Effect of unbleached pulp Kappa number on the kinetics of chlorine dioxide delignification

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Chlorine dioxide delignification of different unbleached kraft pulps from *Eucalyptus globulus*, having Kappa numbers of 12 to 18, was studied in the temperature range of 285 K to 358 K. The effect of the unbleached pulp Kappa number on the initial fast phase of delignification was investigated with respect to the depletion factors for Kappa number and chlorine dioxide concentration, as proposed by Barroca et al. (*2*). Furthermore, the behaviour of the floor lignin content of the pulp, or the floor Kappa number, was analysed within this range. The results show that all pulps exhibit a similar pattern, with respect to temperature, in depletion factors for Kappa number and chlorine dioxide concentration. The degree of normalised delignification and chlorine dioxide consumption is very similar and independent of the Kappa number of the unbleached pulps. Moreover, the results reveal that there is a strong correlation between the floor lignin content and the temperature, and that this correlation is applicable to a wide range of unbleached pulp Kappa numbers, since the residual Kappa number is independent of its initial value. The results enable the general application of a kinetic model to kraft pulps with different unbleached Kappa numbers.

Keywords
Bleaching, *Eucalyptus globulus*, kraft pulp, kinetics, chlorine dioxide, mathematical model, unbleached pulp Kappa number, floor Kappa number

Nowadays the trend in bleached pulp manufacturing is towards bleaching technologies that are free of elemental chlorine (ECF). Although environmental concerns are beginning to introduce new chemical bleaching alternatives in the first bleaching stage, chlorine dioxide is still the most widely used reactant in the prebleaching stage. Its characteristics, and in particular its high selectivity, ensure a good level of delignification of the pulp while preserving pulp physical and chemical properties. Until recently chlorine dioxide was mainly used in combination with chlorine in the first bleaching stage and this explains why several kinetic models have been proposed in the literature to describe chlorine delignification with or without chlorine dioxide substitution. The main conceptual differences among the proposed models are associated with the use of lignin having different reactivities, and with the consideration of a floor lignin concentration. The kinetic expression proposed by Germgard (*3*), Germgard and Lindberg (*4*), Germgard and Karlsson (*5*) and Teder and Tormund (*8*) are based on the concept of a single structural unit for the lignin macromolecule having a constant reactivity along the fibre wall. In contrast to this general approach, Ackert et al. (*1*) and Tessier and Savoie (*7*) developed a model for prebleaching where lignin is considered to consist of two main components with different reactivities: a fast and a slow reacting lignin. This implies that two simultaneous reactions are taking place in parallel between lignin and chlorine dioxide and thus the global rate of delignification is the sum of the two partial rates. In these studies the authors arbitrarily assumed all partial orders of reaction with respect to each reactant to be one, in order to simplify the estimation of both the activation energies and the frequency factors for the fast and slow lignin reactions. In addition to this, the initial distribution of lignin composition, between the fast and slow lignin content, must also be defined to best fit their experimental data.

The application of both types of kinetic models requires knowledge of the reaction stoichiometry and of the floor level of lignin, which has been considered as a constant parameter, independent of the operating conditions. The stoichiometry, which represents the consumption of chlorine dioxide per unit Kappa number drop, has also been traditionally assumed as a constant. However, Germgard (*3*) has shown that this is a non-linear function of the Kappa number drop, although such observation was based on measuring the Kappa number of the pulp after a standard alkaline extraction stage (E_1). Unfortunately, in most of the previous investigations the kinetics of delignification was studied by using both chlorine and chlorine dioxide and the majority is only concerned with softwood kraft pulp.

In a recent paper Barroca et al. (*2*) proposed a kinetic model for chlorine dioxide delignification of hardwood kraft pulps, more specifically of an unbleached pulp from *E. globulus*. Their model is based on the measurement of the Kappa number immediately after D_0 and all kinetic parameters are estimated using a special technique in order to improve the quality of the optimal estimates. A set of two new parameters, K_θ and $[ClO_2]_\theta$, identified as depletion factors, were proposed to characterise the initial fast phase of delignification, and a new non-linear relationship between chlorine dioxide consumption and the decrease of Kappa number was introduced in their study. Moreover, the floor Kappa number was identified as a strong linear function of temperature. Although the model revealed excellent prediction capabilities for both Kappa number and chlorine dioxide concentration for a D_0 stage, it was only applied to a single unbleached pulp with a fixed initial Kappa number. Since in an industrial situation one can observe important variations in the initial unbleached pulp Kappa number, the present study extends the above model to pulps with Kappa numbers ranging from 12 to 18.

MATERIALS AND METHODS

The unbleached pulps used in this work were produced in different laboratory kraft cooks of *E. globulus* chips from the same lot of wood and their resulting Kappa numbers, after disintegration and full washing, varied between 12 and 18. The production of pulps with low Kappa numbers was carried out by prolonging the cooking time with the same white liquor charge. All bleaching experiments were carried out in a temperature con-

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trolled 3-litre glass reactor at low pulp stock concentration (0.7%) and chlorine dioxide charge (3% on o.d. pulp). The stirring rate of 600 rpm, as established in previous experiments (2), ensured that there are no interphase mass transfer limitations. The pulp suspension was continuously stirred and just before the addition of chlorine dioxide, sulfuric acid was fed into the vessel, in order to fix the desired value of pH at the beginning of the reaction (pH 4). This was kept constant throughout the experiment by continuously adding a solution of sodium hydroxide. Temperature was controlled by means of a recirculating thermal fluid. At the end of each experiment a liquid sample was taken with a syringe fitted with a special glass filter and immediately cooled prior to chemical analysis. Meanwhile, the pulp suspension was quickly withdrawn from the reactor and the fibres immediately washed with cold water to stop the bleaching reaction. The pulp was then further washed with an excess of warm water prior to Kappa number determination. Each run was comprised of a set of interrupted reaction experiments enabling the measurement of chlorine dioxide concentration and Kappa number as a function of reaction time (15 and 30 seconds, 1, 2, 3.5, 5, 7.5, 10, 15, 22.5 and 30 minutes). To investigate the relationship between the floor Kappa number and the initial Kappa number of the pulp, and the temperature of reaction, a set of several non-interrupted experiments was conducted under the same conditions for four hours.

Chlorine dioxide was produced by reacting a concentrated solution of sodium chlorite with sulfuric acid, and no chlorine was detected in the resultant solution.

RESULTS AND DISCUSSION

Modelling strategy

Recently Barroca et al. (2) proposed a simple methodology by which two sequential reaction stages were considered to take place during the delignification with chlorine dioxide. Their strategy led to a robust model, with excellent prediction capabilities for an unbleached pulp with an initial Kappa number of 12.7. The first period of the process was assumed to last for a short period of $\theta \cong 15$ seconds, where the Kappa number drop and the corresponding consumption of chlorine dioxide are both exclusive functions of temperature, thus resembling a zero order reaction. In the second period a typical chemical reaction is considered to be the dominant step. This slow regime was best described by a model, whose state variables are Kappa number after D_0 and the concentration of chlorine dioxide in the liquid. In addition to this, the integrated form for stoichiometry was described by a polynomial relationship and the floor lignin by a single linear function of temperature.

To extend the above kinetic model to hardwood pulps with different initial Kappa numbers, a set of experiments was carried out at several temperatures and chlorine dioxide charges with different unbleached pulps.

The profiles of the initial drop in Kappa number and in chlorine dioxide consumption with temperature are shown in Figures 1 and 2, respectively. As would be expected from previous results, the four pulps exhibit a similar behaviour with respect to this operating variable, and the general pattern can be described by an equation of the type proposed previously by Barroca et al. (2).

For a given temperature, the initial delignification and chlorine dioxide consumption rates increased with the initial Kappa number due to the higher lignin content in the pulp. However, as highlighted in Figure 3, the behaviour of the four pulps is very similar and independent of the initial values of their Kappa number when the initial drop in Kappa number is normalised with respect to the unbleached pulp Kappa number. Thus, one can conclude that an unbleached pulp always shows the same degree of normalised delignification, regardless of its initial Kappa number. A similar procedure was adopted for the initial consumption of chlorine dioxide, but in this case the depletion factor was normalised with respect to both unbleached pulp Kappa number and the initial concentration of chlorine dioxide. This pattern is illustrated in Figure 4 where, again, one can see a common behaviour for all pulps.

In accordance with the approach proposed by Barroca et al. (2) these two normalised depletion factors were correlated with temperature by means of the following equation:

$$y = \beta_1 + \beta_2 e^{-\beta_3 T} \quad [1]$$

Where:

y = normalised initial depletion factors as shown in Table 1.
T = reaction temperature (K).
$\beta_1, \beta_2, \beta_3$ = parameters.

The best parameter values for both normalised chlorine dioxide consumption and Kappa number drop in the fast regime are shown in Table 1.

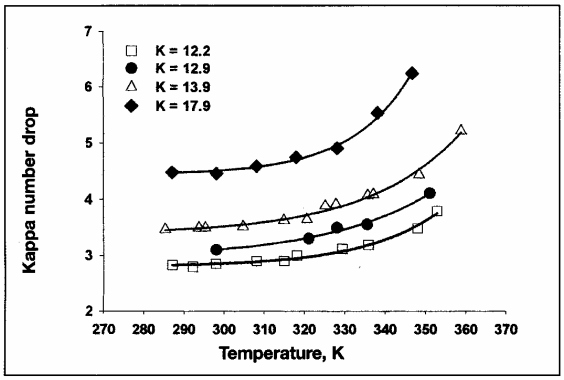

Fig. 1 Initial Kappa number drop for different unbleached pulps at different temperatures.

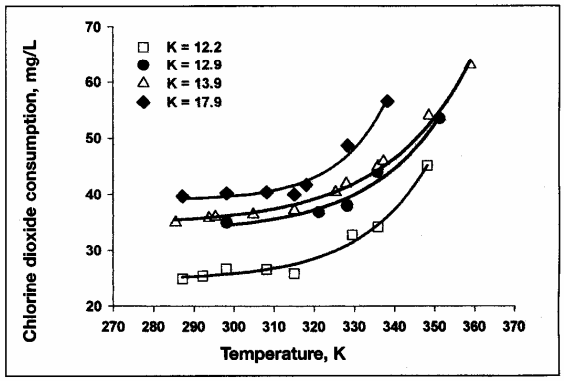

Fig. 2 Initial chlorine dioxide consumption for different unbleached kraft pulps at different temperatures.

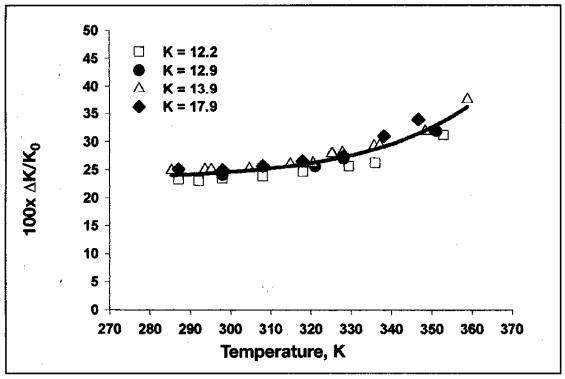

Fig. 3 **Normalised Kappa number drop at different temperatures.**

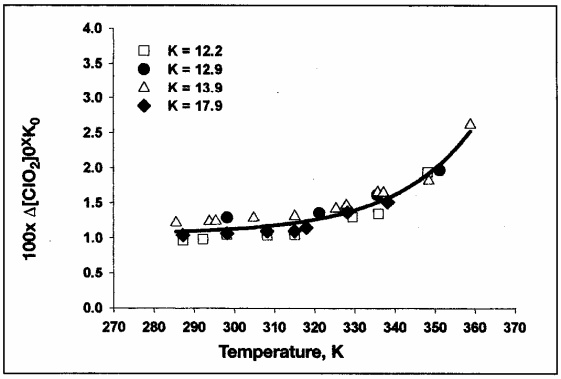

Fig. 4 **Normalised chlorine dioxide concentration at different tempreatures.**

Table 1
Optimal estimates for the normalised initial depletion factors for chlorine dioxide and Kappa number.

Parameter	$100 \times \frac{[ClO_2]_0 - [ClO_2]_\theta}{[ClO_2]_0 \times K_0}$	$100 \times \frac{K_0 - K_\theta}{K_0}$
β_1	1.061	23.324
$\beta_2 \times 10^{-6}$	0.0122	8.176
β_3	0.052	0.040

In order to model the second stage of the delignification process it is essential to know the stoichiometry and the floor Kappa number. In a recent work by Barroca et al. (2) it was shown that the differential stoichiometry of the reaction is not a constant, as advocated in most studies concerning D_0 bleaching, and that it is not influenced by temperature in the range 278 to 343 K. Furthermore, in its integrated form, it was best described by a polynomial relationship of the Kappa number drop, confirming the observation that the longer the delignification time the higher the specific consumption of chlorine dioxide.

In the same study the authors identified a clear relationship between the floor lignin content of the pulp and the temperature. To evaluate the effect of initial Kappa number of the unbleached pulp on the residual lignin content, a set of experiments was performed for four hours at different temperatures with pulps having different initial Kappa numbers. The results are illustrated in Figure 5, and show that at each temperature the final lignin content in the pulp is similar for all pulps, thus confirming that the total lignin removal increases with the initial Kappa number. This figure also confirms that the floor lignin content is independent of the unbleached pulp Kappa number and it is only a function of temperature. As a result of this, the correlation between the floor Kappa number and temperature (K),

$$K_\infty = 33.880 - 0.0932xT \quad [2]$$

proposed previously by Barroca et al. (2), can be used over a range of Kappa numbers that cover most situations for kraft mills processing hardwood species.

CONCLUSIONS

The effect of unbleached pulp Kappa number on the initial fast phase of chlorine dioxide delignification was investigated. The results revealed that all pulps exhibited a similar pattern, with respect to temperature, and that the normalised depletion factors were independent of the unbleached pulp Kappa number. Furthermore, the results confirmed that at each temperature the residual lignin content in the pulp was similar for all pulps and, thus, the floor Kappa number is independent of the initial Kappa number. These results provide the foundations for the general application of the kinetic model proposed by Barroca et al. (2) for the chlorine dioxide delignification of hardwood kraft pulps covering a range of initial Kappa numbers.

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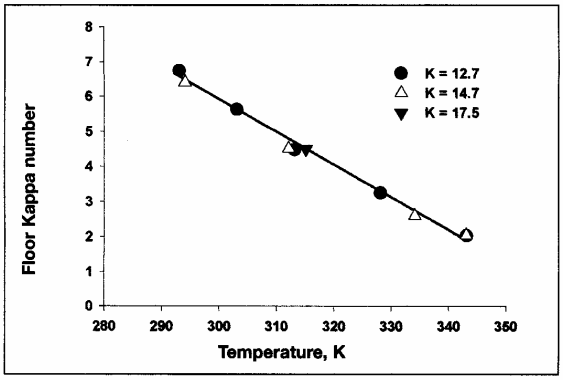

Fig. 5 **Variation of floor lignin, K_∞ with reaction temperature for different unbleached pulp Kappa numbers.**

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The effectiveness of the Hydrocol system was highly dependent on the dosage of the cationic PAM. This alone explains over 60% of the first pass retention changes in the trials. The bentonite dosage did not affect the retention level significantly. The dosing delay was not optimised, but the results show that Hydrocol needs a longer adsorption time.

The dual polymer was quite different in its mechanism. The flocs made by the C-PAM were connected by very long chain A-PAMs. The C-PAM used here was a longer chain than the usual C-PAMs and it needed more adsorption time. The dosage of the cationic polymer was as important as the dosing delay. Since the anionic polymer was such a long chain and so anionic, it was deemed that the dosage of 4.0 kg/t was too much.

The dual polymer system filler retention was strongly affected by the cationic polymer dosage. The reflocculation ability of the dual polymer system was not as good as with the microparticle system, so the filler retention decreased at higher speeds. The A-PAM had a negative influence on the filler retention at the 4.0 kg/t dosage.

The HSR-Tester can be used as a powerful tool for the optimisation of retention systems. The results with multivariable trials using a fractional factorial design showed the most important factors affecting retention. In more specific optimisation trials such experiment designs are not as useful, and other multivariable schemes should be used. This means increasing the number of test points, where the HSR-Tester gives good mean values.

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