MOLYBDENUM CATALYZED ACID PEROXIDE BLEACHING OF EUCALYPTUS KRAFT PULP

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Molybdenum catalyzed peroxide bleaching (P_{Mo} Stage) consists of pulp treatment with hydrogen peroxide under acidic conditions in the presence of a molybdenum catalyst. Molybdenum is applied in catalytic doses (50-200 mg/kg pulp) and may originate from various sources, including $(NH_4)_6Mo_7O_{24}.4H_2O$, $Na_2MoO_4.2H_2O$, siliconmolybdate, etc. This work is aimed at optimizing the P_{Mo} stage and evaluating its industrial application in the OAZDP sequence. Optimum P_{Mo} stage conditions for bleaching eucalyptus pulp were 90 ºC, pH 3.5, 2 h, 0.1 kg/adt Mo and 5 kg/adt H_2O_2. The P_{Mo} stage was more efficient to remove pulp hexenuronic acids than lignin. Its efficiency decreased with increasing pH in the range of 1.5-5.5, while it increased with increasing temperature and peroxide and molybdenum doses. The application of the P_{Mo} stage as replacement for the A-stage of the AZDP sequence significantly decreased chlorine dioxide demand. The P_{Mo} stage caused a decrease of 20-30% in the generation of organically bound chlorine. The quality parameters of the pulp produced during the P_{Mo} stage mill trial were comparable to those obtained with the reference A-stage.

Keywords: Activated hydrogen peroxide; Molybdenum; Light-ECF bleaching; Mill trials

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INTRODUCTION

There has been a growing demand for light elemental chlorine free (light-ECF) pulps, particularly in Europe, in order to replace the very expensive totally chlorine free (TCF) pulps. There is no clear definition for the so-called light-ECF pulps, but the market tends to accept under this denomination the bleached pulps that contain less than 50-60 g Cl^-/adt pulp of organically bound chlorine substances (OX), as measured by a standard test method such as SCAN-CM 52:94, PTS-RH 012/90, ISO 11480, etc. Such a low bound chlorine target requires that ECF bleaching be implemented under unusual operational conditions, i.e., with very low chlorine dioxide charges (Colodette et al. 2006; Colodette et al. 2008). Many bleaching alternatives have been evaluated to minimize chlorine dioxide use for eucalyptus kraft pulps, one of them being the so-called molybdenum activated hydrogen peroxide stage (P_{Mo}) (Hämäläinen et al. 2003; Suchy and Argyropoulos 2002).

Eucalyptus kraft pulps are usually cooked to kappa number 16-20 and oxygen delignified to kappa 9-12. Further drop in kappa number is usually difficult because a large fraction (4-6 units) of the pulp kappa number is comprised of hexenuronic acids

(Costa et al. 2001; Li and Gellerstedt 1998). Subsequent bleaching of such pulps to full brightness with ECF sequences of the A/D(PO)DP and AZDP types consume about 35-45 kg/adt total active chlorine (including H_2O_2), which is equivalent to a bleachability level of about 4 kg/adt total active chlorine per kappa unit (Colodette et al. 2008). Pulps produced with this much total active chlorine tend to contain OX values slightly over 100 g Cl^-/adt pulp, unless large doses of hydrogen peroxide are applied in the P stages and low doses of chlorine dioxide are used in the D stages.

In order to minimize OX values, one needs either decreasing kappa number after O-stage or increasing pulp bleachability level. Kappa number entering the bleach plant can be reduced in the digester or in between the digester and bleach plant through improved brown stock washing and oxygen delignification. The option of extending cooking in the digester has been tried in the past but yield penalties showed this practice to be counterproductive. Oxygen delignification technology has seemingly reached maturity, and the low lignin content of eucalyptus pulps leaves little room for improvement in this phase of the process. More efficient brown stock washing systems can certainly help decrease kappa number by improving subsequent oxygen delignification, but modern mills are equipped with top-notch washing systems that already work at high efficiencies, i.e., 40-60 kg COD/adt entering the O-stage (Colodette et al. 2006; Colodette et al. 2008).

An alternative that has been successful to reduce eucalyptus pulp kappa number prior to bleaching has been the so-called hot acid hydrolysis stage (A), (Henricson 1997; Vuorinen et al. 1996). However, the acid stage presents some problems, since it decreases the reactivity of the remaining lignin (Tran 2006). Besides, the acid stage diminishes pulp viscosity. Thus, alternatives to the acid stage have been sought after, including treatments such as xylanase enzymes (Yang et al. 1993), peroxymonosulfuric, or peroxyacetic acid that has been distilled, generated by equilibrium, or *in situ* produced from glucose penta-acetate (Kang and Ni 2001; Kang et al. 2004), and metals activated acid peroxide (Eckert 1982; Sundman 1988; Mounteer et al. 1991; Hämäläinen et al. 2003).

Eckert (1982) pioneered the study of acid peroxide stages activated by various metals including W, Mo, Os, Cr, and Se and concluded that the molybdenum-H_2O_2 system is the most efficient to delignify hardwood pulps and that the Mo and W filtrates were the least toxic of all. Continuing the studies of Eckert, Sundman (1988) studied the reactivity of various lignin models and residual kraft lignin with peroxide in the presence of tungsten or molybdenum. It was determined that molybdenum was a more effective activator than tungsten both at pH 2 and 5, and that lignin models containing a free phenolic hydroxyl group were significantly more reactive than those etherified. Both Mo- and W-activated peroxide systems were capable of oxidizing phenolic groups to ortho- and para-quinones, but further degradation of these quinones to corresponding muconic acids did not take place.

The delignification action during the P_{Mo} stage is ascribed to the ability of the molybdate, in acid conditions, to form together with the hydrogen peroxide an active complex, resulting in the generation of the diperoxi-molybdenum complex (Fig. 1). Several different molybdenum-containing species are catalysts, including sodium and ammonium molybdate, molybdenum trioxide, siliconmolybdate, etc.
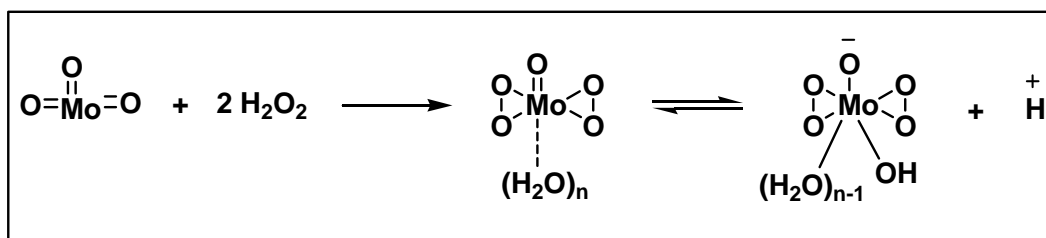
Fig. 1. Reaction for the formation of the diperoxi-molybdenum structure under acid aqueous conditions (Sundman 1988)

It has been shown for ECF bleaching of Scandinavian hardwood and softwood pulps that the use of the P_{Mo} stage can decrease the chlorine dioxide demand up to 6 kg/adt of pulp (Hämäläinen et al. 2003). The great advantage of this stage in relation to other stages run under acidic conditions is the minimum formation of oxalic acid that can cause scaling in the bleach plant. Oxalic acid is produced through acid hydrolysis that occurs when an acid stage (e.g. ozone and chlorine dioxide) is used to remove pulp hexenuronic acids (Begnor-Gidnert et al. 1998).

The presence of molybdenum in the bleaching filtrate causes no significant damage to the effluent system nor to the recovery system, because of the low amount of molybdenum used in the stage (catalytic levels), and part of the filtrate of this stage can be reused in the stage to replace the loss of molybdenum (Kubelka et al. 1992; Hämäläinen et al. 2003).

In a recent study Milagres et al. (2007) evaluated the sodium molybdate activated peroxide stage (P_{Mo}) for full bleaching of an oxygen delignified eucalyptus kraft pulp, containing large amount of hexenuronic acids (HexA groups). Two- to four-stage ECF and TCF sequences such as $P_{Mo}DP$, $P_{Mo}D/P$, $P_{Mo}D(PO)$, $P_{Mo}Q(PO)$, and $XP_{Mo}Q(PO)$ were compared. Among the ECF alternatives, the two-stage $P_{Mo}D/P$ sequence proved attractive without significantly affecting pulp viscosity in relation to the traditional D(EPO)DP sequence. Besides, it produced better quality effluent in relation to the reference. However, a four-stage sequence, $XP_{Mo}Q(PO)$, was required to achieve full brightness using the TCF technology. The TCF sequence was not cost-effective, although it produced pulp of acceptable viscosity.

The objective of this work was to optimize, at both the laboratory and mill scale, the application of the molybdenum-activated peroxide stage for bleaching an hexenuronic acid rich eucalyptus kraft pulp, aiming at minimizing operational costs and pulp organically bound chlorine (OX) content, while maintaining unaltered the product quality and environmental load.

EXPERIMENTAL

Materials

This work is divided into two parts, with the first being on the optimization of the P_{Mo} stage and the second on its laboratory and industrial application in light-ECF bleaching. The optimization of the P_{Mo} stage was carried out on oxygen delignified pulp derived from an industrial unbleached eucalyptus kraft pulp. The

unbleached pulp was collected from a fiber line operating with a wood mix of *Eucalyptus grandis* and *Eucalyptus urograndis*. The characteristics of the pulps before and after oxygen delignification are described in Table 1. The P_{Mo} stage optimization was carried in the two phases, which are described in Table 2.

Table 1. Characteristics of the Brown and Oxygen Delignified Eucalyptus Kraft Pulps

Parameters	Brown Pulp (Industrial)	Oxygen Delignified Pulp (Laboratory)*
Brightness, %ISO	37.2	50.5
Viscosity, dm^3/kg	1451	1156
Kappa number	16.2	11.0
Hexenuronic Acids, mmol/kg	62.1	60.2
*Oxygen stage conditions (carried out in a Quantum Mixer/reactor, model Mark V): 100 ^{o}C temperature; 60 min; 12% consistency; 20 kg NaOH/adt pulp; 20 kg O_2/adt pulp; and 3 kg $MgSO_4.7H_2O$ /adt pulp.		

Table 2. Parameters and Conditions Evaluated in the P_{Mo} Stage

First Optimization	
Time, h	2 ; 3 ; 4
Temperature, ºC	70 ; 90
Molybdenum doses, kg/adt pulp	0 ; 0,1; 0;2; 0,4
H_2O_2 doses, kg/adt pulp	10
pH	3,5
Consistency, %	11
Second Optimization	
pH	1,5; 3,5; 4; 4,5; 5; 5,5
H_2O_2 doses, kg/adt pulp	3; 5; 7; 10
Molybdenum doses, kg/adt pulp	0,1
Molybdenum source	$(NH_4)_6Mo_7O_{24}.4H_2O$, $Na_2MoO_4.2H_2O$
Time, h	2
Temperature, ºC	90, 95
Consistency, %	11

After complete optimization, the P_{Mo} stage was applied in the $P_{Mo}ZDP$ light-ECF bleaching having as reference the AZDP sequence, under the conditions described in the result tables. The pulps were characterized using the TAPPI T236 cm-85 standard for kappa number, the SCAN-CM 15:99 standard for intrinsic viscosity, and the TAPPI T525 om-86 standard for brightness. Pulp heat reversion was measured after aging the handsheets in an oven (4 h, 105±3 °C, 0% moisture content); the handsheets were previously conditioned for 12 h in an acclimatized room (23 ± 1 ºC, 50 ± 2 % moisture content). The hexenuronic acids were analyzed by UV spectroscopy on hydrolysates derived from pulp treatment with formic acid, according to Tenkanen et al. (1999).

The degree of association among variables was estimated *via* correlation coefficients (r). Correlation significance was measured by the so-called *p*-value, which is the probability that a sample could have been drawn from the population(s) being tested.

A p-value of 0.05 indicates a 5% chance of drawing the sample being tested if the null hypothesis is actually true (iSixSigma 2003). In the experiments the correlations were considered non-significant (ns) when *p*-values were higher than 5% and significant (*) otherwise. The statistical analysis was carried out using the S*tatistica* software.

In the mill trial the acid stage of the AZDP sequence was replaced by the P_{Mo} stage. Figure 2 illustrates the P_{Mo} stage application during the trial, which started on March 1, 2005 and ended on March 31, 2005. In this period, there were a few interruptions of the P_{Mo} stage. The general bleaching conditions used during the trial are shown in Table 3. The operational conditions applied in the P_{Mo} stage were similar to those used for the acid stage (A), except for the addition of hydrogen peroxide and sodium molybdate.

Table 3. General Bleaching Conditions Used During the Mill Trial

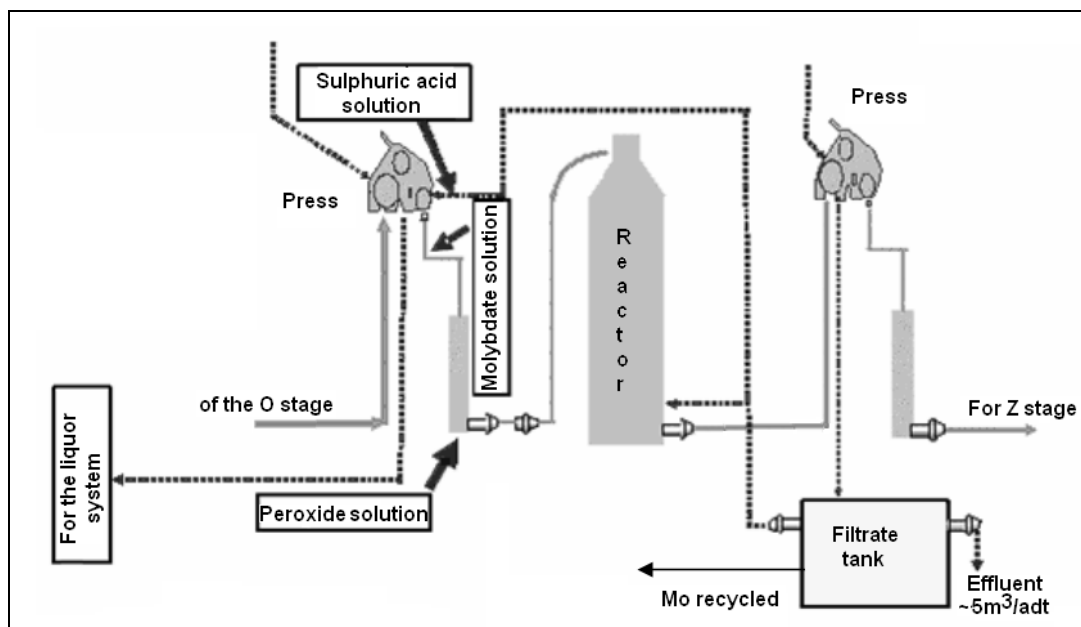| Operational Parameters	Bleaching Stages				
	A	P_{Mo}	Z	D	P
Time, min	120	120	1	40	90
Temperature, ^{o}C	95	95	40	85	90
pH	3.5	3.5	2.5-3.0	4.5	10.5
Initial Mo dose (first hours), kg/adt pulp	---	0.1	---	---	---
Make up Mo (steady state), kg/adt pulp	---	0.06	---	---	---
H_2O_2, kg/adt pulp	---	5	---	---	---

Fig. 2. Illustration of the P_{Mo} stage as applied during the mill trial

The molybdenum applied to the system was initially 0.1 kg/adt pulp, but this value was dosed only in the first hours of the trial until the system reached steady state. After that, the molybdenum dose was controlled to keep the concentration of the elemen-

tal molybdenum (Mo) around 0.1 kg/adt pulp in the suspension. During the mill trial about 40% of the molybdenum was recycled. Therefore, 60% of the salt was carried over with the effluent. No detectable amounts of molybdenum were found in the pulp. A hydrogen peroxide load of 5 kg/adt pulp was used during the whole trial. Residuals of peroxide were maintained in the system so that the Mo was kept in solution. Such control was done in the press filtrates.

For the evaluation of pulp physical and mechanical properties, four levels of beating were used (0, 750, 1,500, and 3,000 revolutions) in a PFI mill. All pulp quality parameters including physical, mechanical, chemical, optical, and morphological essays, were carried out according to TAPPI standard procedures. Effluent AOX loads were measured before and after the treatment station and before disposal to the river. The AOX and OX determinations in the effluent and pulp were done according to the SCAN W9:89 and P69:94 standard procedures, respectively, and were carried out in a Euroglass analyzer.

RESULTS AND DISCUSSION

Optimization of the Molybdenum Activated Peroxide Stage (P_{Mo})

Figure 3 shows that pulp kappa and HexA groups removal increased with increasing P_{Mo} stage temperature, time, and molybdenum dose. These parameters showed poor correlation with molybdenum dose, with *p-values* not being significant (ns) at 5% probability, regardless of time and temperature. It is apparent that Mo doses above 0.1 kg/adt had little effect on kappa and HexA groups removal. The positive effect of raising the temperature from 75 to 90 °C on kappa and HexA groups removal became less evident at long retention times. The significant effect of temperature seen at two hours reaction became almost not perceptible at four hours. Hence, two hours reaction at 90 °C seems to represent the best compromise. Table 4 shows that under the more severe conditions (90 °C, 4 h, 0.1kg/adt Mo) the P_{Mo} stage decreased kappa number by 7.5 units, while the acid stage decreased it by only 3.4 units. The greater part of the kappa number removal during the P_{Mo} stage was indeed from HexA groups. Of the 7.5 kappa units removed, about 5.3 derived from pulp HexA groups. It was assumed that 10 mmol/kg of HexA groups corresponds to about one kappa unit (Vuorinen et al. 1996).

Table 4. Composition of Kappa Number Removed across the P_{Mo} Stage (10 kg H_2O_2/adt Pulp, 0.1 kg/adt Mo, 11% Consistency and pH 3.5) and A Stage (11% Consistency, pH 3.5, no Mo).

Treatment	Kappa Units Removed		
	HexA groups*	Lignin**	Total (HexA groups + Lignin)
Acid Stage	2.0	1.4	3.4
P_{Mo} Stage	5.3	2.2	7.5

* HexA groups kappa = 10 mmol/kg of HexA groups is equivalent to one kappa unit (Vuorinen et al., 1996).
**Lignin kappa = total kappa units – HexA groups kappa units.
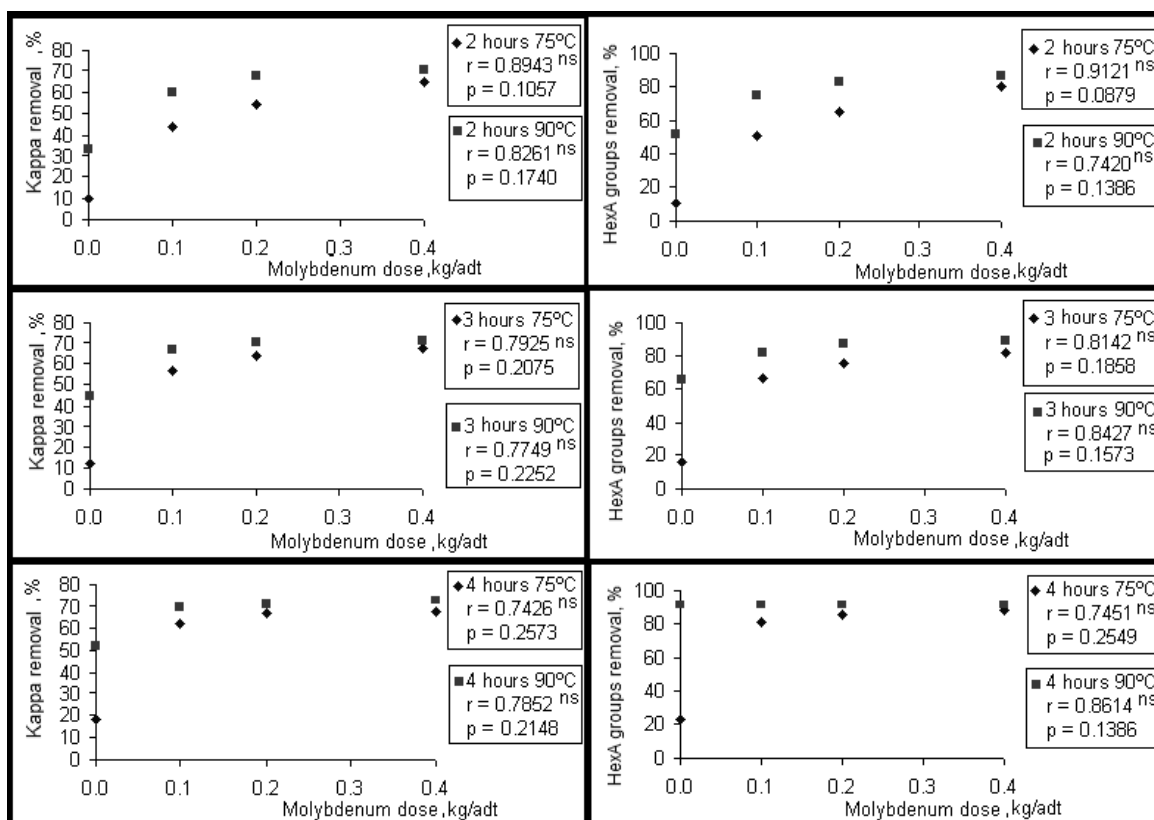
r: correlation coefficient; p: *p*-value; ns: non-significant at 5% probability.

Fig. 3. Effect of P_{Mo} stage time, temperature, and molybdenum dose on kappa and HexA groups removal (10 kg H_2O_2/adt pulp, 11% consistency, pH 3.5).

The reaction of the peroxymolybdate complex with the hexenuronic acids likely occurs through the formation of the epoxide with the double bond of these acids and the further decomposition of the complex, resulting in formic acid (Hämäläinen et al. 2003). According to Heikkilä *et al*. (1998), the peroxyacids can react with hexenuronic acids linked to xylans. The reactions may involve both nucleophilic and electrophilic attack. In the electrophilic attack there occurs hydroxylation of the double bond, and in the nucleophilic, the hydroxylated compounds are first hydrolyzed and converted to carbonyl groups, which are further oxidized by nucleophilic attack.

The effect of the P_{Mo} stage on pulp lignin content was small but significant (2.2 kappa units removal). The P_{Mo} effect on lignin has been attributed (Sundman 1988) to removal of lignin fragments resistant to oxygen delignification, such as biphenyl groups, which are mainly demethoxylated in the P_{Mo} stage. The peroxymolybdate can react also with olefin (Fig. 4), involving a reversible coordination of the metal with the olefin, with displacement of one bond (Mimoun 1980). In the complexation, the olefin loses its nucleophilicity due to the lack of bonding capacity of the metal *d* shell. The electrophilic olefin is then attacked by the nucleophilic oxygen by a 1-3 dipolar mechanism. The reaction rate increases with decreasing pH since under acidic conditions the epoxide is hydrolyzed to the corresponding glycol.
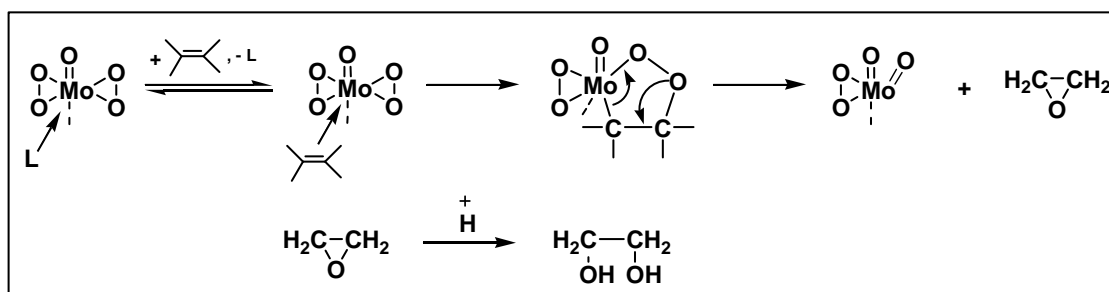
Fig. 4. Reaction of olefin with peroxymolybdate (Mimoun 1980)

Figure 5 shows that viscosity loss increased with increasing P_{Mo} stage temperature, time, and molybdenum dose, but no significant correlations (ns) were observed between viscosity loss and these parameters. The most significant negative effect on viscosity was caused by Mo dose up to a charge of 0.1 kg/adt. The effect of time was rather small, and temperature had a more significant effect in the reference pulp (acid treated) than in the P_{Mo} treated ones. The P_{Mo} stage improved pulp brightness significantly (Fig. 5).
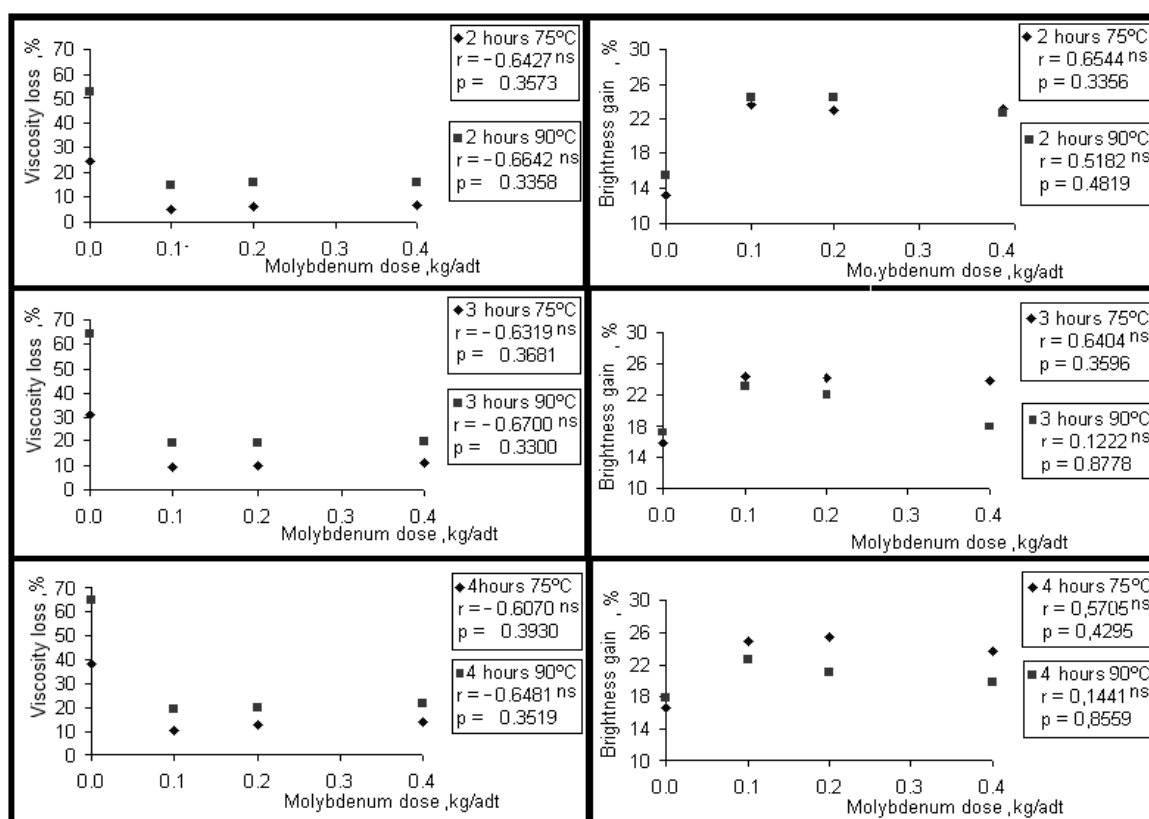
r: correlation coefficient; p: *p*-value; ns: non-significant at 5% probability.

Fig. 5. Effect of P_{Mo} stage time, temperature and molybdenum dose on viscosity loss and brightness gain (10 kg H_2O_2/adt pulp, 11% consistency, pH 3.5)

At the 0.1 kg/adt Mo dose, 2 h, and 90 °C, an 11% ISO brightness gain was achieved in relation to the reference acid stage without Mo. This gain is attributable to the removal of the 2.2 kappa units derived from lignin, since the removal of HexA groups should not affect brightness. The correlation between brightness gain and Mo dose was quite low and not significant at 5% probability. In fact, brightness gain reached a peak at the 0.1 kg/adt Mo dose and then decreased. A possible explanation for this finding is that at very high Mo doses, the severe attack of the molybdenum-diperoxi complex on HexA groups leads to the formation of chromophores, thus decreasing brightness. Increasing time from 2 to 4 h also decreased brightness gain, particularly at 90 °C. Likely, the more severe condition triggered lignin darkening reactions.

Sodium and ammonium molybdate salts were compared as activators in the P_{Mo} stage. They were evaluated under two reaction temperatures, 90 and 95 °C (Fig. 6). No significant differences in kappa removal were observed between the P_{Mo} stages run with the sodium or ammonium salts, but better efficiencies were achieved at the temperature of 95 °C, as should have been expected. HexA groups removal was slightly lower (4% less) for the sodium salt at the 90 °C temperature. In the experiments 10 kg H_2O_2/adt pulp was used according to values previously reported in the literature (Eckert 1982; Suchy and Argyropoulos 2002).
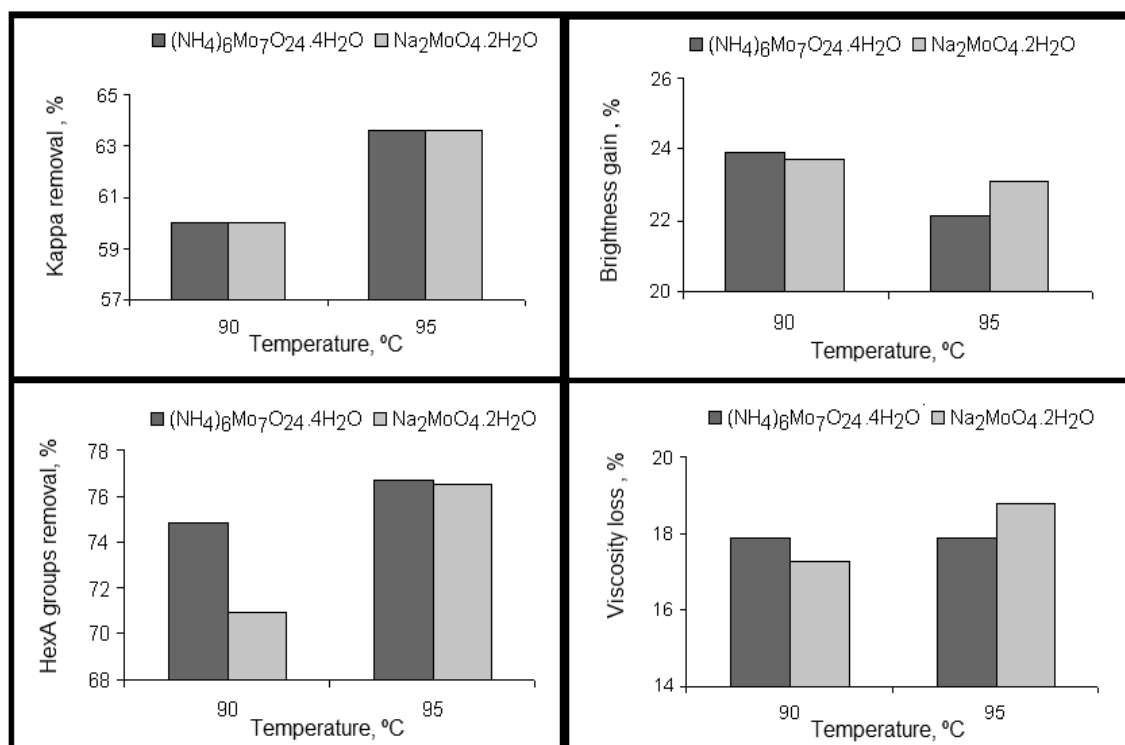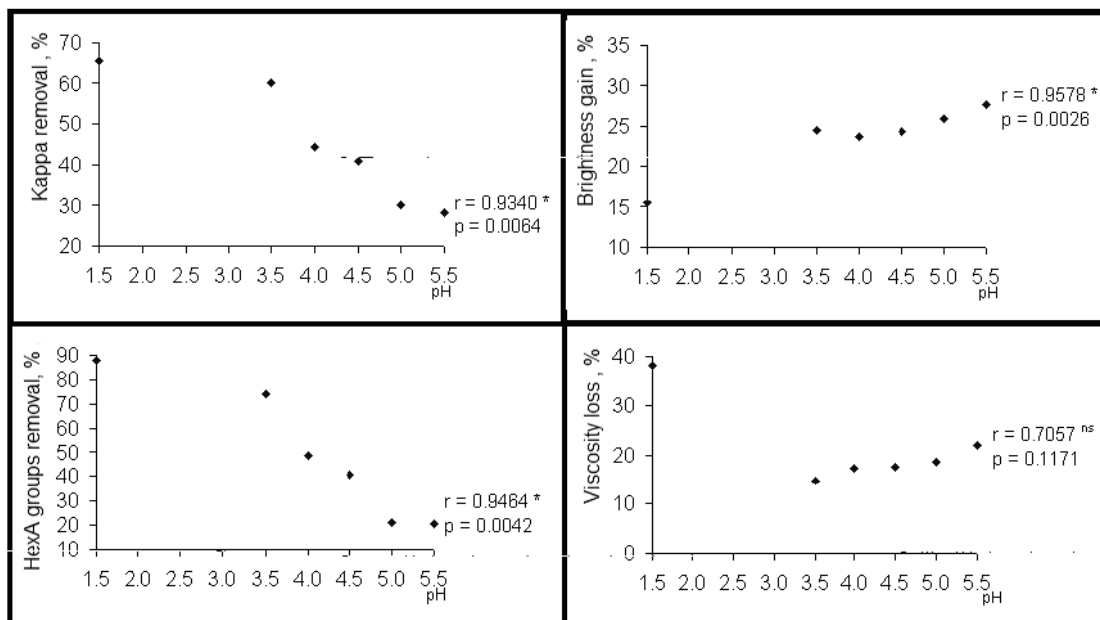

Fig. 6. Effect of P_{Mo} stage molybdenum source (sodium or ammonium molybdate) on kappa and HexA groups removal, brightness gain, and viscosity loss (10 kg H_2O_2/adt, 0.1 kg Mo/adt, 11% consistency, pH 3.5 and 2 h)

According to results in Figs. 3 and 5, the optimal operational conditions to run the P_{Mo} stage were 90°C, 2 h, and 0.1 kg/adt molybdenum. These conditions were used for optimization of reaction pH (1.5-5.5), and peroxide dose (3-10 kg/adt pulp). Figure 7 shows that increasing pH in the range 1.5-5.0 decreased kappa and HexA group removal significantly, at 5% probability. For these parameters the correlations were negative at 0.4-0.6% significance levels (p=0.004-0.006). Pulp brightness correlated positively and significantly (p=0.003) with pH in the 3.5-5.5 interval. Viscosity loss also correlated positively but not significantly (p=0.12) with pH. It is apparent that increasing pH from 3.5 to 5.5 hurt most of the important parameters, with the only benefit being a slight increase in pulp brightness. Therefore, this pH was considered optimal for the subsequent studies. The pH value of 1.5 resulted in pulp of very low brightness and viscosity, although it showed the highest efficiency to remove kappa number and HexA groups. The pH values in the range of 1.5-3.5 were not investigated in this study but are worth trying.

Figure 8 shows the behavior of the P_{Mo} stage as related to the H_2O_2 dose. The values of kappa drop and HexA groups removal correlated positively but not significantly (ns) with peroxide dose. The benefits of peroxide tended to decrease rather sharply over the 5kg/adt H_2O_2 dose. Both brightness gain and viscosity loss correlated positively and significantly with peroxide dose (p=0.03-0.04). These results were expected and reflected the greater formation of the active species, the molybdenum-diperoxi complex. The choice of H_2O_2 dose is entirely dependent on process economics. In this study the choice was to apply a 5 kg/adt charge because the 10 kg/adt proved less economically attractive in our previous studies. In other words, the kappa drop and brightness gain improvements when the H_2O_2 dose is increased from 5 to 10 kg/adt are not sufficiently high to pay for the additional peroxide. Another interesting point is related to the lower degradation of carbohydrates at the 5 kg/adt dose.

r: correlation coefficient; p: *p*-value; ns: non-significant at 5% probability.
Fig. 7. Effect of P_{Mo} stage pH on kappa and HexA groups removal, brightness gain and viscosity loss (10 kg H_2O_2/adt pulp, 0.1 kg Mo /adt pulp, 11% consistency, 90 °C, 2 h)
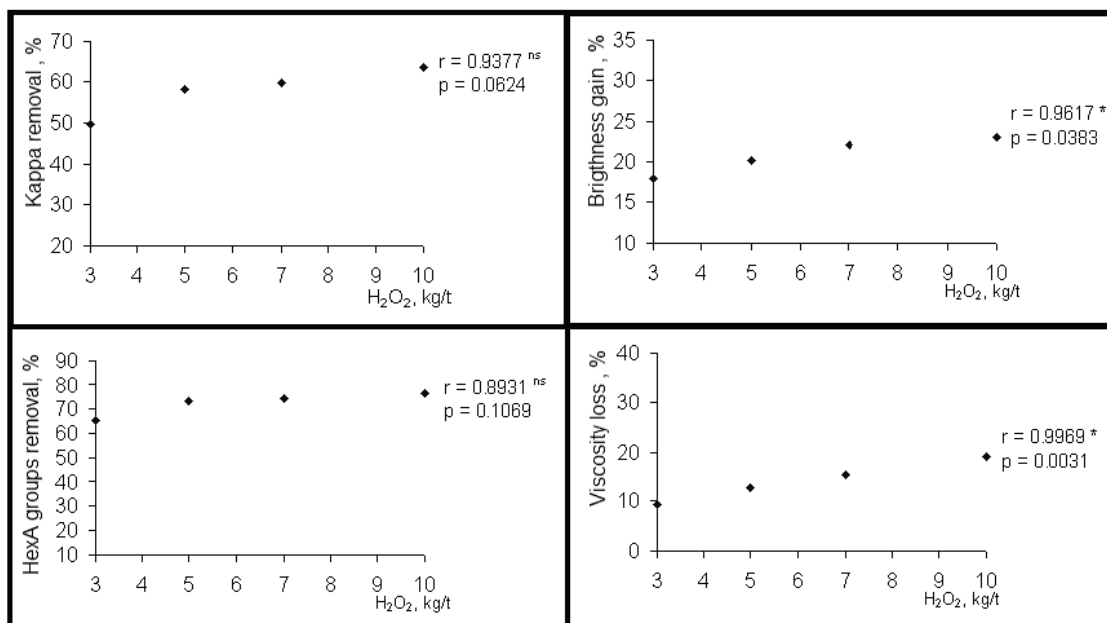
r: correlation coefficient; p: *p*-value; ns: non-significant at 5% probability.
Fig. 8. Effect of P_{Mo} stage hydrogen peroxide dose on kappa and HexA groups removal, brightness gain and viscosity loss (0.1kg Mo/adt pulp, 11% consistency, pH 3.5, 90 °C, 2h)

Application of the Molybdenum Activated Peroxide Stage (P_{Mo}) in the Light-ECF AZDP Sequence

After the optimization of the P_{Mo} stage, the replacement of the hot acid stage (A) of the AZDP sequence by the P_{Mo} stage was evaluated in laboratory scale. The P_{Mo} stage decreased kappa number by about 3 units more than the A stage (Table 5). As a consequence, the kappa number after the Z stage was also reduced, but not in the same proportion (2.1 units). This behavior had been observed before by other workers (Mounteer et al. 1991; Hämäläinen et al. 2003). It is worth noting that at least one half of the three kappa unit difference observed can be ascribed to HexA groups removal differences in the two cases. While the HexA groups content after the A-stage was ~30 mmol/kg, the one after the P_{Mo} stage was ~16 mmol/kg. This difference represents approximately 1.5 kappa units (Vuorinen et al. 1996).

The pulp brightness after the P_{Mo} stage was 6% ISO higher in relation to the A stage, and that reflected on the brightness across the whole sequence (Table 5). In fact, a 3.7% higher ISO brightness was obtained after the D stage of the sequence P_{Mo}ZDP, despite the fact that it used 2.3 kg ClO_2 less per air-dry ton of pulp. Final brightness was similar for the AZDP and P_{Mo}ZDP sequences, but the hydrogen peroxide dosed to the last stage was much lower for the sequences having the P_{Mo} stage. The final bleached pulp viscosities were slightly higher for the P_{Mo}ZDP sequence in relation to the reference, reflecting its lower demand of oxidants to reach full brightness. No significant differences were observed in brightness stability between the two pulps.

The chlorinated organic content of pulps and effluents derived from the P_{Mo}ZDP sequence were much lower than those of the reference sequence. The pulp OX and effluent AOX values were 25-30% and 20-25% lower, respectively. These results are

explained by the high efficiency of the P_{Mo} stage in removing pulp HexA groups, which are the major source of AOX during bleaching of eucalyptus pulps (Costa and Colodette 2007; Bjorklund et al. 2002; Gomes et al. 2007). The bound Cl content of the $P_{Mo}ZDP$ bleached pulps were 50-60 g Cl⁻/adt, which characterizes the so-called light-ECF pulps.

The hydrogen peroxide doses applied to the last bleaching stage (P1, P2, and P3) were varied so that the brightness targets 90, 91, and 92% ISO could be achieved. The doses of ClO_2 and hydrogen peroxide were lower for the $P_{Mo}ZDP$ sequence in relation to the reference. For example, for the target brightness of 90% ISO, the $P_{Mo}ZDP$ sequence used 2.3 kg/adt less chlorine dioxide in the D stage and 2.5 kg/adt less hydrogen peroxide in the P stage than the AZDP one. Of course, the former sequence used 5 kg/adt H_2O_2 and 0.06 kg/t Mo in the P_{Mo} stage, which was not required in the reference case. In order to compare the two sequences more adequately, the total active chlorine consumption was calculated, and the results indicated that the $P_{Mo}ZDP$ sequence is less demanding for oxidants than the reference, regardless of the brightness target (Table 5).

Mill Trial Results

The P_{Mo} stage optimized according to the results previously discussed was evaluated in a mill scale operation with 1200 tpd production capacity. The industrial bleach plant was operating with the AZDP sequence and replaced the A stage by the P_{Mo} stage. After process stabilization, a decrease in chlorine dioxide was observed, and hydrogen peroxide and sodium hydroxide demands decreased by 1.0, 1.7, and 2.8 kg/adt pulp, respectively (Table 6). The reduction in oxidant requirements reflects the higher kappa removal in the P_{Mo} stage in comparison to the conventional acid stage. Sodium hydroxide demand diminished due to lower loads of chlorine dioxide and hydrogen peroxide applied to D and P stages. The chemical cost analysis indicates that the overall cost was about U\$1.00/adt lower during the P_{Mo} trial period, reflecting the use of less total active chlorine and caustic (Table 6).

The average pulp chemical, optical, morphological, physical, and mechanical characteristics during the reference and P_{Mo} trial periods are shown in Tables 7 and 8. In regard to chemical and optical properties, no significant differences were seen between the pulps produced during the two periods. In relation to morphological properties it is apparent that the pulp produced during the P_{Mo} trial period showed a decrease in pulp fines content. An important behavior observed in the physical essays was the decreased air resistance (inverse porosity) and increased Klemm capillarity and Bendtsen smoothness values of pulp sheets (Table 7). These property changes were all related to the lower fines content of the pulp produced during the P_{Mo} trial and they were all positive since they improve eucalyptus pulp quality for its main applications, which are tissue and printing and writing grades. In relation to the mechanical essays, the samples collected during the P_{Mo} trial period showed slightly lower mechanical properties than those of the reference period, for the same number of PFI revolutions, but the differences were not significant. The AOX in the effluent discharged to the river (end-of-pipe) decreased by about 20% during the mill trial, reflecting the lower usage of chlorine dioxide and the fact the P_{Mo} stage was highly effective to remove HexA groups, which are the major source of organically bound chlorine (Costa and Colodette 2007). Notice that molybdenum was not detected in the bleached pulps (Table 8).

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Table 5. Conditions and Results for Light-ECF Bleaching with the Sequences AZDP and $P_{Mo}ZDP$

Conditions and Results	AZDP						$P_{Mo}ZDP$					
	A	Z	D	P1*	P2*	P3*	P_{Mo}	Z	D	P1*	P2*	P3*
Time, min	120	1	40	90	90	90	120	1	40	90	90	90
Temperature, °C	95	40	85	90	90	90	95	40	90	90	90	90
End pH	3.2	2.9	4.2	9.9	9.6	10.3	3.5	2.8	4.5	10	9.8	10.5
Consistency, %	11	11	11	11	11	11	11	11	11	11	11	11
Mo, kg/adt	-	-	-	-	-	-	0.1	-	-	-	-	-
H_2O_2, kg/adt	-	-	-	3.5	6	9	5	-	-	1	2	6
O_2, kg/adt	-	-	-	-	-	-	-	-	-	-	-	-
NaOH, kg/adt	-	-	7	6.5	7.5	9	-	-	5.8	3	4	5
O_3, kg/adt	-	4	-	-	-	-	-	4	-	-	-	-
$MgSO_4.7H_2O$, kg/adt	-	-	-	2	2	2	-	-	-	2	2	2
H_2SO_4, kg/adt	7.5	2	-	-	-	-	7	2	-	-	-	-
ClO_2, kg/adt	-	-	6.1	-	-	-	-	-	3.8	-	-	-
Total Act. Chlorine, kg/adt**	-	-	-	41.1	46.3	52.6	-	-	-	40.3	42.4	50.8
Oxidant Consumed, %	-	77.4	100	82.5	85.6	85.8	100	80.2	100	97.2	80.7	75.2
Kappa Number	7.6	3.4	-	-	-	-	4.6	1.3	-	-	-	-
HexA groups, mmol/kg	29.7	9.79	2.23	-	-	-	15.8	4.02	1.18	-	-	-
ISO brightness, %	56.2	71.8	84.4	90.5	91.1	92.1	62.2	77.6	88.1	89.8	90.8	91.9
ISO bright. reversion, %	-	-	-	1.4	1.6	1.7	-	-	-	1.4	1.4	1.5
Viscosity, mL/g	1025	889	824	786	718	691	999	888	851	844	805	786
Pulp OX, g/adt	-	-	-	85	83	80	-	-	-	61	60	58
Effluent AOX, g/adt***	-	-	-	90	94	98	-	-	-	72	72	75

*P1, P2 and P3 refer to peroxide stages carried out with different peroxide doses.
**Total active chlorine (kg/adt) = ClO_2 (kg/adt)*2.63 + O_3 (kg/adt) * 4.44 + H_2O_2 (kg/adt) * 2.09.
***For the whole sequence.

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Table 6. Chemical Cost Analyses for the Reference and P_{Mo} Trial Periods.

Chemical	Unit Price, US$/kg	Reference Period (Feb. 2005), AZDP		P_{Mo} Mill Trial Period (March 2005), P_{Mo}ZDP	
		Reagent, kg/adt	Cost, US$/adt	Reagent, kg/adt	Cost, US$/adt
Chlorine dioxide	1.00	9.30	9.30	8.30	8.30
Hydrogen peroxide	1.05	12.2	12.8	10.50	11.0
Ozone	1.52	4.80	7.30	4.70	7.15
Sulfuric acid	0.16	8.60	1.38	8.70	1.39
Sodium hydroxide	0.57	11.3	6.44	8.50	4.85
Sodium molybdate, as Mo	60.0	0.00	0.00	0.06	3.50
Total Cost, US$/adt	-	-	37.2	-	36.3

Table 7. Physical and Mechanical Properties of Pulps for the Reference (Feb 1-28, 2005) and P_{Mo} Trial (March 1-31, 2005) Periods vs. Pulp Refining Degrees

Reference Period - AZDP				
PFI revolutions	0	750	1500	3000
Drainage resistance , °SR	22	29	38	62
Sheet density, kg/m³	547	658	727	806
Bulk, cm³/g	1.83	1.52	1.38	1.24
Air resistance, s/100 mL	1.74	6.43	20.0	197
Bendtsen smoothness, mL/min.	318	157	95.7	41.4
Tensile index, N.m/g	24.4	55.1	73.7	90.1
Stretch, %	1.78	3.10	3.76	4.15
Tensile energy absorption, mJ/g	316	1199	1875	2518
Burst index, kPa.m²/g	0.99	2.99	4.53	6.03
Tear index, mN.m²/g	4.30	8.42	8.99	8.41
Opacity, %	80.4	77.1	74.7	70.9
Capillarity Klemm, mm/10 min.	93.9	59.0	40.7	18.0
Water retention values, %	163	203	231	264
P_{Mo} Trial Period - P_{Mo}ZDP				
PFI revolutions	0	750	1500	3000
Drainage resistance , °SR	22	29	37	59
Sheet density, kg/m³	564	657	717	792
Bulk, cm³/g	1.77	1.52	1.39	1.26
Air resistance, s/100 mL	2.14	5.54	13.0	112
Bendtsen smoothness, mL/min.	365	173	113	52.7
Tensile index, N.m/g	24.3	51.9	69.4	90.2
Stretch, %	1.66	3.02	3.74	4.02
Tensile energy absorption, mJ/g	287	1097	1772	2434
Burst index, kPa.m²/g	1.09	2.91	4.19	6.10
Tear index, mN.m²/g	3.97	8.27	8.50	8.55
Opacity, %	80.4	76.8	74.1	70.7
Capillarity Klemm, mm/10 min.	87.0	65.0	55.3	32.7
Water retention values, %	167	210	215	251

Table 8. Chemical, Morphological, and Optical Properties of Pulps Produced during the Reference (Feb 1-28, 2005) and P_{Mo} Trial (March 1-31, 2005) Periods

	Reference Period AZDP	P_{Mo} Trial Period P_{Mo}ZDP
ISO brightness, %	89.7	89.8
ISO brightness reversion, %	1.72	1.70
Viscosity, dm³/kg	771	761
Organically bound chlorine, g/adt	90	68
Dirt count, mm²/kg	1.06	0.98
DCM extractives, %	0.07	0.06
Ash, %	0.54	0.59
Pentosans, %	13.9	14.1
Molybdenum, mg/kg	not detected	not detected
Coarseness, mg/100m	6.50	6.72
Fiber /g, n° x 10^6	22.9	23.5
Average fiber length, mm	0.82	0.79
Fines (Britt Jar), %	9.92	6.64
AOX of treated effluent, mg/L*	3.08	2.45

*measured at effluent discharged to water stream (end-of-pipe).

CONCLUSIONS

1. Optimum operational conditions to bleach eucalyptus pulp with molybdenum activeated peroxide (P_{Mo} stage) are: 90 ºC, 2 h, pH 3.5, 5 kg/adt H_2O_2, and 0.1 kg/adt Mo.
2. The P_{Mo} stage showed greater delignification rate in relation to a conventional acid stage, but most of its effect on kappa number comes from HexA groups removal.
3. When applied to the AZDP sequence in replacement to the A stage, the P_{Mo} stage decreased the total active chlorine demand and the cost to bleach the pulp to full brightness, both in the laboratory and at mill scale.
4. Mill trial results revealed no significant impact of the P_{Mo} stage on morphological, optical, chemical, and physical properties of the bleached pulp.
5. The application of the P_{Mo} stage in the bleach plant decreased pulp OX and effluent AOX by 20-30%.
6. The P_{Mo} stage is technically applicable for production of light-ECF eucalyptus pulps.

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