

TCF bleaching of Eucalypt kraft pulp with oxone

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SUMMARY

TCF delignification and bleaching of kraft eucalypt pulp using ozone and oxone under alkaline conditions has been investigated. The pulp samples were bleached in two stages of oxone (Ox) treatment using an AZOx₁Ox₂ sequence. Pulp brightness greater than 84% ISO was achieved. The effects of oxone charge, alkali charge, bleaching temperature and time on the bleaching response were studied. The colour removal was determined from the chromaticity coordinates (L*, a* and b*) and 98% colour removal was achieved. Accelerated ageing experiments showed excellent brightness stability with very little brightness reversion (or thermal degradation) of the oxone treated pulp. Improvements in pulp strengths compared to ozone and acid treatments were achieved along with significant HexA removal demonstrating the feasibility of oxone in TCF bleaching.

KEYWORDS

Oxone, TCF Kraft bleaching, Ozone, kappa number, and accelerated ageing

INTRODUCTION

Chlorinated chemicals have been the workhorse of bleaching for many years due to their strong oxidising power on residual lignin. Some chlorine bleaching chemicals are known to cause environmental damage as they release organochlorines into the environment. The use of chlorine dioxide in ECF (elemental chlorine free) bleaching has largely replaced chlorine. In recent years, mills have been looking at alternatives to

replace chlorinated chemicals and some are also striving for 'total chlorine free' (TCF) bleaching.

The current world production of TCF bleached pulp represents only about 6% of total bleached pulp production. There are a number of factors that discourage more widespread use of TCF bleaching. These include a higher bleaching cost, a lower final pulp strength, poorer removal of hexenuronic acid and greater brightness reversion than ECF pulps.

The main bleaching chemicals used in TCF bleaching are oxidants such as oxygen, ozone, and hydrogen peroxide. A variety of more exotic bleaching chemicals including peroxyacetic acid (1), peroxyformic acid (1), potassium peroxymonosulphate (oxone) (1-4), potassium peroxyphosphoric acid (5) and dimethyldioxiranes (6) are also being explored in different bleaching sequences.

Oxone is an attractive alternative because of its stability, simple handling, non-toxic nature and versatility (7). Oxone is a solid tri-salt of potassium peroxymonosulphate (2KHSO₅·KHSO₄·K₂SO₄). The active component, potassium monopersulphate (KHSO₅) is a salt from Caro's acid H₂SO₅. Oxone has long been used as a mild and sole oxidant in organic conversions/synthesis (8-10) and has been used to release peroxymonosulphuric acid in strong acidic medium in pulping and bleaching. (2-4, 11-15). There have been suggestions that peroxymonosulphuric acid can be used as a pre-treatment to oxygen delignification to enhance the selectivity of delignification (11-13, 16-17). Peroxymonosulphuric acid has also been effectively used for the removal of hexenuronic acid and lignin (18). Mill-scale trials have been conducted to verify the effectiveness of peroxymonosulphuric acid as a bleaching agent (19).

In this study eucalypt kraft pulp was first delignified with ozone and then bleached with an aqueous solution of oxone under alkaline conditions. A two stage bleaching sequence AZOx₁Ox₂ was designed after optimizing the Oxone addition (Ox), alkali, temperature and bleaching time. The effect of the bleaching variables on the optical and strength (tensile

and burst index) properties, brightness reversion, kappa number, HexA content and pulp viscosity were studied.

EXPERIMENTAL

Materials

Oxone (potassium peroxymonosulphate), obtained from Aldrich, was prepared by dissolving it in distilled water.

Laboratory produced Eucalypt kraft pulp from *Eucalyptus globulus* was provided by the R & D Laboratories of Gunns Limited, Burnie, Tasmania, Australia. The pulp was stored at 4°C throughout the course of the bleaching experiments to minimize any change in pulp properties. The kappa number of the unbleached kraft pulp was 18, viscosity 45.0 cP and ISO brightness (R457) 25.3%.

The pulp was screened through a #20 mesh screen to remove shives and then acidified to pH 4.0 with 2.0 M H₂SO₄ at a 10.0% pulp consistency for 10.0 minutes at room temperature. After acidification, the pulp was washed with distilled water and then pressed using a mechanical hand press to increase the consistency to ~30%. The consistency of the pressed pulp was determined with an infrared moisture determination method. The metal content (Fe, Mn and Cu) of the acidified washed pulp was determined by flame atomic absorption.

Ozone delignification: The pulp was fluffed using a domestic food processor (Sunbeam Oskar II). 30.0 g o.d of pulp was charged with different concentrations of ozone (Z) at 30.0% consistency to delignify the pulp. After the ozone treatment, the pulp was washed to neutral pH with deionised water.

Bleaching: Pulp samples from ozone delignification (at 1.0% ozone on o.d. basis) were bleached at different concentrations of oxone under aqueous alkaline conditions at 12.0% consistency in polythene zip lock bags for 2.0 hrs at 65°C (Table 1). After each oxone treatment the pulps were washed to neutral pH.

After optimizing the oxone charge to be used in the different bleaching stages, the effect of alkali charge (NaOH), temperature and reaction time on the bleaching response were studied.

Physical Testing: Hand sheets pre-

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pared by TAPPI method T 205 sp-95 were conditioned for 24 hrs prior to testing. An Elrepho 2000 Spectrophotometer was used to measure the colour (L^* , a^* and b^*) and brightness, R457 (T 452 om-98) of the hand sheets. Three independent readings for each set of handsheets were averaged. Accelerated ageing ISO 5630-1 method was used to test the brightness stability of bleached samples by dry heating at 105°C for 24 hrs \pm 10.0 min. The tensile strength of the handsheets was determined using ISO 1924-1: 1992 (E) while the bursting strength was measured according to TAPPI Test method T 403 om-97.

Chemical Properties: The Kappa number was determined using TAPPI test method T236 om-99. A UV spectrophotometric method developed by Chai *et al.* (20) was used to quantify the HexA content ($\mu\text{mol/g}$) in 0.05 g of hydrolysed pulp samples. The 10.0 mL hydrolysis solution consisted of equal volumes of 0.6 HgCl_2 (22.0 mmol/L) and 0.7% $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ solutions. The contents of the sample vials were mixed thoroughly by hand shaking, heated for 30 minutes at 60-70°C and filtered. The UV absorption of solutions at 260 nm and 290 nm were measured in a 10.0 mm path length silica cell. The HexA contents were then calculated (20) as

$$C_{\text{HexA}} = 0.287 [V(A_{260} - A_{290}) / w]$$

Where

0.287 is the calibration factor for dual wavelength measurement

Table 1
Effect of Ozone treatment on pulp brightness

Ozone charge, % on o.d. fibre	% ISO brightness
0.0	26.4
0.5	32.0
1.0	36.1
2.0	42.2

V = volume of hydrolysed solution (mL)
w = weight of o.d pulp (g)

Viscosities of the pulp samples were determined using TAPPI Test method T230 Om-94.

RESULTS AND DISCUSSION

Ozone pretreatment of unbleached kraft eucalypt pulp was undertaken prior to bleaching with oxone because of its effectiveness in producing pulps of high brightness and low kappa number (21-28). The results in Table 1 show that a 10 unit increase in brightness occurs at 1% ozone charge. Increasing the ozone charge to 2% increased the brightness by a further 6 units only, compared to a 1% ozone charge. Thus a 1.0% ozone charge was used for subsequent experimentation and also to avoid any pulp deterioration.

After deciding on the optimal ozone concentration, a series of experiments were undertaken to determine the optimum number of bleaching stages to achieve maximum brightness with the use of oxone. The results in Table 2 show that

two stages of oxone bleaching, $[\text{AZOx}_1\text{Ox}_2]$ achieved a brightness of 83.4% compared to 63.0% brightness with a single oxone bleaching stage. The kappa number was found to be significantly decreased reaching a level of 0.03 with two stage bleaching with 10% oxone charge in each stage. Three stages or more of oxone bleaching were found to have little further impact on the brightness.

The effects of chemical levels (oxone and alkali) and bleaching conditions (bleaching temperature and bleaching time) were further investigated in order to determine the appropriate conditions to achieve maximum brightness in each stage of a two stage bleaching sequence. Figure 1 shows that increasing the alkali (NaOH) charge to 5% resulted in a significant increase in brightness from 49.7 to 69.5% ISO. The brightness was found to change very little at higher alkali charges.

The effect of the reaction temperature was studied using the optimum alkali charge determined in Figure 1 (5.0% NaOH). Brightness was found to increase to 71.8% ISO when the pulp was heated to 50°C as shown in Figure 2. Increasing the temperature above 50°C was found to have little effect on improving the brightness.

The effect of reaction time was investigated at 5% NaOH and 50°C reaction temperature. The results in Figure 3 show that the pulp brightness increased as the bleaching time increased to 60 minutes and then plateaued at higher reaction times.

The optimal conditions determined during the first stage bleaching experiments in Figures 1-3 (10% Oxone, 5.0%

Table 2
Effect of different oxone bleaching sequences and stages on % ISO brightness and Kappa number

Exp. No	Bleaching sequences and stages	Ox (% on o.d.) in different stages					NaOH (% on o.d.) in different stages					% ISO brightness	Kappa number
		1st	2nd	3rd	4th	5th	1st	2nd	3rd	4th	5th		
1	AZOx	10	--	--	--	--	0	--	--	--	--	51.6	13.09
2	AZOx	10	--	--	--	--	3	--	--	--	--	60.9	10.9
3	AZOx	20	--	--	--	--	3	--	--	--	--	62.0	9.60
4	AZOx	30	--	--	--	--	3	--	--	--	--	63.0	8.77
5	AZOx ₁ Ox ₂	10	10	--	--	--	3	3	--	--	--	78.6	4.80
6	AZOx ₁ Ox ₂	5	5	--	--	--	5	5	--	--	--	76.6	5.57
7	AZOx ₁ Ox ₂	8	8	--	--	--	5	5	--	--	--	81.4	0.51
8	AZOx ₁ Ox ₂	10	10	--	--	--	5	5	--	--	--	83.4	0.03
9	AZOx ₁ Ox ₂ Ox ₃	5	5	5	--	--	5	5	5	--	--	79.6	3.60
10	AZOx ₁ Ox ₂ Ox ₃	8	8	5	--	--	5	5	5	--	--	82.6	0.35
11	AZOx ₁ Ox ₂ Ox ₃ Ox ₄	3	3	3	3	--	5	5	5	5	--	72.4	0.57
12	AZOx ₁ Ox ₂ Ox ₃ Ox ₄	2	2	3	5	--	5	5	5	5	--	76.9	5.51
13	AZOx ₁ Ox ₂ Ox ₃ Ox ₄ Ox ₅	3	3	3	3	5	5	5	5	5	5	81.9	0.53

All pulp samples were acidified (A) at pH ~ 4.0 to remove any metal content before bleaching. There is a washing stage in between each bleaching stage.

Reaction condition for all these 13 experiments were:

Z = 1.0% on o.d, Consistency = 12.0%, Temperature = 65°C and reaction time = 120 \pm 5 minutes

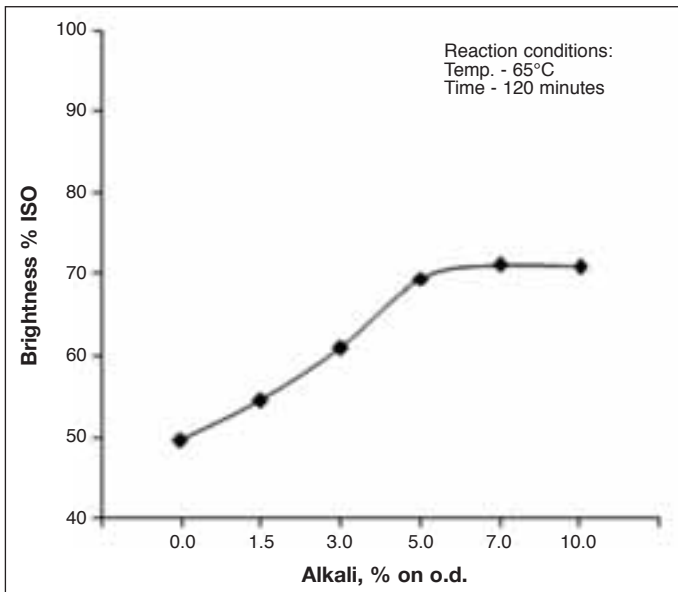


Fig. 1 Effect of alkali charge on first stage bleaching with 10% Oxone charge.

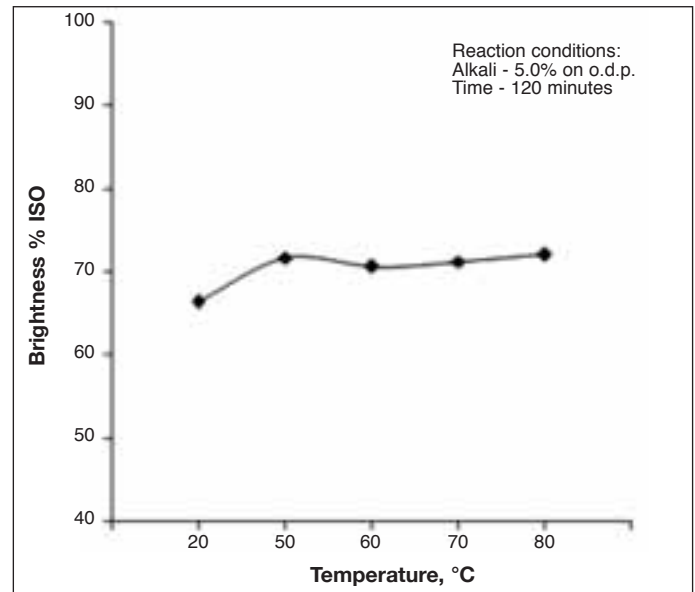


Fig. 2 Effect of bleaching temperature on the first stage bleaching response at 10% Oxone charge.

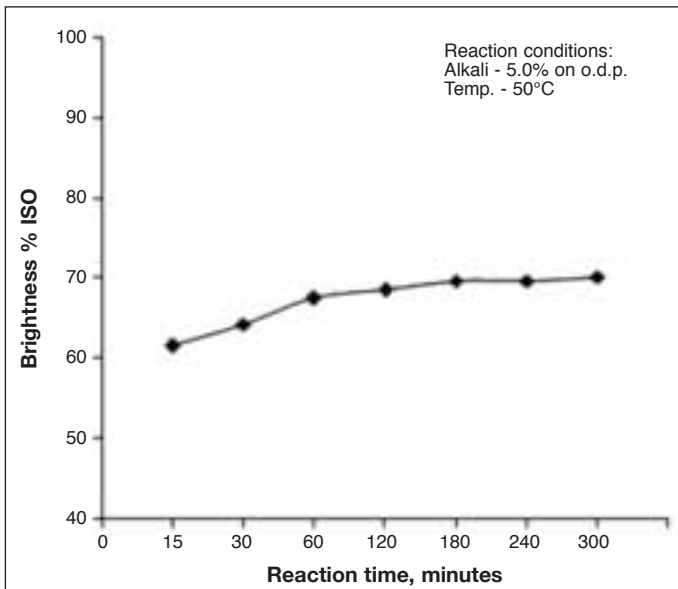


Fig. 3 Effect of bleaching time on first stage with 10% Oxone charge

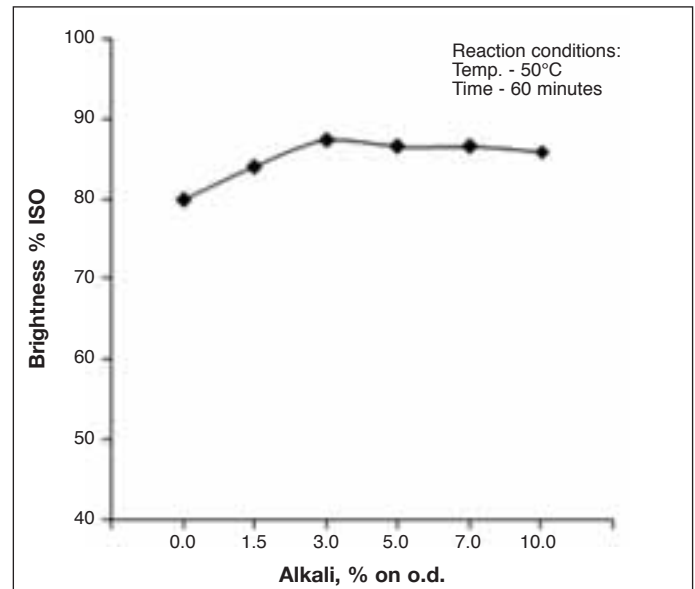


Fig. 4 Effect of alkali on bleaching response in second stage with 10% Oxone. (First stage optimized bleaching conditions were 10% Oxone, 5% alkali charge on o.d. pulp; 50°C and bleaching time was 60 minutes).

NaOH, 50°C and 60 minutes bleaching time) were used to prepare the pulp for the second stage bleaching experiments. The alkali charge, temperature and reaction time were varied in this second stage to find the optimal bleaching conditions at a 10% oxone charge. The results in Figures 4 and 5 show the same trends as observed in the first stage experiments in Figures 1-3. The optimum conditions were found to be 3.0% NaOH on o.d. pulp, T = 50°C and t = 60 minutes. A maximum brightness of 84.3% ISO was achieved using these conditions.

The temperature and reaction time conditions found to be optimal are milder than conditions reported in the literature for per-

oxide bleaching. Hydrogen peroxide needs temperatures > 70 - 90°C and bleaching times of ~ 2.0 hrs to achieve similar brightness levels. Pan *et al* demonstrated that the two main benefits of using oxone as an alternative to hydrogen peroxide were enhanced bleaching efficiency and decreased pulp yield loss (29). Hydrogen peroxide alone has been found to be a relatively ineffective means of bleaching kraft pulp (30). To achieve fully bleached pulp the use of hydrogen peroxide is usually explored in ECF bleaching sequences (30-31). Conventional bleaching sequence, involving hydrogen peroxide, for eucalypt

pulp is four stages D₀EopD₁D₂ to achieve 90+ ISO brightness (32).

Accelerated Aging: One of the drawbacks of TCF and also ECF bleaching processes has been the issue of brightness stability. Although the overall brightness reversion is much smaller in a kraft pulp compared to mechanical pulp, chemical modifications due to the bleaching reactions do occur. Some of these reactions can result in the formation or modification of chromophoric groups which increase the reversion process.

Most TCF bleaching chemicals introduce carbonyl and carboxylic groups to

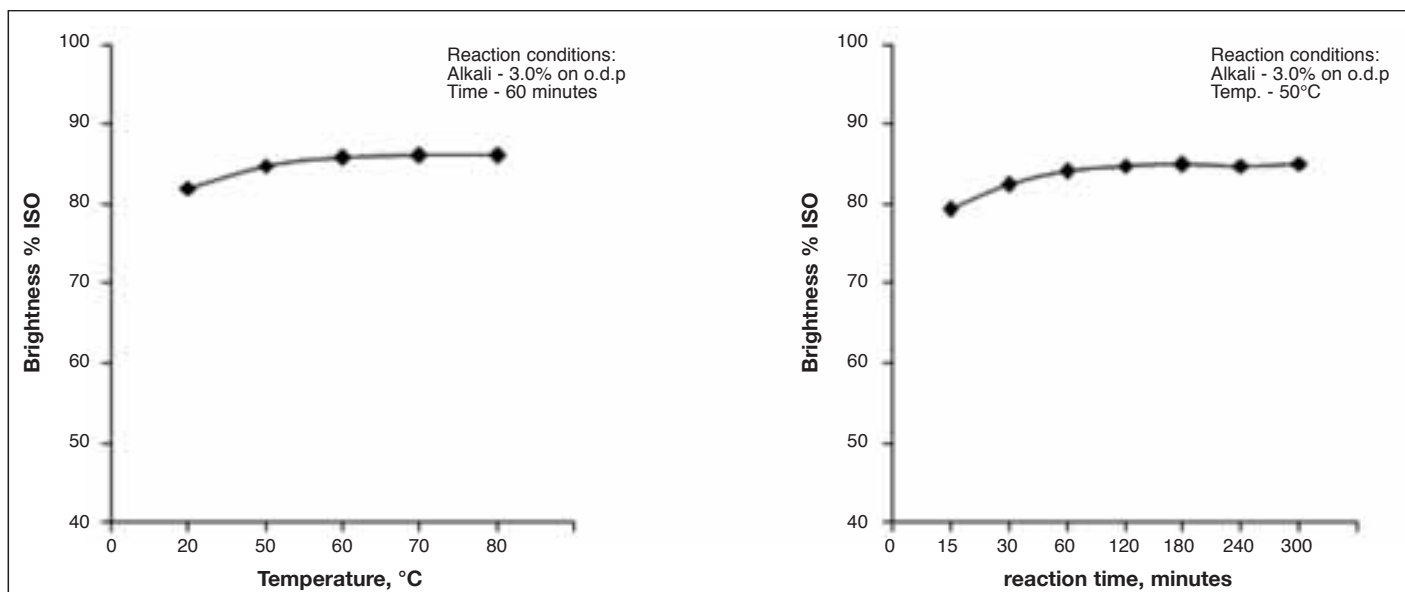


Fig. 5 Effect of reaction time temperature and time on the bleaching response in the 2nd stage of bleaching.

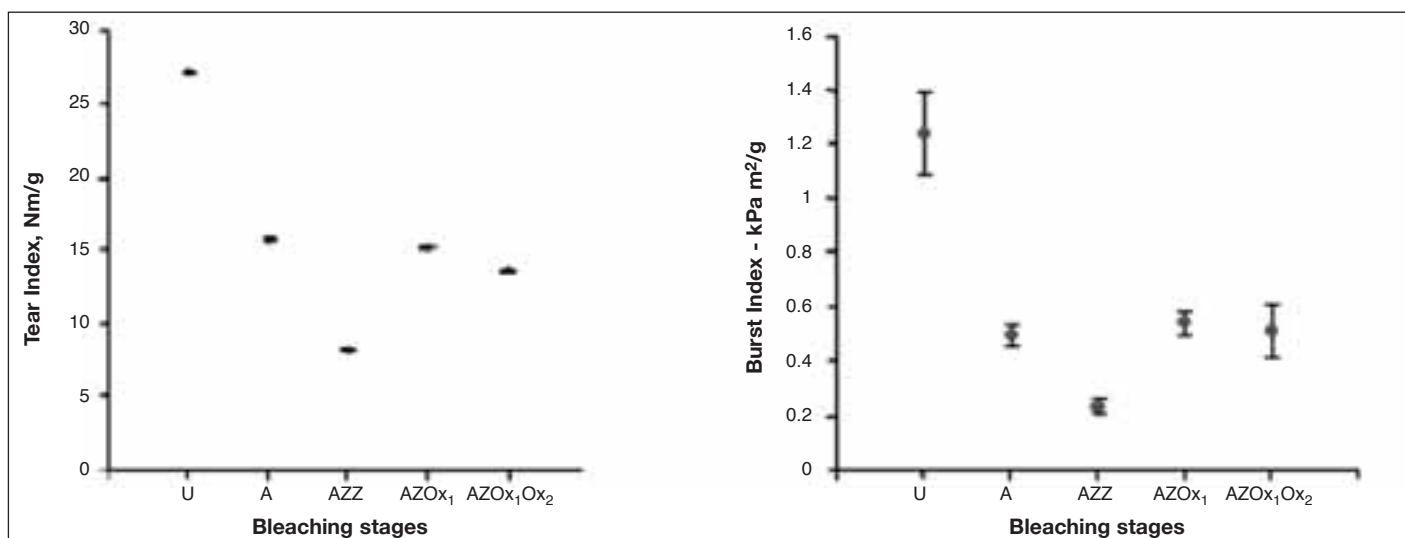


Fig. 6 Effect of acidification, ozonation and oxone bleaching on the tensile index and burst index of pulp handsheets

the pulp which may participate in colour-forming reactions. Oxygen and ozone bleaching of pulp causes the formation of carboxyl group usually at the C1, C2, C3 and/or C6 position of the carbohydrate structures which is detrimental to brightness stability upon heat exposure (33-35). Several studies (32,36) have reported brightness reversion occurring in bleaching sequences using hydrogen peroxide.

A series of accelerated aging experiments were undertaken on the handsheets prepared from the various bleached pulps. Handsheets were subjected to heating at 105°C for 24 hours. Table 3 presents the percentage decrease in ISO brightness of hand sheets. The percentage decrease was determined by comparing the average results before and after heating. A student t-test was performed to determine if the

Table 3
Ageing properties: Brightness stability of bleached pulp

Stages	% decrease in ISO brightness aged at 105°C for 24 hrs ± 10 min						
Unbleached	Un	A	AZ				
	0.59*	1.44*	0.41*				
1st Stage oxone bleaching	E = 0.0	1.5	3.0	5.0	7.0	10.0	
	0.82*	0.11	0.11	0.13*	0.18*	0.11	
	T = 20°C	50°C	60°C	70°C	80°C		
	0.12*	0.33*	0.44*	0.11*	0.25*		
	t = 15 min	30 min	60 min	120 min	180 min	240 min	300 min
	0.62*	0.0622	0.162	0.162*	0.342*	0.142*	0.342*
2nd stage oxone bleaching	E = 0.0	1.5	3.0	5.0	7.0	10.0	
	0.48*	0.12	0.08	0.09	0.37*	0.16	
	T = 20°C	50°C	60°C	70°C	80°C		
	0.07	0.46*	0.41*	0.07	0.07		
	t = 15 min	30 min	60 min	120 min	180 min	240 min	300 min
	0.18*	0.30*	0.18*	0.39*	0.12	0.15*	0.26*

*Student t-test showed differences in means before and after heating were statistically different at 95% confidence level.

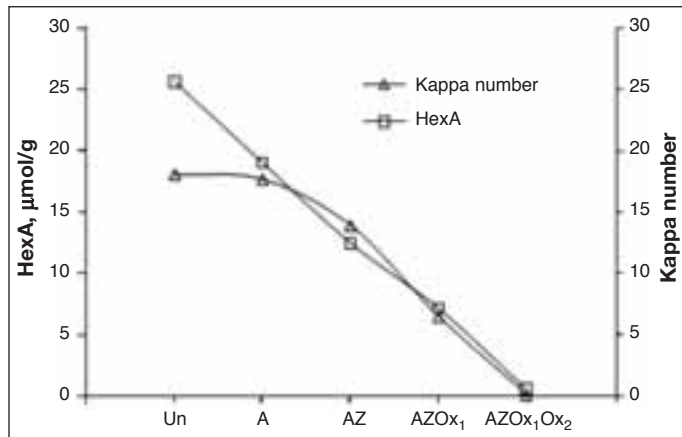


Fig. 7: Corrected Kappa number (TAPPI method) (11) and HexA $\mu\text{mol/g}$ (UV method) (20).

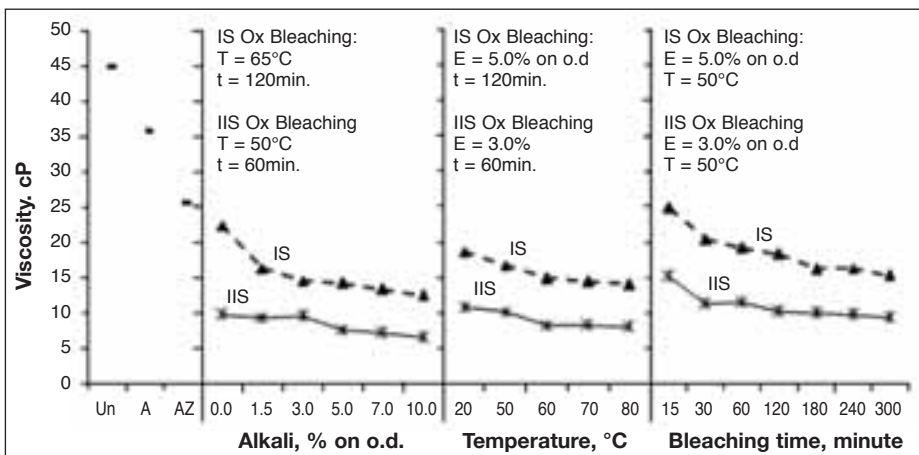


Fig. 8: Effect of acidification, ozonation and oxone bleaching conditions on pulp viscosity. (Un is unbleached; A stands for acidified pulp at pH ~ 4.0; Z is 1.0% ozone on o.d. pulp; IS is 1st bleaching stage with 10.0% Ox on o.d. pulp; IIS is 2nd.

differences between the mean values were statistically different at the 95% confidence level. The results in Table 3 show that the oxone treatment in the bleaching sequence, AZOx₁Ox₂, resulted in a bleached pulp showing very small brightness loss of 0.03 units during accelerated thermal aging as compared to the unbleached sample. The brightness reversion due to thermal aging was more noticeable in acidized (A) and ozonised (AZ) samples. The alkali addition with oxone appears to be protecting the pulp hand sheets from thermal degradation.

Strength Properties: Tensile index and Burst index were determined for five different handsheets: unbleached (Un), acidified only (A), acidified and ozone treated (AZ), one stage of oxone bleaching (AZOx₁) and two stages of oxone bleaching (AZOx₁Ox₂) (Figure 6).

Handsheets prepared from unbleached eucalypt kraft pulp were found to have a higher tensile index and burst index than handsheets made from the treated pulp. Upon acidification at pH 4.0, there is a

significant decrease in tensile index and burst index. Delignification with 1.0% ozone further reduced the tensile index and burst index, however with addition of oxone to the sample in the first stage of bleaching, the tensile index and burst index increased at 5.0% alkali, 50°C and 60 minutes bleaching. A very slight decrease was observed in the handsheets prepared from pulp produced after the second stage of Ox bleaching at 3.0% alkali, 50°C and 60 minutes bleaching.

The apparent regain of pulp strength with alkaline oxone bleaching observed in the first stage of bleaching represents an advantage of this process over other TCF bleaching chemicals such as ozone. Korpela (37) also noticed the improvement in pulp strength due to alkali addition which improves the fibre bonding and flexibility during peroxide bleaching.

Effect of bleaching on lignin content, HexA and cellulose depolymerisation

The effects on the chemical bleaching

treatments on the residual lignin and hexenuronic acid (HexA) contents on the pulps were also determined. The results are presented in Figure 7.

Mild acid treatment of unbleached pulp (Un) has the expected result of almost no effect on the kappa number but removal of some of the HexA content.

Greater than 75% of HexA content (7.12 $\mu\text{mol/g}$ at first stage) was removed by single stage bleaching (AZOx₁) with a corrected kappa number of 6.42. With the employment of a second bleaching stage (AZOx₁Ox₂), both the corrected kappa number and HexA content of the bleached pulp became negligible.

The presence of HexA groups formed in xylan chains are known to cause decreased brightness, greater brightness reversion, poor metal removal in bleached pulp and increased bleaching chemical consumption (38). The results in Figure 7 show the effectiveness of oxone in removing both lignin and HexA. Breuilh *et al.* (18) found a similar effect with peroxymonosulphuric acid.

During bleaching, cleavage of the cellulose chains can occur (39). This decrease in molecular mass of the cellulose chains can be studied by measuring pulp viscosity. The results in Figure 8 show that a considerable decrease in pulp viscosity from 45 cP to 25 cP occurred when the pulp underwent acidification (A) and acidification/ozone (AZ) treatment. This represents a 44% drop in degree of polymerization (DP). Although the decrease in pulp viscosity is less between the first and second stage of oxone bleaching (a decrease from 19.3 cP to 11.5 cP), the relationship between pulp viscosity and DP is logarithmic and so this represents a 40% decrease in DP. Although the AZOx₁Ox₂ sequence yielded a low viscosity (11.5 cP) it is comparable to other bleaching sequences involving hydrogen peroxide. A viscosity of 11 cP was reported for an O/ODEopDED process (36) and viscosity values of 13.2 cP and 10.2 cP were reported for Z/D₀EopD₁ and Z/D₀P processes respectively (32).

CONCLUSIONS

A two stage oxone bleaching sequence following ozone pre-treatment of eucalypt kraft pulp was found to result in pulp brightness greater than 84% ISO. Pulp brightness in the first stage was found to increase with alkali charge up to 5.0%

NaOH. Increasing the bleaching temperature to 50°C and reaction time to 60 minutes were found to result in the maximum brightness of 67.6% ISO in the first stage. Similar trends in alkali charge, bleaching time and temperature were observed with the bleaching response in the second stage. Maximum brightness of 84.3% ISO was achieved using 3.0% NaOH at 50°C for 60 minutes.

Ageing experiments at 105°C for 24 hrs ± 10 min showed that alkaline oxone bleaching prevented thermal degradation (brightness reduction) from occurring as compared to the untreated sample and acidified and ozone treated pulp. Similarly, the AZOx₁Ox₂ bleaching sequence was found to be effective in regaining some of the strength lost during acidification and ozone treatment of eucalypt pulp. A decrease in lignin contents to a negligible level and removal of HexA groups was also demonstrated and together with all of the other results indicates the feasibility of oxone bleaching as an environmentally favourable alternative TCF bleaching sequence, certainly comparing well with chlorinated bleaching approaches and also other TCF bleaching sequences.

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