

MODELING OF *EUCALYPTUS GLOBULUS* KRAFT PULPING

H. Sixta¹, E.W. Rutkowska²

¹R&D director, Lenzing AG Process Innovation, Werkstraße 1, 4860 Lenzing, Austria, ²PhD student, Kompetenzzentrum Holz GmbH, St.-Peter-Str. 25, A-4021 Linz, Austria

ABSTRACT

The optimization of kraft pulping covering both continuous and batch processes demands kinetic models suitable for advanced control and offline optimization of the cooking operation.

This work contributes to an improved kinetic model for kraft cooking of *Eucalyptus globulus* suitable for advanced control of modern displacement cooking processes such as the continuous batch cooking process (CBC). After impregnation where the initial lignin has been removed, the bulk and residual delignification have been studied in a batch reactor as a function of the $[\text{OH}^-]$, $[\text{HS}^-]$, ionic strength, $[\text{Na}^+]$, and temperature. The underlying kinetic expressions are similar to those used in the Andersson model also including a mechanism for determining the distribution of lignin and carbohydrate species 2 and 3 as a function of the cooking conditions. The kinetic equations were successfully validated against experimental data from a pilot plant digester applying conventional batch cooks.

Keywords: *E. globulus*, CBC pulping, delignification kinetics, cellulose degradation kinetics.

INTRODUCTION

The majority of kinetic studies have been performed with softwoods. So far, only basic informations about the kinetics of *E. globulus* kraft pulping are available. Santos et al. (Santos *et al.*, 1997) developed expressions for the initial and the bulk delignification phase. His work was continued by Gilarranz et al. (Gilarranz *et al.*, 2002) who investigated the residual phase and also modeled the lignin conversion value at the transition point from the bulk to the residual phase. However, none of the presented models was able to meet all necessary requirements for modeling *E. globulus* CBC kraft pulping. CBC is a new pulping method, which allows to change the alkali profile and other important reaction conditions during the cooking process (Hepp, 1997). The model of choice seems to be the model proposed by Andersson et al. (Andersson *et al.*, 2003a). This model considers the influence of varying cooking conditions by introducing an appropriate algorithm for determining the distribution of lignin and carbohydrate species 2 and 3 as a function of the relevant cooking conditions. The aim of this study was to develop a comprehensive kinetic

model for kraft pulping of *E. globulus* based on the concept of Andersson to provide an appropriate tool for the optimization of cooking processes in practice.

EXPERIMENTAL

For the kinetic studies *E. globulus* chips received from ENCE, M'Bopicua, Uruguay, with an average thickness of 4 mm were further cut in the laboratory. After screening their average dimensions were reduced to 9.6 mm in length, 4.9 mm in width and 1.9 mm in thickness. The wood chemical composition was as follows: 22.1 % Klason lignin (KL) (T 222 om-98), 4.6 % acid soluble lignin (T om-250), 47.3 % cellulose (C), 2.2 % glucomannan (GM), 21.8 % 4-O-methylglucuronoxylan (X) (AEC with PAD detection after total hydrolysis with H_2SO_4) and 2.0% resins and ash (T 211 om-93; ISO 14453:1997). The hexenuronic acid (HexA) content in the pulp was determined by a selective hydrolysis of the glycosidic linkage between the hexenuronic acid group and the xylan chain followed by oxidation and conversion to a coloured compound for colorimetric determination (Gellerstedt *et al.*, 1996). The kappa number <20 was determined according to T236 cm-85, and >20 according to SCAN-C 1:00, the viscosity according to SCAN 15:88. The cooking liquors were prepared from $\text{NaOH}(\text{s})$, $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}(\text{s})$ and $\text{NaHS}(\text{s})$. The sodium concentration was adjusted by gravimetric addition of NaCl . Effective and residual alkali concentrations were analyzed according to SCAN-N 30:85 and sulfidity according to SCAN-N 31:94.

Prior to the kinetic investigations, the wood was subjected to a uniform impregnation stage in a 10 L-digester at 100 °C for 60 min with $[\text{OH}^-] = 0.37$ mol/L, $[\text{HS}^-] = 0.16$ mol/L, $[\text{Na}^+] = 1.5$ mol/L at a L/S ratio of 10:1. With a yield loss of 6.5%, the composition of the impregnated wood changed to 18.9 % KL, 5.3 % acid soluble lignin (T om-250), 47.1 % C, 0.7 % GM, 17.9 % X, 1.5 % resins and ash and 2.1% unknown. KL can be calculated from kappa number by a factor of 0.183 (18.9/103.3).

After drainage of the impregnation liquor, the chips were transferred to a 400 ml-Parr reactor to proceed with the kinetic investigations. The stainless steel pressure vessel was provided with an external heating system and measurement and control of both pressure and temperature. The temperature was increased at a rate of about 5 °C per minute to the preset cooking temperature. The heating-up time and any deviation from the target cooking temperature were corrected for isothermal conditions using the following expression:

$$t_{T_0} = \int_{t_{T_i}}^{t_{T_0}} \text{Exp} \left(-\frac{E_A}{R} \left[\frac{1}{T_t} - \frac{1}{T_{T_0}} \right] \right) \cdot dt \quad [1]$$

in which T_i refers to the initial temperature, T_t to the temperature during heating-up, T_0 the target temperature, t_{T_0} the reaction time at target temperature (corrected for isothermal conditions), and E_A the activation energy which was assumed to be 134

kJ/mol. The numerical integration has been carried out by using an Excel sheet. The experiments were accomplished at an L/S ratio of 40:1 in order to keep constant concentration of chemicals throughout the cooks. Time series at four different temperature levels (140, 150, 160 and 170°C), five different [OH⁻] levels (0.1, 0.27, 0.52, 0.94 and 1.23 mol/L), three different [HS⁻] levels (0.17, 0.29, 0.64 mol/L) and three different [Na⁺] levels (0.8, 1.5 and 2.5 mol/L) were conducted to provide the necessary database for the evaluation of the kinetic models for delignification, carbohydrate degradation and cellulose chain scissions.

The pilot plant trials were carried out in a 10-L digester with forced liquor circulation. The mean thickness of the industrial chips was 4.0 ± 1.5 mm and the chips had a moisture content of 35%. After a short steaming phase (8 min, final temperature 98 °C), white liquor was introduced to a total L/W ratio of 2.96 L/kg. The effective alkali charge was set to 19% NaOH on oven dry wood (odw). The sulfidity was 26.5% resulting in initial [OH⁻] and [HS⁻] of 1.60 mol/L and 0.245 mol/L, respectively. The conventional batch cooking procedure was characterized by a heating-up time of 90 min to a cooking temperature of 160 °C. Four cooks were performed comprising H-factors of 300, 450, 600 and 800.

RESULTS AND DISCUSSION

Kinetics of delignification and carbohydrate degradation

The general structure of the delignification and carbohydrate degradation models is derived from the model introduced by Andersson et al. (Andersson *et al.*, 2003a). The advantage of this model is that it accounts for any subsequent changes in cooking conditions as occurring in industrial batch and continuous cooking processes (see also (Sixta, 2006). It is commonly agreed that the single wood species such as lignin (L) and (CH) can be divided into three species with different reactivity (L1, L2, L3 and CH1, CH2, CH3) representing their different chemical and supramolecular composition. The model is based on the assumption that all species react in parallel throughout the cook. Assuming that a great part of species 1 (L1, CH1) is easily degraded during impregnation it is suggested to consider only species 2 and 3 (L2, L3, CH2, CH3) for both delignification and carbohydrate degradation models. In the case of non-isothermal industrial cooks, the initial chemical wood composition (L₀, CH₀) has to be used as starting values to account for the overall consumption of active cooking chemicals ([OH⁻], [HS⁻]).

A general rate equation for both lignin and carbohydrate degradation can be expressed according to Eq. 2:

$$\frac{dW_{i,j}}{dt} = -k_{W_{i,j}} \cdot W_{i,j} \quad [2]$$

for W_i = L for lignin and CH for the sum of carbohydrates comprising cellulose (C), glucuronoxylan (X) and glucomannan (GM), for j = species 2 and 3 for both L and CH and for k = rate constants.

The general solution for these first-order rate equations is given in Eq. 3:

$$W_{i,tot} = \sum_{j=2}^3 W_{i,j}^0 \cdot \text{Exp}(-k_{W_{i,j}} \cdot t) \quad [3]$$

W_{ij} represents the species j of wood component i; W_i⁰ = L and CH concentrations after impregnation for the evaluation of the kinetic models and initial wood composition for modelling of industrial cooks. The dependency of the rate expressions, k_{W_{ij}}, on the reaction conditions can be described according to Eq. 4:

$$k_{W_{i,j}} = A_{W_{i,j}} \cdot \text{Exp}\left[\frac{E_{A_{W_{i,j}}}}{R} \cdot \left(\frac{1}{443} - \frac{1}{T}\right)\right] \cdot c_i \quad [4]$$

$$c_i = \left([OH^-]^a [HS^-]^b [Na^+]^c + k_r\right)$$

for A = pre-exponential factor, E_A = activation energy [kJ/mol], R = gas constant [kJ/(mol.K)], a, b, c, are constants and k_r, a rate constant reflecting the observation of carbohydrate degradation even at very low alkali concentrations.

The experimental results have been fitted by nonlinear regression using Scientist® as data fitting software. Scientist employs a least squares minimization procedure based on a modification of Powell's algorithm. The fitting yields the results shown in Table 1:

Table 1. Kinetic constants for delignification and carbohydrate degradation of *Eucalyptus globulus*

Component	L ₀	CH ₀	A	E _A	a	b	c	factor	k _r
	% odw	kappa#	% odw	(l/(M*min))	kJ/mol				l/(min)
Lignin including HexA									
L1*	3,2								
L2	17,1	93,5		0,4527	131,4	0,63	0,32	-0,63	1,3 0,00
L3	1,8	9,8		0,0402	133,0	1,47	0,00	-0,68	0,5 0,00
Lignin excluding HexA									
L1*	3,3								
L2	17,6	96,2		0,4565	132,4	0,63	0,35	-0,60	0,00
L3	1,2	6,8		0,0464	133,9	1,52	0,00	-1,01	0,00
CH1*			5,6						
CH2			15,3	0,2415	140,9	1,54	0,00	0,00	1,0 0,11
CH3			50,3	0,0031	174,6	2,35	0,00	0,00	2,0 0,00

* calculated from mass balance

The coefficients of the kinetic rate equation are only slightly affected when the lignin content of the *Eucalyptus globulus* kraft pulp is corrected for its HexA content assuming that 11.6 mmol/kg contributes to one kappa number unit (Li *et al.*, 1997).

Table 1 shows that the activation energies are in the range reported for kraft pulping, except in the case of carbohydrate degradation of species 3, whose activation energy is significantly higher as published for the same reaction in spruce (174.6 kJ/mol compared to 144 kJ/mol reported by Andersson et al. (Andersson *et al.*, 2003a)). Moreover, the kinetic

order of the hydroxide ion concentrations, particularly for L3 and CH3, are far higher as reported in the literature (Sixta, 2006). The results from the kinetic study confirm that an increase in the ionic strength decreases the rate of delignification considerably as shown for birch by Lindgren and Lindström (Lindgren *et al.*, 1997) and in Figure 1.

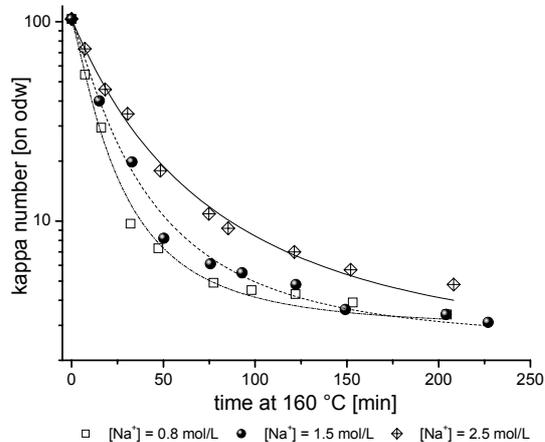


Figure 1. Course of kappa number during kraft pulping of *E. globulus* at 160 °C. $[OH^-] = 0.52$ mol/L, $[HS^-] = 0.28$ mol/L, and increasing $[Na^+]$. Lines represent the calculated values.

The influence of salt content on the rate of delignification may be estimated on the basis of the Donnan theory (Donnan, 1912, Donnan *et al.*, 1911). Recently, it was shown that leaching of dissolved lignin is promoted by decreasing the salt content following the Donnan equilibrium theory (Andersson *et al.*, 2003b, Rasanen, 2003). Since dissolved lignin moieties reveal anionic properties under alkaline conditions, they should be expelled from the fiber wall at low ionic strength (fiber modelled with a pK_a -value of 3.4 according to (Lindgren, 2000)). Consequently, the degraded lignin gradually accumulates within the fiber wall liquor volume with increasing ionic strength of the free accessible suspension liquor. It may then be speculated that the delignification rate slows down when the concentration of the dissolved lignin increases in the entrapped liquor due to a decreasing Donnan distribution coefficient, λ , between the two water phases (fiber volume and suspension liquid). Carbohydrate degradation, however, shows no dependency on ionic strength of the cooking liquor, but is much more affected by hydroxyl ion concentration as compared to delignification (Figure 2). As illustrated in table 1, the dependency of carbohydrate degradation is particularly high at very low lignin level.

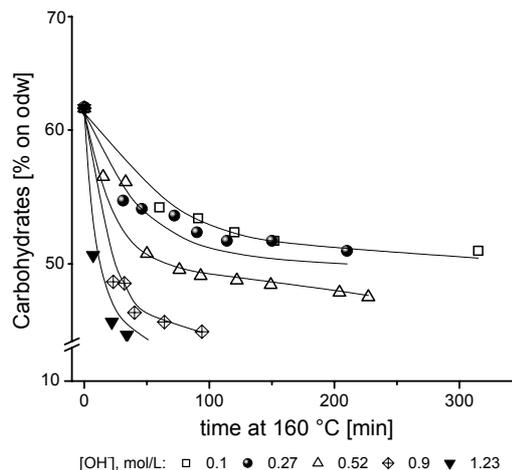


Figure 2. Amount of carbohydrates (C+X) as a function of time at five different levels of $[OH^-]$ during kraft pulping of *E. globulus*. Constant conditions: temperature = 160 °C, $[HS^-] = 0.28$ mol/L, $[Na^+] = 1.5$ mol/L. Lines represent the calculated values.

To allow for changes in the main reaction conditions such as $[OH^-]$, $[HS^-]$, $[Na^+]$ and temperature, the distribution model proposed by Andersson *et al.* has been implemented in our cooking model. This model shows that the species W_2 and W_3 interchange reversibly and that the equilibrium between both species is dependent on certain reaction conditions. The intersection is the level of wood component where W_2 equals W_3 and is termed W^* . Multiple regression analysis provides an expression for W^* as a function of the reaction conditions. The expressions for L^* and CH^* are given in Eq. 5 and 6, respectively, in which the temperature T is expressed in °C:

$$L^* = 0.001487 \cdot ([OH^-] + 0.025)^{-0.625} \cdot ([HS^-] + 0.045)^{-0.308} \cdot ([Na^+] + 5.0)^{4.106} \quad [5]$$

$$CH^* = 55.44 + 68.45 \cdot [OH^-] - 0.48 \cdot T \cdot [OH^-] \quad [6]$$

Surprisingly, no clear influence of L^* on temperature has been observed, while CH^* was clearly influenced by temperature and $[OH^-]$ but not by $[HS^-]$ and $[Na^+]$. The way of determining the proportions of W_2 and W_3 follows the procedure given by Andersson *et al.* (Andersson *et al.*, 2003a, Sixta, 2006)

Kinetics of cellulose chain scissions

The kinetics of carbohydrate degradation, observed as viscosity loss or cellulose chain scissions, can be followed by a very simple approach with reasonable precision. Equation 7 describes the cellulose chain

scissions as a function of temperature, effective alkali and sodium ion concentrations and time (Sixta, 2006):

$$\left(\frac{1}{DP_{n,t}} - \frac{1}{DP_{n,0}} \right) = A \cdot \text{Exp} \left(- \frac{E_{Ac}}{R} \frac{1}{T} \right) \cdot [\text{OH}^-]^d \cdot [\text{Na}^+]^e \cdot t \quad [7]$$

Using this simple expression, it is permissible to use DP_v , calculated from intrinsic viscosity according to SCAN-CM-15:88, instead of DP_n . Nonlinear regression using least square minimization procedure yields the coefficients for the applied kinetic model shown in Table 2:

Table 2: Kinetic constants for chain scissions during kraft pulping of *E. globulus*.

Model parameter	Units	Value
$DP_{n,0}$		4900
$\ln A$	min^{-1}	36,5
E_A	$\text{kJ} \cdot \text{mol}^{-1}$	180,3
d		1,1
e		0,7

Unlike carbohydrate degradation, an increase in ionic strength at a given $[\text{OH}^-]$ is connected with an increase in cellulose degradation as illustrated in Figure 3.

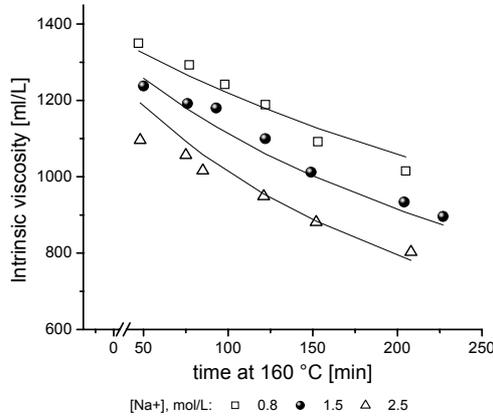


Figure 3. SCAN-Viscosity as a function of time at three different levels of $[\text{Na}^+]$ during kraft pulping of *E. globulus*. Constant conditions: temperature = 160 °C, $[\text{OH}^-] = 0.52 \text{ mol/L}$, $[\text{HS}^-] = 0.28 \text{ mol/L}$. Lines represent the calculated values.

These results clearly reflect the detrimental impact of ionic strength on delignification selectivity as illustrated in Figure 4 in a viscosity-kappa number plot.

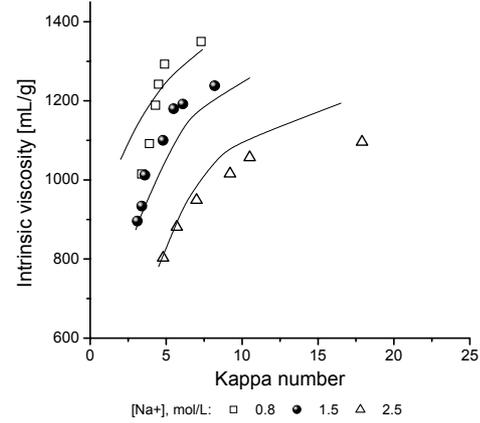


Figure 4. Selectivity plot of *E. globulus* kraft pulping at three different levels of $[\text{Na}^+]$. Constant conditions: temperature = 160 °C, $[\text{OH}^-] = 0.52 \text{ mol/L}$, $[\text{HS}^-] = 0.28 \text{ mol/L}$. Comparison of predicted (lines) and experimentally determined values (symbols).

The reason for the reinforced cellulose degradation may be attributed to a positive salt effect on the heterogeneous alkaline hydrolysis of cellulose. In the case of heterogeneous acid hydrolysis of cellulose it has been shown that the addition of sodium chloride resulted in an increase in the hydrogen ion concentration in the cellulose phase, and hence an increased rate of hydrolysis (Zaranyika *et al.*, 1989). According to Donnan's theory of membrane equilibrium, the difference in the hydrogen ion concentration in the two phases can be minimized by the addition of an inert electrolyte. Similarly, it can be expected that the hydroxyl ion concentration in the fiber phase is increased by raising the ionic strength in the suspension liquor. However, it has to be qualified that the positive salt effect resulted in an increased cellulose degradation rate while no additional yield loss of the polysaccharide fraction was observed. Obviously, more research in this field is needed to better explain the observed results.

Effective concentration of cooking chemicals

Chip dimensions and the level of cooking chemical concentrations in the bulk liquor influence the concentration profiles of the cooking chemicals within the wood. The $[\text{OH}^-]$, $[\text{HS}^-]$ and $[\text{Na}^+]$ across the chip thickness (one-dimensional chip model) were calculated by using the diffusivity parameters of McKibbins solving Fick's second law of diffusion corrected with respect to pH and lignin content according to equation 8 (McKibbins, 1960, Gustafson *et al.*, 1983):

$$D = 0.057 \cdot \sqrt{T} \cdot \text{Exp} \left(- \frac{2452.4}{T} \right) \cdot \left(0.00364 \cdot \kappa\# + 0.13 \cdot [\text{OH}^-]^{0.55} + 0.58 \right) \quad [8]$$

Where D is the diffusion coefficient in $\text{cm}^2 \text{min}^{-1}$ and T the temperature in K.

The reactive cooking chemicals, $[\text{OH}^-]$ and $[\text{HS}^-]$, are transported from the bulk phase to the boundary layer and finally through the water layer of the cell wall and pit membrane structure under the influence of their concentration gradient in the entrapped and free liquor. The model considers only the diffusion of alkali in a one-dimensional wood chip through the chip thickness (radial direction). The diffusion of $[\text{OH}^-]$ is described by Fick's second law of diffusion. The concentration of the active cooking chemicals in the entrapped liquor (bound liquor) must be determined to provide the necessary data for a reliable kinetic study which may be used to predict the course of pulping reactions in pilot or even commercial digesters.

At the beginning of the cook (but after complete impregnation), at $t = t_0$, the average $[\text{OH}^-]$ in the entrapped liquor depends on the wood density (ρ_{dc}) and the moisture content (MC_w) of the wood according to Eq. 9:

$$[\text{OH}^-]_{\text{EL}} = \left(1 - \frac{\text{MC}_w}{(100 - \text{MC}_w) \cdot \left(\frac{1}{\rho_{\text{DC}}} - \frac{1}{1.53} \right)} \right) \cdot [\text{OH}^-]_{\text{FL}} \quad [9]$$

where FL is the free or bulk liquor, EL the entrapped or bound liquor.

During pilot plant or industrial cooking, where L/S ratios range between 2.5 and 5, the concentration of cooking chemicals decreases as a result of the consumption of chemicals by the reaction products. Thus consumption of active cooking chemicals must be considered to predict the extent of delignification and carbohydrate degradation accurately. The specific consumptions of $[\text{OH}^-]$ were determined as 0.20 NaOH/kg degraded lignin and 0.45 kg NaOH/kg degraded carbohydrates, respectively, which are only slightly higher as reported by Christensen et al. for similar reactions of softwood components (Christensen et al., 1983).

The concentration profiles for the effective alkali in both free (FL) and entrapped (EL) liquors (average concentration) during a conventional batch kraft cook using *E. urograndis* as a raw material have been calculated by the model. Additionally, the minimum effective alkali concentration in the centre of the 4 mm-chip (CC) is shown in Figure 5.

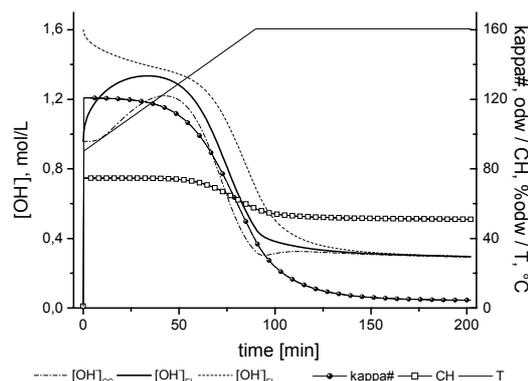


Figure 5. Course of effective alkali concentrations in the free (FL) and entrapped cooking liquor (EL) during a conventional *E. globulus* kraft cook. The conditions were taken from pilot plant cooking (KA440): chip thickness 4.0 mm, chip moisture content, $\text{MC}_w = 35\%$, chip density, $\rho_{\text{DC}} = 0.50$; $[\text{OH}^-]_{t=0} = 1.60 \text{ mol/L}$, $[\text{HS}^-]_{t=0} = 0.245 \text{ mol/L}$, $\text{L/S} = 3.15 \text{ kg/kg}$. [10]

The effective alkali concentration in the bound liquor reveals an increase during the first third of the heating-up phase, approaching the maximum value after 33 min at 115 °C, indicating that diffusion is the dominating process. The effective alkali, however, is rapidly consumed by the chemical reactions which start predominantly in the second third of the heating-up period. The hydroxyl ion concentration inside the chips approaches that outside the chips only after 30 min reaction time at cooking temperature. The calculated residual hydroxyl ion concentration (after $t = 90 + 112 = 202 \text{ min}$) of 0.300 mol/L agrees perfectly with the experimentally determined residual hydroxyl ion concentration of 0.296 mol/L.

Validation of the Model

One of the key advantages of the distribution model from Andersson is that it accounts for changes in the reaction conditions appropriately.

Therefore, in a first set of experiments the influence of a sudden increase of $[\text{OH}^-]$ from 0.1 mol/L to 1.0 mol/L after a reaction time of 45 min at 160 °C and a L/S ratio of 40:1 on the course of the degradation of wood components was simulated.

Figure 6 displays the comparison between predicted and experimentally determined kappa numbers. Even though only a few experiments were carried out so far, the agreement between calculated and measured kappa numbers is satisfactory. The (calculated) course of $[\text{OH}^-]$ in both the bound liquor and the chip centre is quite comparable due to the high L/S ratio.

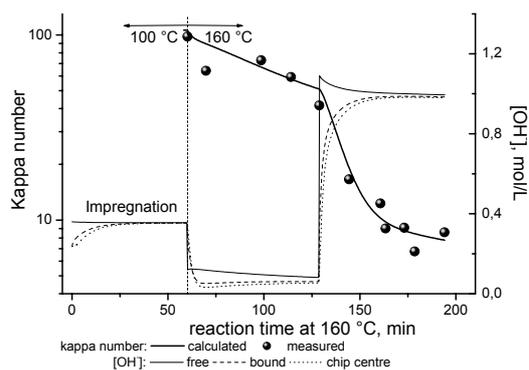


Figure 6. Comparison of predicted and experimentally determined kappa numbers in the course of kraft pulping of *E. globulus* during a step change of $[\text{OH}^-]$ from 0.1 mol/L to 1.0 mol/L after 60 min at 160 °C. Impregnation at 100 °C, $[\text{OH}^-] = 0.36$ mol/L, $[\text{HS}^-] = 0.16$ mol/L, $[\text{Na}^+] = 0.52$ mol/L. Constant cooking conditions: chip thickness 1.9 mm, chip moisture content, $\text{MC}_W = 31.6\%$, chip density, $\rho_{DC} = 0.50$; L/S = 40:1, $[\text{HS}^-] = 0.30$ mol/L, $[\text{Na}^+] = 1.5$ mol/L, $T = 160$ °C.

The aim of the second set of experiments was the prediction of the unbleached pulp quality derived from *E. globulus* kraft pulping using a conventional batch process. Please note, that similar to Andersson et al., the pre-exponential factors A were modified by a “factor” reflecting the differences between constant composition cooks and pilot plant cooking (see table 1). Figure 7 illustrates an acceptable agreement between simulated and experimentally determined kappa numbers and viscosity values.

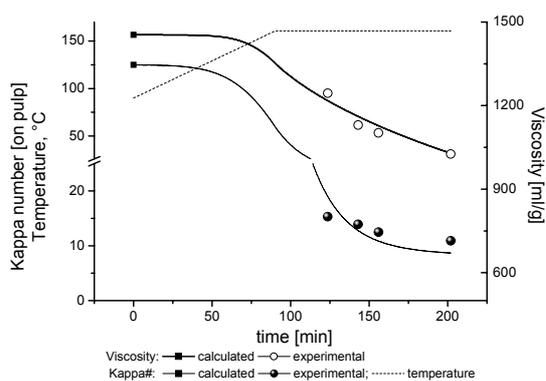


Figure 7. Measured and predicted kappa numbers and viscosities as a function of H-factors of conventional batch kraft cooking of *E. globulus*. The conditions were taken from pilot plant cooking (KA440): chip thickness 4.0 mm, chip moisture content, $\text{MC}_W = 35\%$, chip density, $\rho_{DC} = 0.50$; $[\text{OH}^-]_{t=0} = 1.60$ mol/L, $[\text{HS}^-]_{t=0} = 0.245$ mol/L, L/S = 3.15 kg/kg.

Even though the modelling of viscosity is based on a very simple approach, the viscosity is predicted more precisely as compared to the kappa number. The latter

reduces only by 3.5 units when increasing the H-factor from 300 to 800. The low change in kappa number during a significant prolongation of cooking time may be attributed to a progressive precipitation of dissolved lignin parallel to a decrease in the effective alkali concentration.

CONCLUSIONS

The proposed kinetic model adequately describes the performance of lignin and carbohydrate degradation and cellulose chain scissions during kraft pulping of *E. globulus*. For the first time also the influence of $[\text{Na}^+]$ was considered in a comprehensive kinetic pulping model. The good correspondence between predicted and experimentally determined unbleached pulp parameters confirms the suitability of the distribution model introduced by Andersson et al. for offline optimization studies of industrial kraft cooks. More effort has to be undertaken to elucidate the effect of ionic strength on delignification and carbohydrate degradation kinetics.

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