The Role of Oxalic Acid in the Ozone Bleaching Kinetics of an Xo-Kraft Pulp

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THE ROLE OF OXALIC ACID IN THE OZONE BLEACHING KINETICS OF AN XO-KRAFT PULP

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ABSTRACT

The effect of oxalic acid on the reaction kinetics of ozone with a Eucalyptus globulus kraft pulp was studied. Xylanase treatment (X) and oxygen delignification (O) were carried out on the pulp before the kinetic study. Ozone treatment was carried out in a special batch reactor at low consistency (0.5% o.d.p.). The main variables were ozone consumption and oxalic acid doses, and the measured responses were kappa number, viscosity and brightness. The positive effect of oxalic acid was shown. First order kinetics for both cellulose degradation and lignin removal were observed. For chromophore degradation, the kinetics were also first order. The addition of oxalic acid increased the rate of delignification and decreased that of cellulose degradation during ozone bleaching.

INTRODUCTION

Ozone is one of the most recent bleaching agents to be introduced industrially. It is a powerful oxidising agent that breaks down residual lignin in

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pulp, but it also tends to react with carbohydrates, causing a reduction in pulp viscosity and fibre strength.[1-3] Proposed ways of decreasing the degradation in the ozone stage include the use of additives. In recent studies it has been found that oxalic acid is one of the best additives in the ozone stage, since it improves selectivity.[4] No information was found on the effect of oxalic acid in ozone kinetics. Therefore, in this paper we study the role of <u>oxalic acid</u> in ozone bleaching kinetics at low consistency to obtain the kinetic expressions which govern this bleaching stage. Selectivity values were obtained from these kinetic expressions.

The incorporation of ozonation into bleaching processes allows the minimisation of halogenated organics (and even their elimination in some cases). However, it is necessary to increase the selectivity of ozone bleaching. Hence, the study of the positive effect of oxalic acid could lead to a better understanding of the improvement in the ozone stage.

There is an ample literature on the bleaching kinetics of oxygen, chlorine dioxide and hydrogen peroxide. However, available data on ozone bleaching kinetics are scarce. In addition, the majority of these studies deal with model compounds of lignin and cellulose. There is some information being available on pulp at high consistency.[5, 6] Moreover, we have found no information on the effect of <u>oxalic acid</u> in ozone bleaching kinetics. Our objective was to evaluate the reaction kinetics of ozone bleaching with a pulp suspension under a simplified system, at low consistency (0.5% o.d.p.). The effects of several oxalic acid additions (0-200 ppm) on the viscosity, kappa number and brightness were also studied.

RESULTS AND DISCUSSION

The behaviour of XO <u>Eucalyptus</u> kraft pulp at several initial concentrations of oxalic acid was compared with ozone stage. Conditions of application and final results after ozone treatment are shown in Table 1.

TABLE 1

Conditions of Application and Final Results of Ozone Treatment (pH=2.5)

Exp.	Ozone consumption[Δ]	Reaction time (s)	Kappa number	Brightness (% ISO)	k/s [*]	Viscosity (cm³/g)	DP$_v$	[Oxal][□] (ppm)
1	1	20	5.6	58.7	0.1453	881	1306	
2	2	41	4.28	61	0.1247	818	1204	
3	3	68	2.8	69.5	0.0669	755	1102	0
4	5	192	1.38	75.2	0.0409	657	945	
5	8	340	1.31	75.9	0.0383	620	886	
6	1	16	5.76	59.3	0.1399	-	-	
7	2	38	3.85	64.6	0.0972	-	-	
8	3	63	2.39	70.6	0.0614	766	1119	0.5
9	5	141	1.53	75.5	0.0399	-	-	
10	8	264	1.49	78.5	0.0295	-	-	
11	1	16	5.38	59	0.1427	953	1425	
12	2	35	3.35	64.1	0.1005	885	1313	
13	3	67	2.18	72.2.1	0.0691	778	1139	2.5
14	5	135	1.52	77.4	0.033	679	980	
15	8	269	1.17	79.3	0.0272	675	973	
16	1	17	4.93	60.4	0.1301	-	-	
17	2	37	3.49	64.6	0.0973	-	-	
18	3	60	2.15	72	0.0503	780	1142	5.4
19	5	137	1.51	77.7	0.0322	-	-	
20	8	274	1.33	78.7	0.0287	-	-	
21	1	16	5.17	58.7	0.1458	974	1460	
22	2	35	3.51	63.9	0.102	895	1329	
23	3	61	2.11	72.9	0.0595	831	1225	35
24	5	141	1.5	77.1	0.0342	725	1053	
25	8	266	1.36	78.6	0.0293	689	996	
26	1	17	5.07	60.8	0.1268	979	1469	
27	2	35	3.5	65.9	0.0886	905	1346	
28	3	62	1.61	73	0.0515	857	1267	101
29	5	142	1.47	77.3	0.0335	759	1108	
30	8	273	1.45	79.1	0.0276	698	1010	
31	1	16	5.81	59.6	0.1372	989	1484	
32	2	35	3.73	64.4	0.0983	937	1398	
33	3	61	1.93	73.2	0.0491	873	1293	187
34	5	129	1.08	78.4	0.0297	756	1103	
35	8	257	1.32	79.7	0.026	699	1012	

(Δ) real ozone charge consumed by the pulp (% o.d.p.), (*) k/s is the Kubelka-Munk coefficient; (□) Initial oxalic acid concentration..

Influence on Kappa Number

The influence of oxalic acid addition on lignin removal was studied. As illustrated in Figure 1, the differences in lignin removal during ozone treatment are significant when oxalic acid is applied, for ozone consumption ranges from 0 to 3% o.d.p. This is in accordance with findings reported in the literature.[7]

The addition of oxalic acid enhances the delignification for ozone consumption of less than 5% o.d.p. For 101 ppm oxalic acid addition and 2% ozone consumption, the kappa number reduction is about 10% greater than without oxalic acid. For 3% ozone consumption, the reduction is about 17% higher. For greater ozone consumption values, no difference in kappa number was found in any of the oxalic acid additions. Stabilisation of kappa number could be explained by: 1) competing reactions with other wood components, such as carbohydrates, 2) other possible reactions with intermediate products of lignin, 3) the existence of a non-reactive lignin whose removal is more difficult in the conditions studied, 4) the presence of hexeneuronic acid groups which are not eliminated during ozone bleaching and could therefore contribute to an erroneously high lignin content,[8] and 5) the remaining fraction of lignin could be located in positions which are less accessible for ozone.

Influence on Viscosity

The influence of oxalic acid on viscosity for different ozone consumption values is shown in Figure 2. The trend of viscosity vs. ozone consumption is similar for the different oxalic doses: viscosity decreases when ozone consumption increases. However, viscosity increases in line with oxalic acid concentration increases. A positive effect on viscosity is obtained when oxalic acid is added in the ozone stage. Viscosity is about 9% higher with addition of oxalic acid at 35 ppm, and about 12% higher at 101 ppm, as compared to 0 ppm. The drop in viscosity
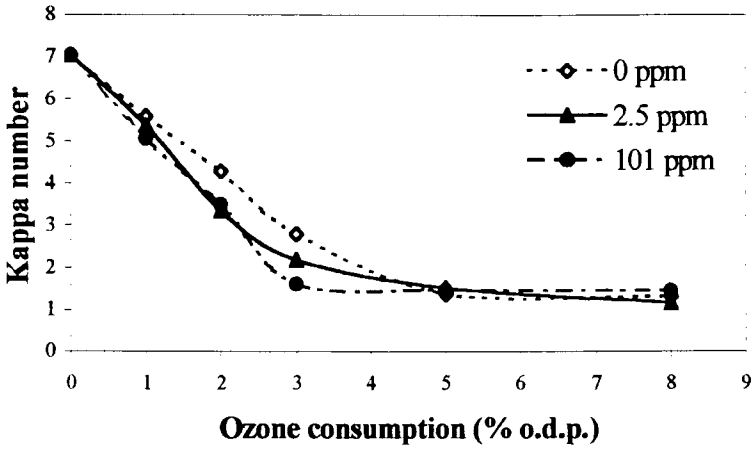
FIGURE 1.   Variation of kappa number with initial oxalic acid concentration at different rates of ozone consumption.
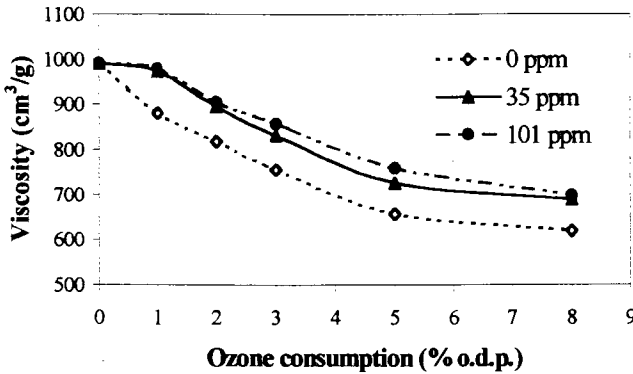
FIGURE 2.   Influence of initial oxalic acid concentration on viscosity at different rates of ozone consumption.

for 0 ppm is about 10% more than for 101 ppm. This means that the degradation value for 101 ppm is about 50% of the degradation without oxalic addition.

The effect of oxalic acid is more significant on viscosity than on kappa number removal. It is possible to obtain a pulp with good viscosity for the same lignin removal if oxalic acid is added.

A theoretical number of cellulose chain scissions can be calculated from the following expression[9]:

$$c = \frac{DP_{v0} - DP_v}{DP_v} \tag{1}$$

where DP_{v0} and DP_v are the degrees of polymerisation calculated from viscosity values (Eq. 12) before and after the ozone stage respectively.

Application of this formula to such a highly dispersed polymer as an aggregate formed by cellulose and hemicelluloses is a rough procedure, but it can be used to assess the total number of scissions which a mass of pulp undergoes.

Figure 3 shows the number of cellulose chain scissions versus ozone consumption for different oxalic acid concentrations. The increase in ozone consumption resulted in a large number of cellulose chain scissions and therefore a higher cellulose depolymerisation. However, there is a clear difference when oxalic acid is applied since fewer cellulose chain scissions take place. Oxalic acid application leads to less cellulose degradation with an adequate delignification.

Viscosity vs. Kappa Number

The relationship between viscosity change and kappa number for different initial oxalic acid concentrations is shown in Figure 4. Viscosity decreases with decreasing kappa number. Oxalic acid has a positive effect since the same kappa number is achieved with less depolymerisation of carbohydrates.

In all cases, the drop in viscosity is very sharp for kappa numbers slightly over 1. Since viscosity must be maintained above a critical value in order to ensure adequate strength properties it is not possible to remove lignin completely from fibres while maintaining an adequate degree of cellulose polymerisation. This confirms that there is a certain fraction of lignin, which is more difficult to remove,[10,11] and which could be located in less accessible positions. It is therefore
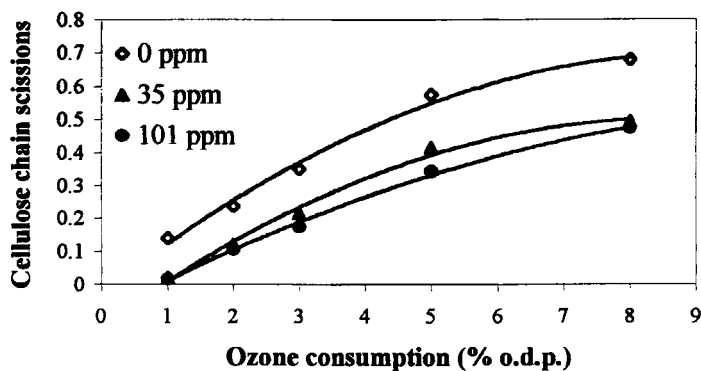
FIGURE 3.   Variation of number of cellulose chain scissions with ozone consumption for different oxalic acid concentrations.
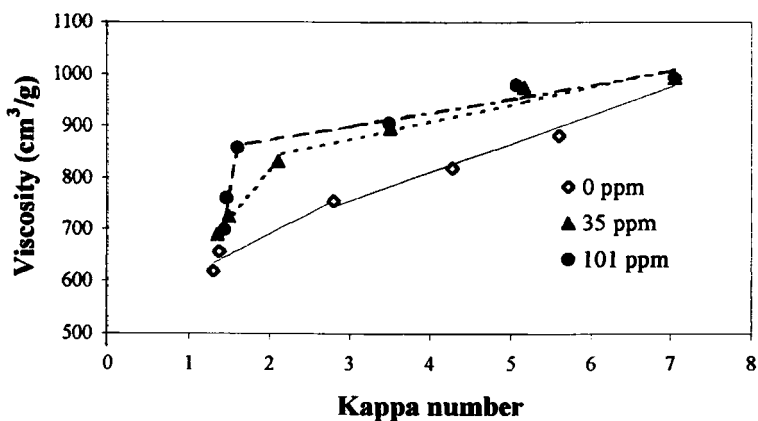
FIGURE 4.   Viscosity variation with kappa number for different oxalic acid doses added.

impossible to reduce the kappa number to zero in these conditions of ozone bleaching, while maintaining viscosity above critical levels.

Moreover, it can be observed that the viscosity change with kappa number is linear. Regression lines and 95% significance ranges are used throughout. The upper line shows two stretches with different slopes, the first for ozone

consumption of 0-3% o.d.p. and the second for higher consumption. The adjustment values are shown in Table 2. In all cases the line viscosity vs. kappa number relationship reaches a point where the slope changes dramatically, showing a significant drop in viscosity for minor decreases in the kappa number.

The adjustment values show that the first slope (0-3% ozone consumption) is smaller when oxalic acid is added. This means that the process selectivity is better. The slope decrease for oxalic acid concentrations of 0-100 ppm is about 52% (55.02 to 26.47). The decrease is less (about 15%) for higher oxalic concentrations (100-200 ppm).

Brightness vs. Kappa Number

Figure 5 shows the variation of brightness with kappa number. Brightness increases when the kappa number decreases. A decrease in kappa number indicates less presence of lignin in the pulp, which means greater brightness of the pulp. The linear variation of brightness with kappa number does not depend on the initial concentration of oxalic acid. The adjusted line with confidence bands, significance 95%, is:

$$\text{Brightness (\% ISO)} = (-4.12 \pm 0.298) \text{ kappa number} + (81.85 \pm 1.22) \qquad (2)$$
$$r = 0.975$$

Viscosity vs. Brightness

The linear change of brightness in line with viscosity could be observed at different oxalic acid concentrations (Fig. 6). The situation is similar to that resulting from the study of kappa number vs. viscosity (Fig. 4). Increases in brightness are accompanied by decreases in viscosity.

TABLE 2

Empirical Relationship for Viscosity vs. Kappa Number.

[Oxal][a] (ppm)	Ozone consumption (% o.d.p.)	Viscosity $(cm^3/g) = a \cdot$ kappa no. + b		
		a	B	r
0	0-3	55.02	590.1	0.989
	3-8	80.85	529.4	0.974
2.5	0-3	41.6	715.2	0.958
	3-8	108.21	535	0.951
35	0-3	33.58	773.3	0.961
	3-8	183.83	443.6	0.998
101	0-3	26.47	819.3	0.962
	3-8	913.62	-607.6	0.965
187	0-3	22.5	838.8	0.980
	3-8	164.58	538.6	0.821

[a] Initial oxalic acid concentration added.
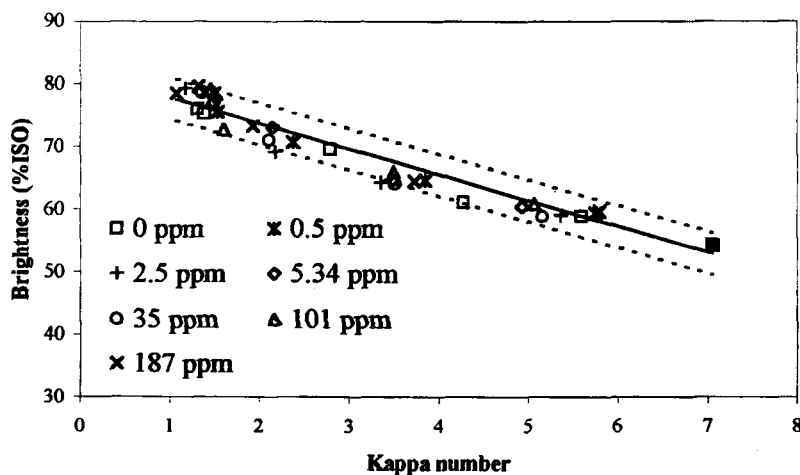

FIGURE 5.   Brightness variation with kappa number, at different initial concentrations of oxalic acid.
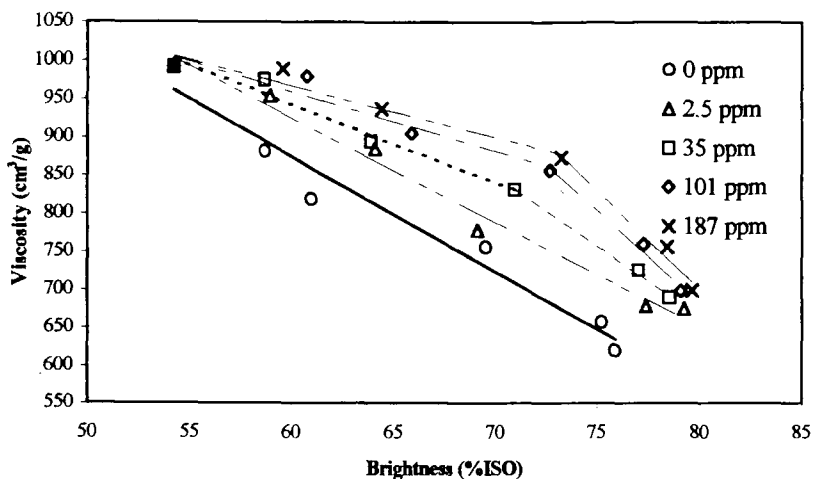
FIGURE 6.   Variation of brightness with viscosity for different initial
concentrations of oxalic acid.

The adjusted lines with confidence bands, significance 95%, are shown in
Table 3. The upper line shows two stretches with different slopes when oxalic acid
is added. The slope decreases when oxalic acid concentration increases. This
means that more brightness can be achieved with a lower depolymerisation of
carbohydrates, when oxalic acid is applied. The positive effect of oxalic acid in
ozone bleaching is evident.

Kinetics

Experiments 1 to 35 in Table 1 provide the data required to study the kinetics
of the reaction. The reactor content was stirred in order to fulfil the hypothesis of
complete mixing, and ozone was present in excess in the bleaching experiments
(see experimental device). To begin with, the indeterminate Equation 3 was
considered:[12]

TABLE 3

Empirical Relationship for Viscosity vs. Brightness.

[Oxal][*] (ppm)	Ozone consumption (% o.d.p.)	Viscosity (cm³/g) = a · brightness + b		
		a	B	r
0	0-8	-15.1	1779.9	0.981
2.5	0-8	-13.61	1741.5	0.993
35	0-3	-10.18	1553	0.986
	3-8	-18.31	2130.8	0.998
101	0-3	-7.84	1429.9	0.962
	3-8	-24.01	2604.2	0.994
187	0-3	-6.71	1369.2	0.968
	3-8	-25.63	2751.5	0.989

[*] Initial oxalic acid concentration added.

$$\frac{dL_T}{dt} = -k_L \ L_T^n \qquad (3)$$

Where L_T is the amount of lignin in the pulp at time t, and k_L is the process rate constant. By solving the differential Equation 3 for different reaction orders (n = 0.5, 1 and 2), the best fit was found to be for n = 1. Therefore, at room temperature and low consistency (0.5%), delignification during ozone treatment was described by the equation:

$$\ln L_T = -k_L \ t + \ln L_{T,o} \qquad (4)$$

where $L_{T,o}$ is the lignin content at $t=0$.

Similarly, we consider

$$\frac{dl}{dt} = -k_{DP} \ l^n \qquad (5)$$

for the cellulose degradation reaction,[13] where l is the number of glycosidic bonds in the system. The relationship between l and the number average degree of polymerisation of cellulose in pulp (DP_v) is:

$$l = N_o \left(1 - \frac{1}{DP_v}\right) \tag{6}$$

where N_o is the number of monomer units in the polymer. DP_v is calculated from Equation 11. Again, the best adjustment was for n=1. By substituting Equation 6 in the integrated form of Equation 5 we derive Equation 7:

$$\ln\left(1 - \frac{1}{DP_v}\right) - \ln\left(1 - \frac{1}{DP_{vo}}\right) = -k_{DP}\, t \tag{7}$$

where k_{DP} is the depolymerisation rate constant, DP_{vo} is the cellulose polymerisation degree at $t=0$, DP_v is the cellulose polymerisation degree at time t and t is the suspension exposure time. Application of Taylor's theorem in Eq. 7 leads to Equation 8:

$$\frac{1}{DP_v} - \frac{1}{DP_{vo}} = k_{DP}\, t \tag{8}$$

when DP_v and DP_{vo} are large enough.[13-15]

Therefore, at room temperature and low consistency (0.5% o.d.p.), cellulose degradation during ozone treatment can be described by Equation 8.

Similarly and in the same conditions, chromophore degradation in pulp calculated from the Kubelka-Munk coefficient (Eq. 13) was described by Equation 9 in which the reaction order was n=1.

$$\ln \left(\frac{k}{s} \right) = -k_{\left(\frac{k}{s} \right)} t + \ln \left(\frac{k}{s} \right)_o \qquad (9)$$

where (k/s) and $(k/s)_o$ are the Kubelka-Munk coefficients at time t and $t=0$ respectively, and $k_{(k/s)}$ is the chromophore removal rate constant.

The results of these kinetic experiments are summarised in Table 4. Rate constant values and reliance ranges, 95% significance, are shown (ozone consumption ranged from 0% to 3% o.d.p.).

The influence of initial oxalic acid concentration on delignification rate constant is shown in Figure 7. This rate constant increases when oxalic acid concentration increases, stabilising at higher oxalic doses (> 40 ppm).

The variation of the chromophore degradation rate constant with the addition of oxalic acid is shown in Figure 8. Increases in oxalic acid doses are accompanied by increases in chromophore removal up to a "ceiling" level. This level is reached at about 40 ppm oxalic acid addition. Since the variation of brightness with kappa number is linear and does not depend on the oxalic acid concentration (Fig. 5), we can consider that delignification increases with increasing oxalic acid addition up to about 40 ppm, remaining constant for higher oxalic doses.

Figure 9 shows the variation of depolymerisation rate constant with initial oxalic acid concentration. This rate constant decreases when oxalic acid increases. This means that oxalic acid has a protective effect on cellulose.

Selectivity values for different oxalic acid doses are also shown in Table 4. This selectivity is defined as k_L/k_{DP}, where k_L is the delignification rate constant and k_{DP} is the cellulose degradation rate constant. Figure 10 shows selectivity values for the different oxalic acid concentrations. An increase in oxalic acid resulted in better selectivity. It is clear then that addition of oxalic acid leads to better delignification and less depolymerisation. The resulting adjusted line with confidence bands, significance 95%, is:

$$\text{Selectivity} = (62.3 \pm 16.4) \, [\text{oxalic concentration}] + (5073.9 \pm 1577.5) \qquad (10)$$

$$r = 0.989$$

TABLE 4

Rate Constants for Delignification, Depolymerisation and Chromophore Removal,
and Selectivity Values for the Several Oxalic Acid Additions.

[Oxal]** (ppm)	k_L (s^{-1})	r_L*	k_{DPv} (s^{-1})	r*$_{DPv}$	$k_{(k/s)}$ (s^{-1})	r*$_{(k/s)}$	Selectivity K_L/k_{DP}
0	0.0136	0.997	$3.42 \cdot 10^{-6}$	0.993	0.0150	0.977	$\sim 3.97 \cdot 10^3$
0.5	0.0174	0.997	-	-	0.0180	0.999	
2.5	0.0179	0.992	$3.15\ 10^{-6}$	0.993	0.0192	0.999	$\sim 5.67 \cdot 10^3$
5.4	0.0196	0.999	-	-	0.0205	0.995	
35	0.0198	0.999	$2.51\ 10^{-6}$	0.986	0.0221	0.994	$\sim 7.88 \cdot 10^3$
101	0.0239	0.995	$2.04 \cdot 10^{-6}$	0.977	0.0216	0.999	$\sim 11.7 \cdot 10^3$
187	0.0217	0.992	$1.32\ 10^{-6}$	0.969	0.0222	0.996	$\sim 16.42 \cdot 10^3$

* denotes correlation coefficients for parameters obtained by regression
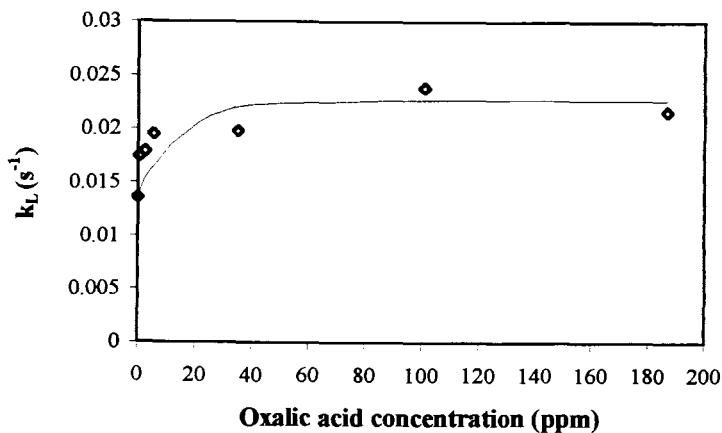analysis; ** initial oxalic acid concentrations.

FIGURE 7.   Influence of initial oxalic acid concentration on delignification rate
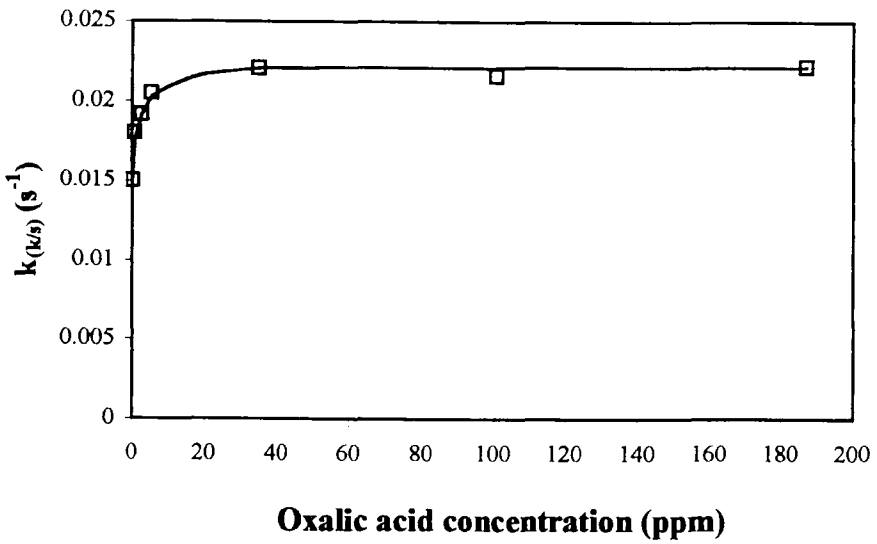constant.

FIGURE 8.   Variation of chromophore degradation rate constant with initial oxalic acid concentration.
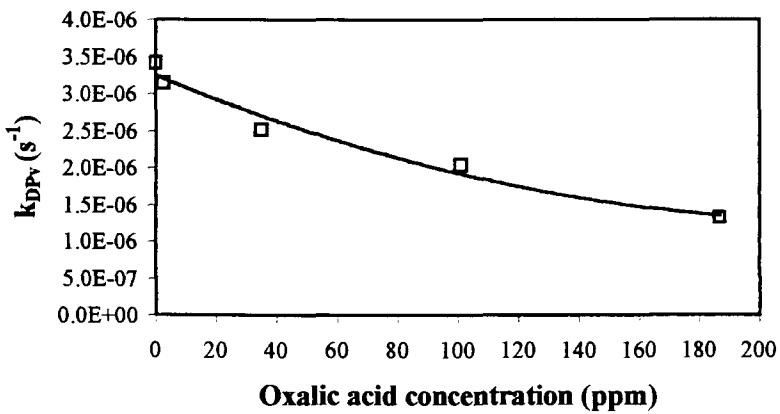

FIGURE 9.   Variation of depolymerisation rate constant with initial oxalic acid concentration.
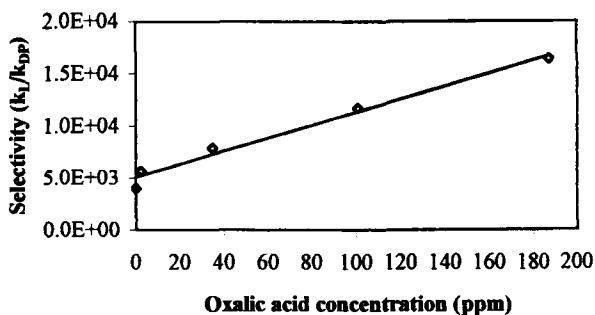
FIGURE 10.   Selectivity values for the various oxalic acid concentrations.

The positive effect of oxalic acid in ozone bleaching could be due to any of the following factors: 1) Oxalic acid might decrease cellulose swelling during ozone bleaching,[7] resulting in a decrease in the accessibility of cellulose to the ozone. Consequently, less degradation of cellulose would take place. Therefore, the ozone would react preferentially with lignin, increasing the delignification. [7] 2) The chelating effect of oxalic acid[16]. It has been reported that the presence of transition metal ions substantially increases radical formation in ozone bleaching experiments[17]. Oxalic acid is a powerful organic acid chelator. Therefore, the effect of transition metal ions could be inhibited by oxalic acid. 3) The combined effects of increased delignification rate and decreased reactivity of cellulose toward ozone. It seems that oxalic acid catalyses the delignification reaction. Oxalic acid may control and regulate the formation of radicals that participate in the degradation of pulp compounds, catalysing the reactions of these radicals with the lignin and inhibiting excessive reaction with the cellulose.

These explanations are suppositions which are currently being studied. These supposed processes might take place in parallel or individually, or one might be a consequence of the others. Moreover, they may have an effect on cellulose degradation and on delignification separately or both together.

CONCLUSIONS

This paper shows the effect of oxalic acid in an ozone treatment of pulp.

The viscosity decreases when ozone consumption increases. However, viscosity data are higher when oxalic acid is added at this stage. The effect of oxalic acid is more significant on viscosity than on kappa number removal. In all cases the line viscosity vs. kappa number relationship reaches a point where the slope changes dramatically showing a significant drop in viscosity for small kappa number decreases.

The linear variation of brightness with kappa number does not depend on the oxalic acid concentration.

This is the first study of the kinetics of the effect of oxalic acid on ozone bleaching of a Eucalyptus globulus kraft pulp.

Delignification, chromophore removal and cellulose degradation during ozone treatment were described by approximate first order kinetics. Increases in oxalic acid doses (0–40 ppm) are accompanied by increases in delignification and chromophore degradation rate constants, while the depolymerisation rate constant decreases for the whole range of oxalic doses.

Addition of oxalic acid in ozone bleaching has a positive effect on the selectivity values which are greater. Possible explanations could be: a) The chelating effect of oxalic acid; b) The decreased accessibility of cellulose to ozone resulting from the decrease in cellulose swelling; c) A catalysing effect of delignification reactions and a protective effect of cellulose degradation.

EXPERIMENTAL

Materials

Pulp. Unbleached Eucalyptus globulus kraft pulp was used. Before the kinetic

study of ozone bleaching, a xylanase pretreatment (X) and an oxygen delignification (O) were carried out. Accordingly, the ozone bleaching experiments were performed with this XO-pulp [brightness 54.2 ISO, kappa number 7.05 and viscosity 992 cm^3/g].

Experimental device

The xylanase pretreatment conditions were as follows: 10% o.d.p. consistency, 45° C, 180 min reaction time, initial pH 6.5-8 and 550 EXU/kg xylanase doses.[18]

The conditions for oxygen delignification were: 10% o.d.p. consistency, 110° C, 60 min reaction time, 1.5% o.d.p. NaOH charge, 0.5% o.d.p. $MgSO_4 \cdot 7H_2O$ charge and 6 MPa O_2 pressure.[19,20]

Ozone bleaching at low consistency (0.5% o.d.p.) was performed at room temperature. Ozone consumption (the real ozone charge that reacts with the pulp) varied from 1.0 to 8% o.d.p. The pulp was previously acidified with H_2SO_4 to pH 2.5 with H_2SO_4 and several oxalic acid charges, varying between 0 and 187 ppm in aqueous suspension.

The reaction was carried out in a special batch reactor the details of which have been published elsewhere.[21] The ozone set-up includes: an ozone generator, two analysers, a flowmeter, a reactor, a PC-Lab Card and a software package created by us (Figure 11). The bleaching system allows for analyser calibration. Calibration was carried out using an iodometric method for the determination of ozone in a process gas. The software calculates the real ozone charge which reacts with the pulp (ozone dose consumed by the pulp) every 1 second, using the inlet and outlet ozone concentration data measured by the two analysers. Moreover, this system allows the bleaching stage to be carried out in an ozone saturated medium, which ensures that ozone was present in excess during the bleaching experiments.
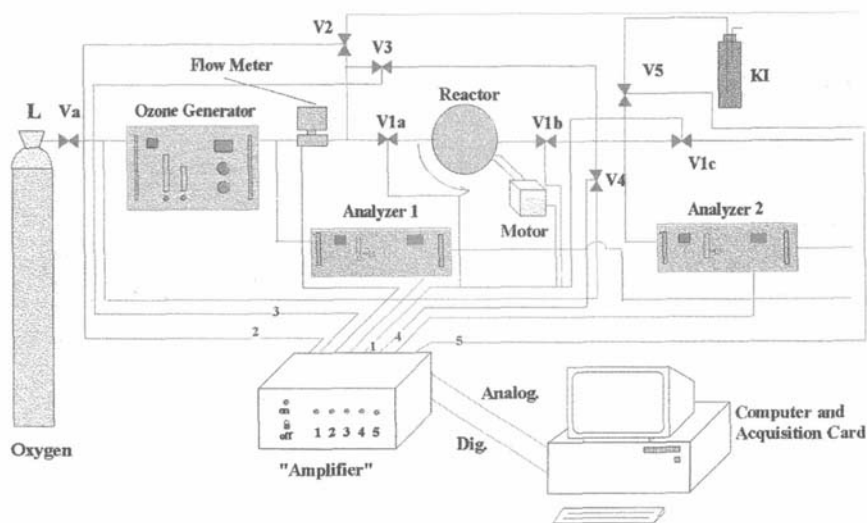
FIGURE 11. Ozone bleaching system.[19]

Ozone consumption at low consistency (0.5% o.d.p.) was approximately ten times higher than at high consistency (40% o.d.p.).

Ozone reaches the reactor through a diffuser, which maintains good mixing and enhances mass transfer. It also ensures the fulfilment of the perfect mix hypothesis. The reaction volume was 0.5L, the ozone inlet concentration was 35 mg/L and the gas flow was 150 NL/h.

Characterisation of the pulps

Kappa number, viscosity and brightness were according to ISO standards (302, 5351/1-2 and 3688 respectively).

The empirical relationship used in this work, between kappa number and lignin content for kraft pulps is:[22]

$$L_T = (0.147) * (\text{Kappa Number}) \qquad (11)$$

where L_T denotes the weight percentage of total lignin in the pulp.

The number-average degree of polymerisation (DP_v) of cellulose in the pulp was calculated from the viscosity values (v). The relationship between the two values is (SCAN C-15:62):

$$DP_v^{0.905} = 0.75 \, v \qquad (12)$$

The Kubelka-Munk coefficient was calculated from brightness values (B, % ISO). The relationship between the two values is:

$$\frac{k}{s} = \frac{(1 - R_\infty)^2}{2R_\infty} \qquad (13)$$

where $R_\infty = B/100$.

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