate equations to determine the specific delignification rate constants. A more recent approach was developed for the delignification of *Arundo donax* L., based on the consideration of *n*-parallel irreversible first-order reactions with similar final product and analysed as a multi-component reaction system [6]. It was found that the kinetics of three lignin fractions would satisfactorily represent the proposed system.

Some undesirable side reactions also occur in the pulping process, such as the degradation of cellulose and hemicelluloses.

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The reactions involved with carbohydrate degradation generally do not involve the hydrogen sulphide ion [7]. The degradation in alkaline solutions of the major cellulose and hemicelluloses in softwood and hardwood were presented in several studies [8–11]. Hemicelluloses (including pentosans) in major wood species appeared to be readily soluble in alkaline solutions in the initial stage of kraft pulping. The degradation of hemicelluloses can be characterised by alkaline hydrolysis, peeling and termination reactions. Cellulose, whose morphological structure is quite different from hemicelluloses, exists in nature in the form of microfibrils arranged in highly ordered (crystalline) regions alternate with less-ordered (amorphous) regions. The amorphous fraction of cellulose is highly susceptible to reaction chemicals and hence it is more readily dissolved during pulping. The crystalline fraction is more resistant to chemical degradation. In kraft pulping cellulose is subjected to not only peeling reactions, which affect the pulp yield, but also alkaline hydrolysis reactions that reduce its molecular weight and subsequently its viscosity. It is anticipated that these two types of reactions are distinctively different. For typical kraft hardwood pulps the depolymerisation of cellulose, unless highly excessive, is not relevant to the use of this pulp for making printing grade on modern paper machines without open draw.

Traditionally, batch kraft cooks are performed at high temperature (∼170 °C) and with a high effective alkali concentration. Extension of kraft cooking to lower the kappa number, which is a frequently used indirect indication of lignin content of pulp, is not always practical due to the accompanied loss of yield. Improving pulp yield, which is essential in modern pulp mills regarding the high cost of the raw materials, has been a key area of research in the pulp and paper industry.

One of the first studies on modified kraft pulping [12] showed that improvements in pulping performance can be achieved by decreasing the concentration of dissolved wood solids throughout the bulk phase of the delignification. The results were later applied and commercialised in a pulping technology called Lo-Solids® by Ahlstrom (Andritz). In this technology, the dissolved solids and alkali profiles are optimized to achieve optimum pulp properties for bleaching. Due to the commercial value of this development, the advantages of such a process have never been fully realised.

The objective of this work is to study the effects of process variables on the dissolutions of the lignocellulosic components under isothermal kraft pulping of thin chips of *Eucalyptus nitens* in flow-through reactors. The pulping conditions are designed to minimize the dissolved solids content in the reactors, imitating the Lo-Solids® pulping conditions. The operating conditions will then be systematically combined using the Nuclei Growth kinetic models, which was previously developed [13]. The results will be used to identify the optimum conditions for kraft pulping of *E. nitens.*

2. Experimental

Wood chips used in the pulping experiments were produced from 20-year-old *E. nitens* supplied by the North Forest Product Tasmanian plantation, Australia. Thin chips were prepared for the pulping experiments. The dimensions of the chips were measured using a pair of vernier callipers. The mean chip dimensions were 1.7 ± 0.5 mm thick, 10.4 ± 4.2 mm wide and 24.4 ± 5.9 mm long. Before the pulping experiments, the chips were thoroughly mixed. Each sample was hand-sorted to remove knots and defective chips.

The cooking unit composes of three parts. The first part includes six 2-l reactors. Each reactor was equipped with a different functional valve system for cooking, washing and isolation. Thermocouples and a flowmeter were used to monitor the cooking temperature and the liquor flow to the cells, respectively. The second part consists of a 50-l vessel which was used for storing and supplying cooking liquor to the system. The cooking liquor temperature was controlled via a heat exchanger which operated with steam. The last part is the scrubber system where the flash steam from the spent liquor was collected and scrubbed with a hypochlorite solution.

At the start of each cook, wood chips were charged into 6 baskets made of 100-mesh gauze covered with 100-mesh lids and positioned inside the reactors. The moisture of the wood chips was determined. The cooking liquor was heated to the target temperature in the 50-l vessel which was equipped with a temperature controller. The SCAN method N2:63 was used to determine the concentrations of active components in the cooking liquor. The liquor delivery rate to each 2-l reactor was controlled at 1.5 l/min to ensure that the dissolved organic content in the cooking liquor was maintained below 2.5%.

A total of 12 series of 6 cooks were carried out to cover ranges of conditions as listed in Table 1. The concentration of hydroxide ions is equal to the effective alkali, which is the sum of sodium hydroxide and half the sodium sulphide. The hydrogen sulphide ion concentration is half the sodium sulphide concentration under aqueous conditions.

When the target cooking time was achieved the reaction was quenched by running cold tap water through the reactors. The cold water was left to run in the reactor until the cooked chips are thoroughly washed (normally after 2 h). The cooked chips were then transferred to 100-mesh bags and subsequently thoroughly washed with warm tap water at 60 °C. The washed pulps were stored in plastic bags at 4 °C for further chemical analyses.

Pulp yields were determined from sample weights and moisture contents. The moisture contents of samples were determined by drying a pre-weighed sample in an oven at 105 °C until constant weight was attained (usually overnight). For the chemical analyses, wood and pulp samples were air-dried and ground

Table 1
Pulping conditions

Process variable	Range
Temperature (°C)	130–165
Hydroxide ion concentration (M)	0.25–1.0
Hydrogen sulphide ion concentration (M)	0–0.12
Time (min)	30–300

in a Wiley mill to pass a screen with 1 mm holes. They were then extracted with methanol, following Australian Standard AS 1301.012s-79 (Standards Association Australia, 1991). The extracted samples were analysed for lignin by AS 1301.011s-78 (SAA, 1991) and TAPPI Useful Method UM250 (TAPPI, 1991), using the specific absorption coefficient of 100 L/g cm. The pentosans content was determined by TAPPI Standard T223cm-84 (TAPPI, 1994). The cellulose content was calculated by subtracting the lignin and pentosans from the extractive-free samples. The cellulose calculated in this manner will also include any hemicelluloses not detected by the pentosans test. The kappa number (*K*) was determined using the following relationship:

$$K = \frac{100L}{0.147Y} \quad (1)$$

where *Y* and *L* are the yield and lignin content of pulp, respectively.

3. Results and discussion

The kappa number of the pulps ranges from 2.7 to 182. The yield of the produced pulps ranges from 40 to 84%. A plot of kraft pulp yield versus kappa number was shown in Fig. 1. It was evident that the pulp yield decreased linearly with kappa number with a regression coefficient, R^2, of 0.96. The scattering of the plot is significant indicating the effects of process conditions on the pulp yield, suggesting that the optimisation of pulp yield requires not only the selection of a target kappa number but also the cooking conditions such as temperature and effective alkali profile.

3.1. Effect of temperature

The kraft pulp yield at different cooking temperatures was plotted against kappa number in Fig. 2a–c. It was found that when the effective alkali concentration was less than 0.52 M, the cooking temperature had insignificant effect on the yield at a target kappa number (Fig. 2a and b). However, when cooked at 1.0 M of effective alkali, the pulp yield decreased by ~4% when the cooking temperature was raised from 150 to 165 °C (Fig. 2c). These results show that it is essential to utilise low cooking temperature in order to obtain uniform and high-yield kraft pulps.

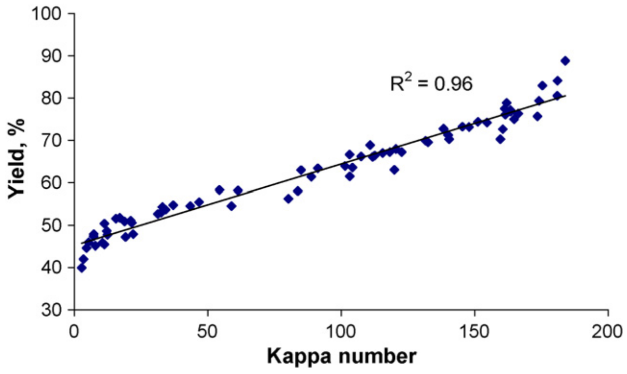

Fig. 1. Kraft pulp yield variation with kappa number.

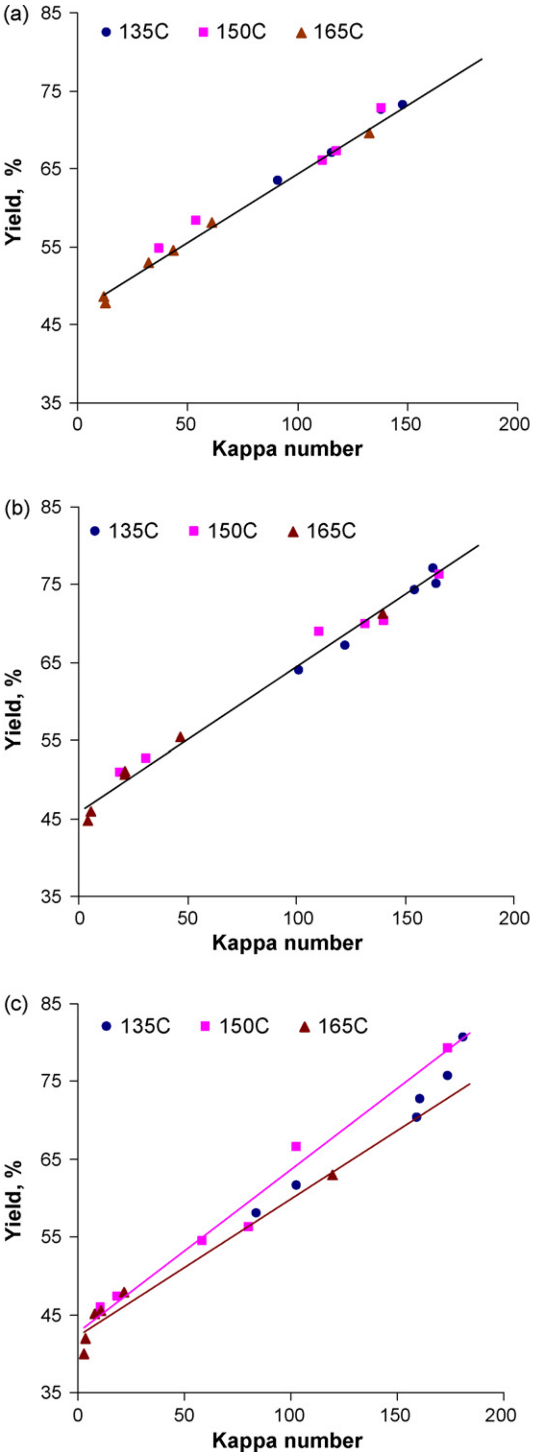

Fig. 2. Effect of temperature at $[HS^-] = 0.05–0.07$ M on kraft pulp yield: (a) $[OH^-] = 0.24–0.29$ M; (b) $[OH^-] = 0.46–0.52$ M; (c) $[OH^-] = 0.98–1.0$ M.

The effect of cooking temperature on the dissolutions of lignin and pentosans contents was also investigated. The changes in lignin and pentosans contents with time at different temperatures were shown in Fig. 3a and b, respectively. Both sets of the results confirm the accelerating effect of temperature on the dissolution rates.

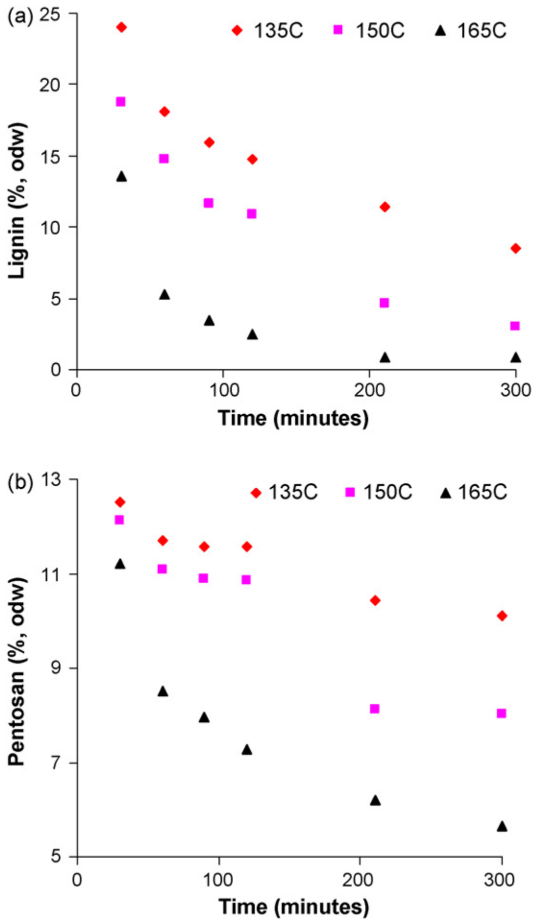

Fig. 3. Effect of temperature on the dissolution of wood constituents: (a) lignin; (b) pentosans.

3.2. *Effect of effective alkali concentration*

The kraft pulp yields at different effective alkali concentrations were plotted against kappa number in Fig. 4a–c. It was evident that at 1.0 M of effective alkali, the effect on kraft yield was profound in all cases with an overall reduction of 3–4%. These results indicate that higher pulp yield can be obtained by cooking at moderately lower effective alkali concentration (<0.5 M). This can be achieved by splitting the alkali addition during the pulping stage.

The changes in lignin, pentosans and cellulose contents with time (at cooking temperature 150 °C) at effective alkali concentrations of 0.25 and 0.98 M were shown in Fig. 5a and b, respectively. It was found that after 300 min of cooking the residual lignin content was less than 4% and 1% at effective alkali concentrations of 0.25 and 0.98 M, respectively. The results clearly showed the selectivity of the kraft process towards the delignification.

Having learnt the effects of cooking temperature and effective alkali concentration, it is now possible to differentiate the data presented in Fig. 1. In Fig. 6, the yield was re-plotted against the kappa number separating the pulping conditions into two sets: one for $T \leq 150\,^{\circ}\mathrm{C}$ and $[\mathrm{OH}^-] \leq 0.5\,\mathrm{M}$ and the other for higher temperature and alkali concentration. It was evident that using these optimal pulping conditions, pulp yield could be improved by at least 1–2% at a target kappa number. On an industrial scale, this represents significant savings.

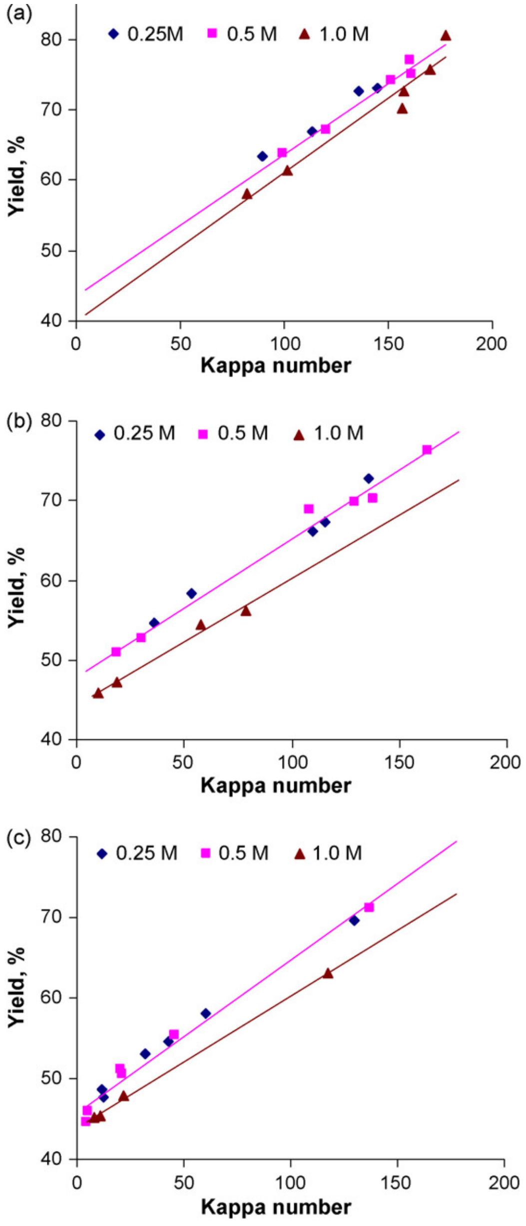

Fig. 4. Effect of effective alkali concentration at $[\mathrm{HS}^-] = 0.05\,\mathrm{M}$ on kraft pulp yield: (a) 135 °C; (b) 150 °C; (c) 165 °C.

3.3. *Nuclei Growth kinetic models*

We attempted to combine all the effects of cooking conditions on the dissolutions of lignocellulosic components using the Nuclei Growth (NG) model, which was previously developed for kinetic studies [13]. The general form of the NG model applied to each component in wood is a first-order rate equation with a time-dependent rate coefficient (Eq. (2)):

$$-\frac{dX}{dt} = a \cdot \left[OH^-\right]^b \cdot \left[HS^-\right]^c \cdot X \cdot t^{n-1} \cdot \left(\exp\left(-\frac{E}{R_u T}\right)\right)^n \tag{2}$$

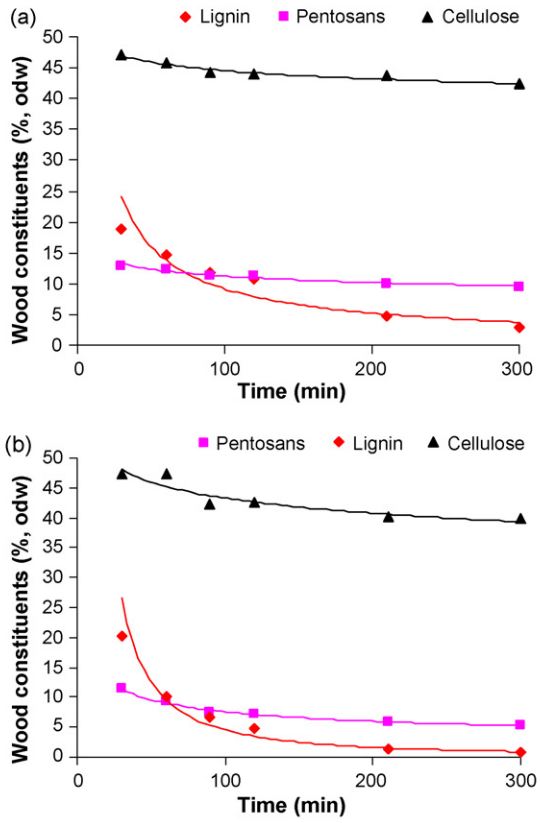

Fig. 5. Effect of effective alkali concentration on the dissolutions of wood constituents at a cooking temperature of 150 °C: (a) $[\mathrm{OH}^-] = 0.25$ M; (b) $[\mathrm{OH}^-] = 0.98$ M.

where X is the lignin, pentosans and cellulose content of pulp (%, o.d.w.); $[\mathrm{OH}^-]$ the effective alkali concentration (M); $[\mathrm{HS}^-]$ the hydrogen sulphide concentration (M); E the activation energy (kJ/mol); t the time (min); T is the temperature (K).

It should be noted that from the development of the NG model, the magnitude of a not only represents the available number of initial reactive sites, I, but also the growth of the reactive area, R. The higher the value of a gives rise to the probability of the spread of reactive area R. The constants b and c are the order of the chemical reactants (e.g. effective alkali and hydrogen sulphide) participating in the pulping reactions. The order of reactants can be positive or negative and can be an integer or a fraction. The values of b and c must be determined from experimental results and not from the stoichiometry of the reactions.

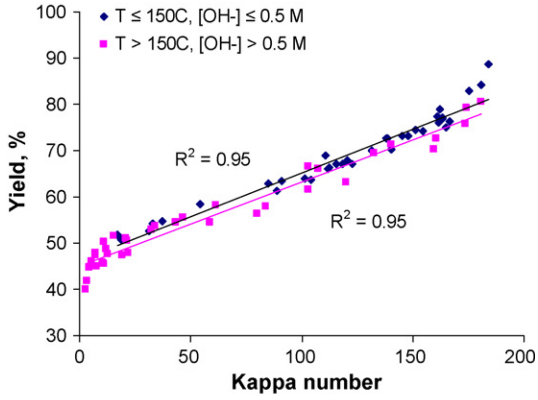

Fig. 6. Improvement of kraft yield at optimal pulping conditions.

Eq. (2) describes a first-order rate equation with a time-dependent rate coefficient. This type of equation can be used to replace the three multiple-phase rate equations. The multiple-phase approach was effective for modelling purpose; however in practice it is not always possible to identify the transition points or the different fractions of lignin. In terms of modelling, the multiple-phase approach requires at least three different sets of kinetic parameters, which creates complexity for simulation.

To minimize conversion time in modelling, the above equation is transformed into a linear form as below:

$$\ln\left(-\ln\left(\frac{X}{X_i}\right)\right) = \ln a + b\ln\left[\mathrm{OH}^-\right] + c\ln\left[\mathrm{HS}^-\right] - \frac{nE}{R_u T} + n\ln t \qquad (3)$$

This linearization ensured that a reproducible single set of estimates would be obtained. Statistica$^{\mathrm{TM}}$ 6.0 (StatSoft Inc., USA) was used to perform the multiple linear regressions to determine the estimates of the model parameters (a, b, c, E and n). The P-values of the regression were also determined to indicate the level of significance associated to each estimate. The regression results associated with the lignin, pentosans and cellulose kinetic models are summarised in Table 2.

The linear form of Eq. (3) applied for the delignification can be graphically presented in Fig. 7. This plot shows a regression coefficient, R^2, of 0.97 for the delignification. The small P-values obtained from the regression analysis indicate that the estimates of model parameters are significant with high levels of confidence. It should be noted that the NG model was developed to represent the kinetics associated with the heterogeneous nature of chemical transport in wood structure [13]. Mathematically, it is possible to produce different predictive models with better regression coefficients, but these do not necessarily represent the mechanism of the delignification. One of the most popular approaches is combining a number of first-order rate

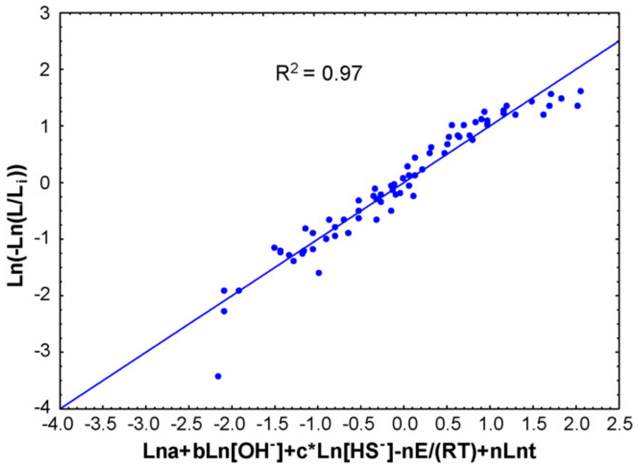

Fig. 7. Validation of the NG model (Eq. (2)) for the delignification during kraft pulping of *Eucalyptus nitens*.

Table 2
Summary of kinetic model parameters

Wood component	*a*	*b*	*c*	*n*	*E* (kJ/mol)
Lignin	8.55×10^9	0.31	0.43	0.93	97.3
P-value	1.77×10^{-6}	1.62×10^{-4}	6.12×10^{-3}	$<10^{-6}$	$<10^{-6}$
Standard error	30	0.02	0.03	0.0246	9.1
Pentosans	156	0.27	n.d.	0.23	92.2
P-value	$<10^{-6}$	$<10^{-6}$		$<10^{-6}$	4.8×10^{-6}
Standard error	1.5	0.02		0.02	8.9
Cellulose	217	0.11	n.d.	0.29	101.0
P-value	$<10^{-6}$	$<10^{-6}$		$<10^{-6}$	$<10^{-6}$
Standard error	1.8	0.03		0.02	7.0

equations to characterise multi-stage, multi-component delignification kinetics. Such an approach requires a large set of data for the determination of the model parameters. The minimum number of data set, which is equal to (number of stage × number of components × number of parameters for each component in each stage), is excessive. In most cases, the activation energy, which is the most important parameter of delignification, can be estimated using different models. This analysis indicated that both $[\mathrm{OH}^-]$ and $[\mathrm{HS}^-]$ have significant effects on the delignification throughout the cooks. The estimated activation energy of the delignification is 97.3 ± 9.1 kJ/mol. This activation energy is approximate the values of 100.5 kJ/mol obtained by Li and Mui [14] and 89–96 kJ/mol for bulk and residual stages of the *Arundo donax* L. delignification obtained by Shatalov and Pereira [6]. It is anticipated that the activation energy depends on both the chemical and physical structure of the wood. For this reason the activation energies are different from different studies. It should be noted that methanol extraction can remove most but not all the extractives. For this reason the results will bear certain error. However, the regression coefficient of the model is significantly high suggesting that this error is not significant.

The validification of the NG model for the dissolution of pentosans can be graphically presented in Fig. 8. The coefficient of the regression R^2 is 0.86. The *P*-values of the regression as listed in Table 2 are low justifying the inclusion of these variables in the regression. The results indicate that the dissolution rate of pentosans is proportional to $[\mathrm{OH}^-]^{0.27}$ and the activation energy is 92.2 ± 8.9 kJ/mol. This activation energy is in the same order of magnitude of previous results obtained for different types of hemicelluloses [8,15,16].

The regression results for the loss of cellulose can be graphically presented in Fig. 9. The coefficient of the regression, R^2, is 0.89. The results indicate that the loss of cellulose is proportional to $[\mathrm{OH}^-]^{0.11}$, and the activation energy of the cellulose dissolution is approximately 101 ± 7 kJ/mol. This activation energy is higher than the activation energies of the delignification and dissolution of pentosans but within the range previously reported [8,15,16]. Although the concentration of the chemical components (i.e. cellulose and hemicelluloses) of the pulp are estimated values, the sum of these is highly relevant to the pulp yield. Results from additional tests such as chromatography for each component, if available, can be used to improve the accuracy of the NG model. However, such improvement is not significant since the model regression coefficient is already significantly high.

The exponential *n*-values for the delignification, pentosans and cellulose dissolutions were found to be 0.93, 0.23 and 0.29, respectively. The *n*-value is an important parameter in fractal-

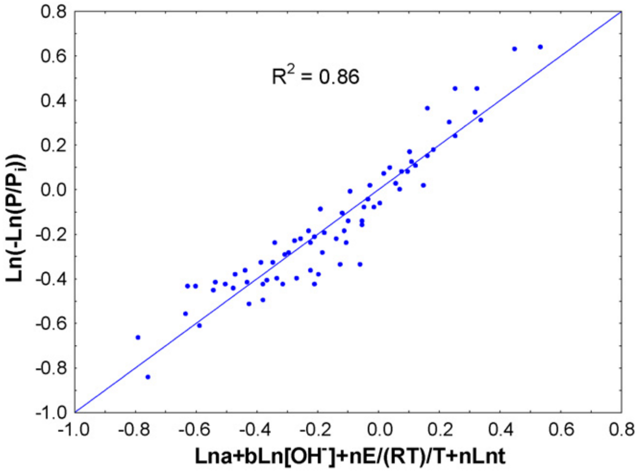

Fig. 8. Validation of the NG model (Eq. (2)) for the dissolution of pentosans during kraft pulping of *E. nitens*.

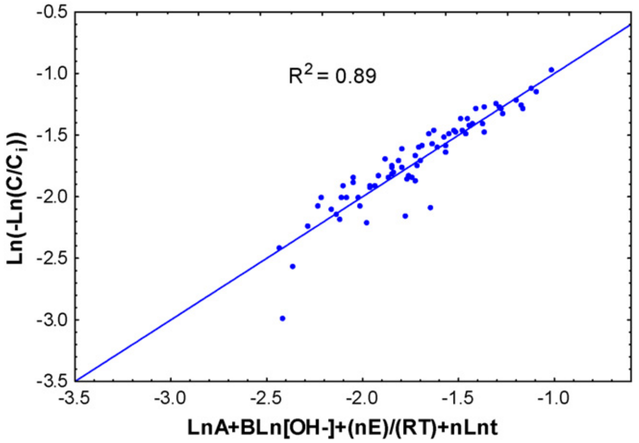

Fig. 9. Validation of the NG model (Eq. (2)) for the dissolution of cellulose during kraft pulping of *E. nitens*.

like (diffusion-limited) kinetics. The variation of n represents the difference in fractal nature of the dissolutions of these lignocellulosic components. Typically, n is less than 1 due to the increasing interferences amongst the growing of reaction zones with cooking time. However, if the growing occurs in zones where the structure is favourable for the spread of chemicals (such as high permitability or low chemical demand by the delignification), n could be larger than 1. The values found here are in good agreement with the range of 0.40–0.90 reported for the lignocellulosics fractionation of corn stalk, alfa, *Populus tremuloides* and *Betula papyrifera* [17].

4. Conclusions

The effects of process variables on the dissolutions of the lignocellulosic components in thin chips of *E. nitens* during kraft pulping in flow-through reactors were studied. It was found that pulping at lower than 150 °C and lower than 0.5 M of effective alkali was favourable in terms of maximising pulp yield at a target kappa number. The Nuclei Growth model, which was previously developed, could be used to combine all the effects of process conditions. The models could be used to optimise and to improve the control of the pulping process.

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