

EFFECT OF LAST STAGE BLEACHING WITH PERACETIC ACID ON BRIGHTNESS DEVELOPMENT AND PROPERTIES OF EUCALYPTUS PULP

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Investigation of last stage bleaching with peracetic acid is the main subject of this paper. Proper conditions were established to apply peracetic acid as the last bleaching stage of the D(Ep)D/Paa, D_{HT}(Ep)D/Paa, A/D(Ep)D/Paa, D_{HT}/Q(PO)Paa and Z/ED/Paa sequences. In addition, the impact of last stage bleaching with Paa on pulp refinability and strength properties was determined. Peracetic acid was consumed relatively fast when applied as the last stage of ECF bleaching sequences. A reaction time of 120 min at 75 °C and pH 5.0 is seemingly adequate regardless of the Paa dose, in the range of 1-5 kg/odt pulp and bleaching sequence. The optimum dose of Paa depends upon the sequence under investigation. In general the Paa application as last bleaching stage caused slight decrease in pulp viscosity, kappa number and HexA content but had no significant effect on pulp reversion and L*a*b* coordinates. The refinability and bonding strength properties of the pulps bleached with the sequences D_{HT}(Ep)DD and D_{HT}(Ep)D/Paa were quite similar when the pH of the last bleaching stage of both sequences were near 5. These properties improved slightly when Paa bleaching pH was raised to 8.5.

Keywords: Peracetic acid; Bleaching; Eucalyptus pulp; Physical-mechanical properties

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INTRODUCTION

Bleached eucalyptus kraft pulp is becoming the most important source of market pulp. Brazil is the 4th largest producer of wood pulps (12.5 million tons in 2008) and the largest exporter of eucalyptus pulps. Almost the totality of the eucalyptus fibres produced in Brazil is bleached. Overall, the main drivers affecting the choice among bleaching technologies are chemical demand, yield, water consumption, effluent load & treatability, pulp OX, brightness stability, refinability and strength, and capital costs. This latter factor is becoming ever more important since new bleach plants are coming in very large sizes. Technologies that permit for elimination of bleaching stages through shortening of bleaching sequences and/or omission of washing between stages has been much sought after.

Eucalyptus pulps are usually bleached to 90% ISO brightness. Although the bleaching has been successfully done with ECF technology, there are few outstanding matters requiring further research. An adequate choice and combination of chemicals can in principle allow for decreasing capital costs. For example, a strong first bleaching stage

applied to eucalyptus pulps can eliminate lignin almost completely, since more than half of the pulp kappa number after the oxygen delignification is comprised of HexA. A pulp containing almost no lignin could in principle be further bleached with only one additional stage, if such stage is well established. As strong first bleaching stage could in principle be picked amongst a variety of choices that include D_0 , D_{HT} , A_{HT}/D , D/Q or Z/E . However, this matter is not well settled.

The final bleaching (brightening stage) should ideally use two different chemistries. The state-of-the-art has been the DP technology, which requires two bleaching stages since washing between D and P is required. The D/D, DD and DED approaches have also been much used. Although D/D approach allows for omission of a washer between stages, it has not been successful due to the similar chemistry of the stages. The DED technology changes chemistries among stages, but it not used for eucalyptus pulps. The D/Paa strategy is compelling in regard to capital investment, since washing between D and Paa can be omitted and yet the chemistries of the two stages are different.

The main objectives of this investigation include: (1) the establishment of proper conditions to apply peracetic acid as the last bleaching stage of ECF sequences, including $D(Ep)D/Paa$, $D_{HT}(Ep)D/Paa$, $A/D(Ep)D/Paa$, $D_{HT}/Q(PO)Paa$, and $Z/ED/Paa$ and (2) the evaluation of the impact of last stage bleaching with peracetic acid on refinability and physical-chemical properties of pulps bleached with the $D_{HT}(Ep)DD$ and $D_{HT}(Ep)D/Paa$ sequences.

Literature Survey

Among the peracids, peracetic acid (Fig. 1) is the most studied. Since the end of the 40`s it has been investigated as a bleaching and delignification agent since it is a stronger oxidant than oxygen and hydrogen peroxide. Peracetic acid is commercialized in slightly acid pH and even in low temperatures it is unstable, so it requires frequent standardization before use.

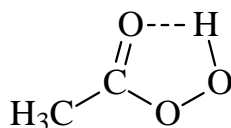


Fig. 1. Peracetic acid (Paa) probable structure

During pulp bleaching, peracids are consumed by lignin/ HexA oxidation reactions and spontaneous decomposition, catalyzed by transition metals (Koubek et al. 1963; Yuan and Van Heiningen 1997). The peracetic acid spontaneous decomposition involves oxygen formation, in accordance to the mechanism proposed by Koubek et al. (1963) (Fig. 2).

The degradation reactions of peracetic acid and hydrogen peroxide catalyzed by transition metals, with the hydroxyl radicals formed further reacting with the peracetic acid (Ball and Edwards 1956; Zhang et al. 1998).

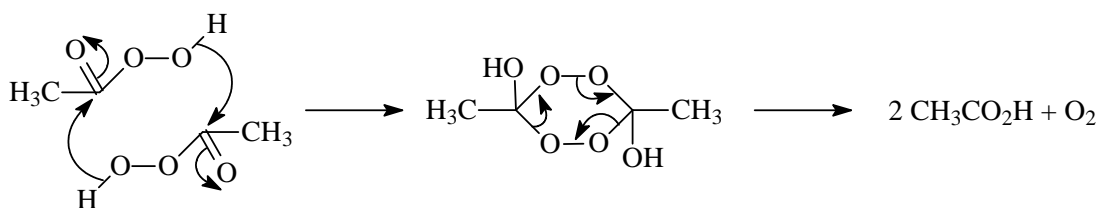


Fig. 2. Peracetic acid decomposition reaction (Koubek et al. 1963)

The peracetic acid can react with lignin mainly through two mechanisms: (1) electrophilic addition and substitution and (2) nucleophilic reactions (Chang 1995). Many authors suggest that the initial reaction between Paa and lignin involves electrophilic hydroxylation in active positions of the aromatic ring, ortho- and para, and oxygenated groups, as shown in Fig. 3. The hydroxylation stage is probably the determinant stage in reaction velocity and some studies propose that it occurs effectively by OH group transference from the peracid, and not by reaction with hydroxyl radicals.

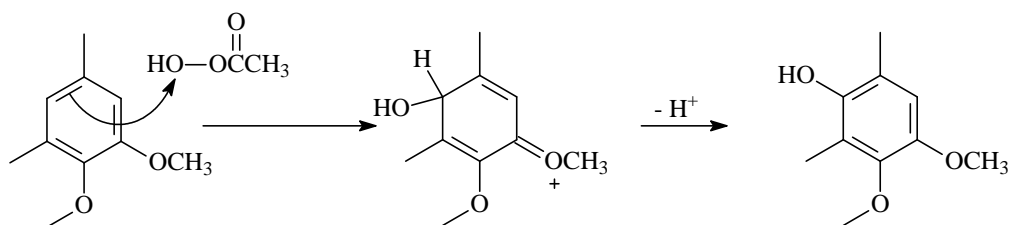


Fig. 3. Aromatic structures hydroxylation by Paa (Johnson 1980)

Aromatic ring hydroxylation can lead to its demethoxylation through an intermediate hemiacetal (Fig. 4). Demethoxylation can lead to quinone formation, and quinones are generally oxidized faster than the initial compounds (Johnson 1980). An increase in Paa concentration promotes higher demethoxylation, generating more o-quinones (Ni and D'entremont 1997). As the quinones show dark color, this author suggested that the peracetic acid charge applied in pulp bleaching must be optimized in order to maximize brightness. In many cases, just p-quinones survive the Paa oxidation and can be isolated, whereas o-quinones are rapidly oxidized by Baeyer-Villiger reactions, creating water soluble products (Davigde et al. 1958). In Paa reactions with phenols and its methyl ethers there occurs formation of quinones, hydroquinones, quinols, muconic acids, and lactones (Davigde et al. 1958; Ni and D'Entremont 1997; Brasileiro 1999).

In Fig. 5, it is shown that the lignin aromatic structures final oxidation stages involve the oxidative cleavage of the rings from quinones, leading to lactones and muconic acids formation. The aromatic ring opening generally occurs between adjacent carbonyl groups, through the hydrolysis of an intermediary cyclic anhydride, formed by the introduction of oxygen, through the Baeyer-Villiger nucleophilic reaction has also been reported (Marshall and Naylor 1974; Brasileiro 1999).

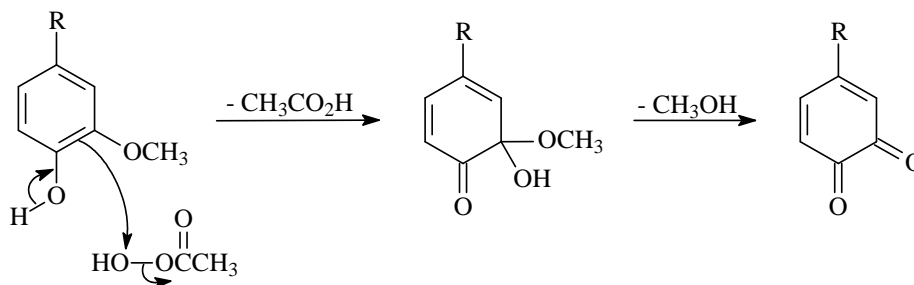


Fig. 4. Aromatic structures demethoxylation by Paa (Ni and D'Entremont 1997)

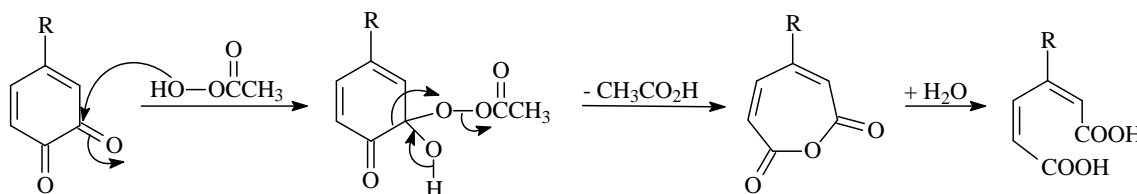


Fig. 5. Aromatic rings opening by Paa, with the formation of muconic acids (Ni and D'Entremont 1997)

In pulp treatment with Paa, the aromatic ring opening makes the oxidized lignin more hydrophilic, contributing to its solubilization in the bleaching liquor (Brasileiro 1999). The acid groups formation also favors lignin fragments solubilization, especially during alkaline extraction stages, because of its ionization.

Peracids can also react with uronic and hexenuronic acids groups mainly linked to xylans (Fig. 6). Heikkilä et al. (1998) demonstrated Paa participation in an electrophilic reaction with the double bond in hexenuronic acid, promoting its hydroxylation, as the nucleophilic attack secondary to the carbonylic groups, formed after hydrolysis of the hydroxylated compounds (Fig. 7). These reactions compete with each other, and with electrophilic reactions between Paa and lignin. Thus, previous removal of uronic acids can favor lignin removal and bleaching efficiency with Paa.

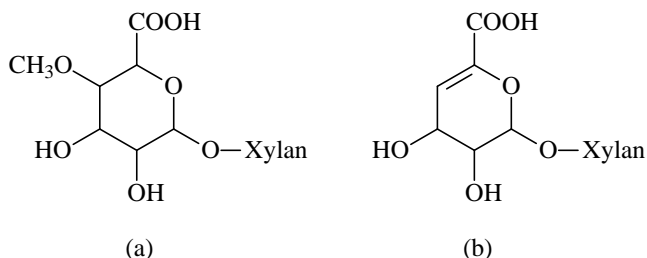


Fig. 6. (a) 4-O-methyl- α -D-glucuronic acid and (b) 4-deoxyhex-4-enuronic acid

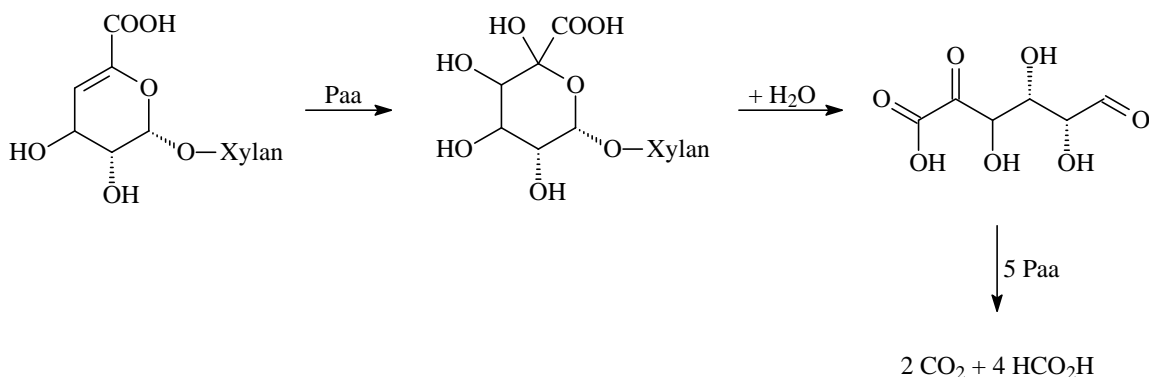


Fig. 7. Hexenuronic acid oxidation by Paa (Heikkilä et al. 1998)

According to results shown by Bailey and Dence (1966) and Hill et al. (1992), the increase in Paa concentration increases pulp delignification. However, higher Paa concentration decreases process selectivity and results in lower viscosity pulps. In neutral or slightly acid pH, the pulp carbohydrate degradation is mainly dependent on Paa concentration (Jääskeläinen and Poppius-Levlin 1998). This degradation is likely caused by reactive species derived from Paa decomposition reactions, which are intensified at higher concentrations of Paa. Another type of reaction that may contribute to carbohydrate depolymerization is the acid hydrolysis in low pH that involves glycosidic linkages cleavage. Cellulose degradation during peracetic acid bleaching can be minimized by pulp pretreatment to remove transition metals (acid washing and chelation) and proper optimization of reaction conditions including pH, temperature, oxidant concentration, and reaction time (Hill et al. 1992).

According to (Barna et al. 1996), peracetic acid shows good potential to displace chlorine dioxide in ECF bleaching of chemical pulps, particularly for pulp mills that are ClO_2 deficient. Furthermore, it is also advantageous to minimize effluent load and toxicity.

EXPERIMENTAL

An industrial oxygen delignified eucalypt kraft pulp (kappa number 10, brightness 55.7% ISO, viscosity 18.3 mPa.s, HexA 49.2 mmol/kg, 25.7 ppm Fe, 13.3 ppm Mn, and 1.2 ppm Cu) was used throughout the study. Except when otherwise stated, *pro analysis* reagents were used throughout the study. Equilibrium peracetic acid was prepared according to the procedure described by Brasileiro et al. (2002) at a concentration of 20% and contained about 4% unreacted hydrogen peroxide. The bleaching sequences described in Table 1 were compared. In all cases a final chlorine dioxide (D_2) or hydrogen peroxide (P) stage was replaced with a Paa stage. In most cases the Paa stage was applied after the D_1 stage without inter-stage washing. Oxidant charges were optimized in the D_1 , P, and Paa stages in order to achieve 90% ISO final brightness.

Table 1. Bleaching Sequences Evaluated

Bleaching sequence reference	Bleaching sequence evaluated
D(Ep)DD	D(Ep)D/Paa
D(Ep)DP	D(Ep)D/Paa
A/D(Ep)DD	A/D(Ep)D/Paa
A/D(Ep)DP	A/D(Ep)D/Paa
D _{HT} (Ep)DD	D _{HT} (Ep)D/Paa
D _{HT} (Ep)DP	D _{HT} (Ep)D/Paa
D _{HT} /Q(PO)	D _{HT} /Q(PO)Paa
Z/EDP	Z/ED/Paa

Hot chlorine dioxide (D_{HT}), pressurize peroxide (PO), hot acid hydrolysis (A), and ozone (Z) bleaching stages were carried out in a model Mark V mixer/reactor (Quantum Technologies Inc.). Conventional alkaline extraction (E), extraction with peroxide (Ep), peroxide (P), chlorine dioxide (D), and peracetic acid (Paa) beachings, as well as chelation treatment (Q) were carried out in polyethylene bags. The main bleaching conditions used are presented in Table 2. After each bleaching stage, run in duplicate, the samples were washed with excess distilled water, except in those cases where the washing step was deliberately omitted. Reagent doses are expressed in kg per oven dried ton of pulp (odt). Concentrations of conventional oxidants and residuals were measured according to Kraft (1967). Concentrations of peracetic acid stock solution and residuals were measured according to Greenspan (1948), through titration of the hydrogen peroxide contamination with ammonium ceric sulfate, followed by iodometric titration of the peracetic acid.

Pulp kappa number, viscosity, brightness and brightness stability values were measured according to TAPPI standard procedures. Hexenuronic acids were measured by UV after their conversion into furoic acid, using acid hydrolysis with formic acid (Vuorinen et al. 1999). Bleached pulp samples were refined in a PFI mill at 0, 1000, 2000, and 2500 revolutions and tested for physical-mechanical properties according to TAPPI (1998) standard procedures. Bleaching chemical costs were obtained by multiplying chemical doses (kg/odt pulp) by chemical prices (US\$/kg chemical). Relative bleaching chemical costs were derived by considering the lowest chemical costs as 100 and whatever higher or lower number as a percentage over this value. The D_{HT}(Ep)DD was the sequence with the lowest bleaching cost. The following chemical prices (US\$/kg of product at 100%) were used to calculate bleaching costs: ClO₂=1.00, H₂O₂=0.85, NaOH=0.50, H₂SO₄=0.15, O₃=1.80, CH₃CO₃H=1.80, DTPA=1.50. Total active chlorine demands were calculated by multiplying the chemical consumptions (kg/odt) by the equivalent active chlorine contained in each one of the oxidants used in the bleaching sequence. The following conversion factors were used: 1 kg/odt ClO₂ = 2.63 kg active Cl₂, 1 kg/odt H₂O₂ = 2.09 kg active Cl₂, 1 kg/odt CH₃COOH = 0.934 kg active Cl₂ and 1 kg/odt O₃ = 4.44 kg active Cl₂.

Table 2. General Bleaching Conditions Utilized

Bleaching Conditions	Bleaching Stage										
	D ₀	A/D	D _{HT}	D/Q	Z/E	(Ep)	D ₁	D ₂	(PO)*	P	Paa*
Consistency, %	10	11/10	10	11/10	40/10	10	10	10	10	10	9
Temp, °C	60	95/90	95	95/90	50/60	80	80	80	90	80	75
Time, min	30	110/10	120	120/30	1/30	90	120	120	120	120	30-120
Pressure, kPa	-	-	-	-	-	-	-	-	500	-	-
Kappa Factor (KF)	0.16	0/0.16	0.16	0.26/0	-	-	-	-	-	-	-
End pH	2.7	2.7/2.7	2.7	2.7/6.5	2.7/10	10.5	3.8	5.5	10	10	5
H ₂ O ₂ , kg/odt	-	-	-	-	-	3	-	-	5-50	2	-
Paa, kg/odt	-	-	-	-	-	-	-	-	-	-	1-5
ClO ₂ , kg/odt	6.1	6.1	6.1	9.9	-	-	2-6	0.8	-	-	-
O ₃ , kg/od	-	-	-	-	6/0	-	-	-	-	-	-
DTPA, kg/odt	-	-	-	0/1.5							

*Oxidant charges were optimized in the D₁, P/(PO) and Paa stages in order to achieve 90% ISO brightness

RESULTS AND DISCUSSION

Paa Performance as Last Bleaching Stage

The D(Ep)DD sequence was the standard bleaching process for eucalyptus pulp mills in the nineties. Currently, there exist a significant number of bleach plants operating with this technology. There has been a trend towards replacing the D₂ stage by a peroxide stage in order to improve pulp brightness stability and refinability. Another possibility is using peracetic acid to replace the D₂ stage. Washing between D₁ and Paa stage is optional, since these two stages operate under similar pH conditions.

One of the objectives of the work was to establish proper conditions for applying peracetic acid as the last bleaching stage of the ECF sequences listed in Table 1, aiming at 90% ISO brightness. Only Paa dose (1-5 kg/odt pulp) and reaction time (30-120 min) were evaluated, with temperature (75°C), pH (5.0), and reaction consistency (9%) maintained constant in all runs.

Optimization of Paa dose and reaction time

Pulp samples were pre-bleached with the D(Ep)D, A/D(Ep)D, D_{HT}(Ep)D, D_{HT}/Q(PO), and Z/ED sequences to brightness values in the range of 86.2-88.2% ISO. These samples were then treated with a Paa stage under the aforementioned conditions. The results in Fig. 8 show the consumption of peracetic acid under these conditions in the sequence D(Ep)D/Paa. It is observed that regardless of dose and reaction time, the Paa consumption reached values over 60%. There was a trend of increasing Paa consumption with increasing time and decreasing Paa dose. For the sequence starting with a D₀ stage, there was no significant effect of washing between D₁ and Paa stages on peracetic acid consumption. Considering that the highest Paa consumption was achieved at the reaction time of 120 min, this time was selected to run the Paa stage for the various sequences.

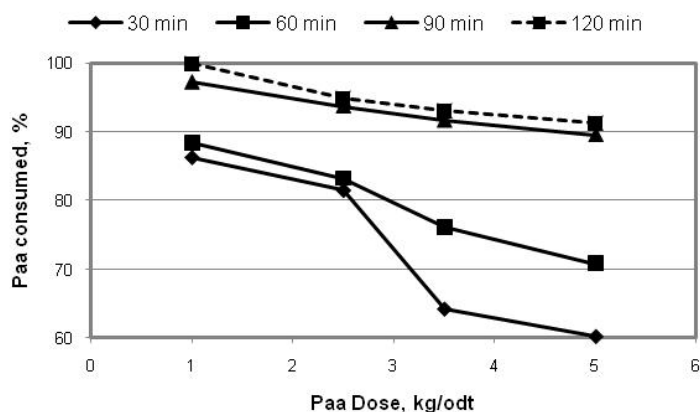


Fig. 8. Effect of Paa dose and reaction time on Paa consumption in the sequence D(Ep)D/Paa (no washing after D₁)

Figures 9 and 10 show the effects of Paa dose and reaction time on brightness development and viscosity loss when applied as the last stage of the D(Ep)D/Paa sequence. Brightness tended to increase with increasing time and Paa dose, with the opposite being verified for pulp viscosity. For the D(Ep)D/Paa sequence, the 90% ISO brightness target was achieved with the dose of 1 kg Paa per ton of pulp over the course of 120 min reaction. The brightness increased from 88.2 to 89.8% ISO, while the pulp viscosity decreased from 18.5 to 13.1 mPa.s. Similar trends were observed for the D_{HT}(Ep)D/Paa sequence, for which 1 kg Paa/odt pulp resulted in a brightness increase of 87.8 to 89.9% ISO (Fig. 11) and a viscosity losses of 15.2 to 10.4 mPa.s (Fig. 12). Viscosity losses are attributable to radical formation from decomposition of the hydrogen peroxide present as contaminant (~4%) in the Paa solution. These significant viscosity losses could have been avoided if distilled peracetic acid were used instead of equilibrium peracetic acid.

The effect of time and reagent dose on Paa stage brightness development when applied to the A/D(Ep)D/Paa sequence is shown in Figure 13. From a brightness of 88.3% ISO after D₁ stage it was possible to reach values up to 89.7% ISO when the Paa stage was run for 120 min at a dose of 1 kg/odt of pulp. The viscosity drop across the Paa stage increased with increasing reaction time and Paa dose (Fig. 14).

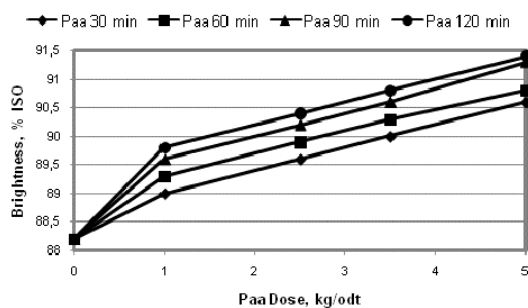


Fig. 9. Effect of Paa stage dose and reaction time on brightness development when applied in the D(Ep)D/Paa sequence

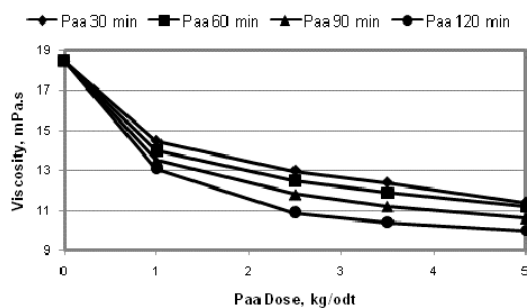


Fig. 10. Effect of Paa stage dose and reaction time on pulp viscosity when applied in the D(Ep)D/Paa sequence

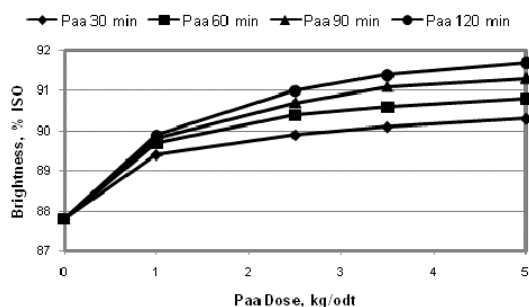


Fig. 11. Effect of Paa stage dose and reaction time on brightness development when applied in the $D_{HT}(Ep)D/Paa$ sequence

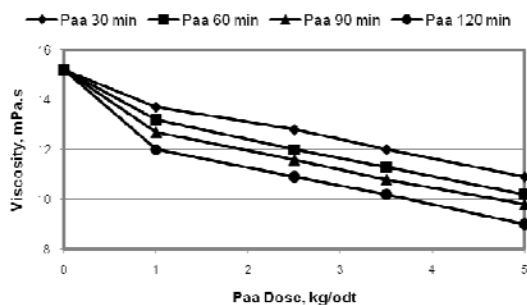


Fig. 12. Effect of Paa stage dose and reaction time on pulp viscosity when applied in the $D_{HT}(Ep)D/Paa$ sequence

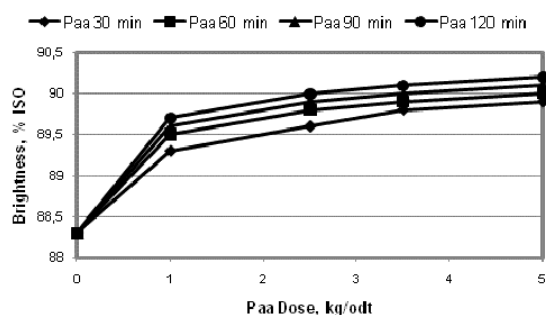


Fig. 13. Effect of Paa stage dose and reaction time on brightness development when applied in the $A/D(Ep)D/Paa$ sequence

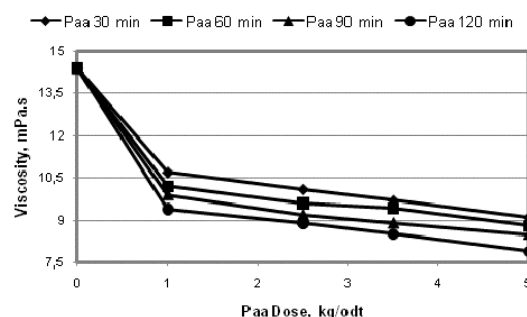


Fig. 14. Effect of Paa stage dose and reaction time on pulp viscosity when applied in the $A/D(Ep)D/Paa$ sequence

The effect of time and reagent dose on Paa stage when applied to the $D/Q(PO)Paa$ sequence is shown in Fig. 15. From a brightness of 86.3% ISO after D_1 stage it was possible to reach values up to 90.1% ISO when the Paa stage was run for 120 min at a dose of 5 kg/odt of pulp. The viscosity drop across the Paa stage increased with increasing reaction time and Paa dose (Fig. 16). Note that a larger dose of peracetic acid was required for this sequence, which is shorter than those previously discussed. Bleaching was more challenging in this case due to low brightness after D_1 . The final viscosity values of the pulp bleached with the $D/Q(PO)Paa$ sequence were lower than those of the four-stage type ones. This was likely due the harmful effects caused by the application of large doses of hydrogen peroxide in the (PO) stage and of peracetic acid in the Paa stage.

The effect of time and reagent dose on Paa stage performance when applied to the $Z/ED/Paa$ sequence is shown in Fig. 17. From a brightness of 87.1% ISO after D_1 stage it was possible to reach values up to 90.0% ISO when the Paa stage was run for 120 min at a dose of 3.5 kg/odt of pulp. Furthermore, no washing was necessary between D_1 and Paa stage. The viscosity drop across the Paa stage increased with increasing reaction time and Paa dose (Fig. 18).

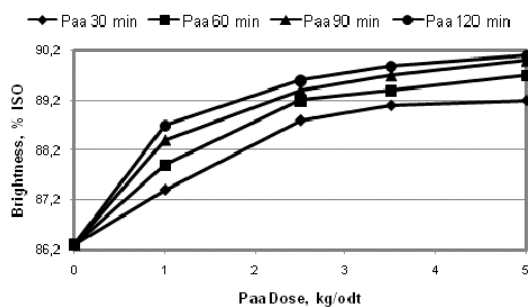


Fig. 15. Effect of Paa stage dose and reaction time on brightness development when applied in the D/Q(PO)Paa sequence

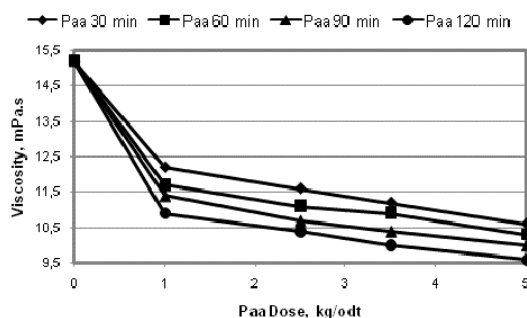


Fig. 16. Effect of Paa stage dose and reaction time on viscosity when applied in the D/Q(PO)Paa sequence

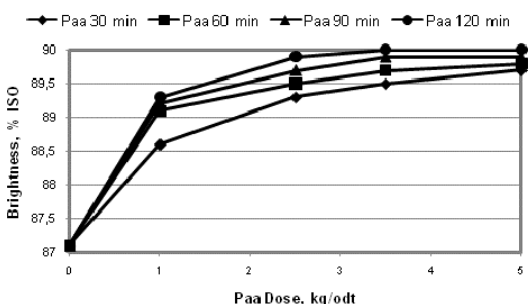


Fig. 17. Effect of Paa stage dose and reaction time on brightness development when applied in the Z/ED/Paa sequence

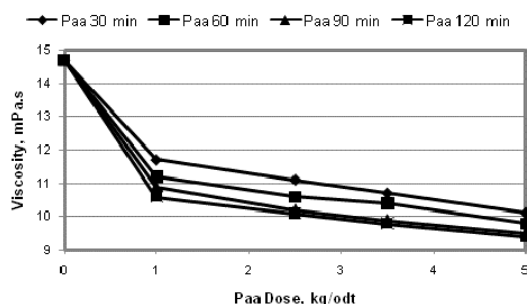


Fig. 18. Effect of Paa stage dose and reaction time on viscosity when applied in the Z/ED/Paa sequence

Summarizing Figs. 9 through 18, one can conclude that peracetic acid was consumed relatively fast when applied at the last bleaching stage of the various sequences investigated. The reaction time of 120 min is seemingly suitable for all sequences, regardless of the Paa dose applied. The proper dose of Paa depends upon the sequence under investigation, with the four-stage type sequences requiring very low doses of Paa (1 kg/odt), while short sequences such as D/Q(PO)Paa and Z/ED/Paa demand more Paa (5 kg/odt and 3,5 kg/odt, respectively) due to the low pulp brightness prior to the Paa treatment. The brightness response to the reaction time at various Paa dosages was different in the three different bleaching sequences (Figs. 9, 11, and 17), possibly due to the difference between the chemical pulps derived from different sequences before entering the Paa stage, although they had similar initial brightness. This difference of chemical pulp is especially the case for the HexA content of the pulp, the carbonyl groups content, and possibly the residual lignin.

Potential Cost Gains and Pulp Quality Benefits Derived from Paa Bleaching

The various sequences containing Paa as their last bleaching stage were compared with reference sequences without this stage. The knowledge established in the previous section was helpful in determining the proper dose of Paa to be used in each sequence.

Wherever applicable, comparisons were run also considering no inter-stage washing between the D_1 and the Paa stage.

Reference bleaching was carried out with the sequences D(Ep)DD, A/D(Ep)DD, D_{HT} (Ep)DD, $D_{HT}/Q(PO)$, D(Ep)DP, A/D(Ep)DP, D_{HT} (Ep)DP, and Z/EDP. All sequences were optimized to achieve minimum bleaching chemical cost for the 90% ISO brightness target. While a 0.16 kappa factor was sufficient for the sequences having four bleaching stages, the $D_{HT}/Q(PO)$ sequence required a 0.26 kappa factor. The results presented in Tables 3 and 4 show that the D_{HT} (Ep)DD and $D_{HT}/Q(PO)$ sequences were the ones of lowest and highest bleaching chemical costs, respectively. The very high cost of the latter sequence was caused by the excessive use of hydrogen peroxide. In practice, this sequence has only two bleaching stages, and that is the major cause for its high chemical cost as compared to the four-stage sequences. The qualities of the 90% ISO bleached pulps measured by kappa number, HexA, viscosity, reversion, and $L^*a^*b^*$ coordinates showed only slight variations. However, an unusually high reversion value was observed for the pulp bleached with the D(Ep)DD sequence (Table 3), and that was likely caused by its reasonably high HexA content associated with the fact that the sequence does not contain a final hydrogen peroxide stage. Sequences containing a final peroxide stage produce bleached pulp of high brightness stability regardless of their HexA contents (Eiras and Colodette 2005). The excess peroxide used in the D/Q(PO) sequence resulted in low final viscosity. There was a trend for low final viscosity, HexA and reversion values in the pulps bleached with sequences containing the D_{HT} stage. The sequences having final peroxide bleaching stages instead of D_2 stages produced pulps of higher brightness stability and HexA contents but showed higher bleaching costs. The variations observed among the pulp $L^*a^*b^*$ coordinate values for the reference bleaching sequences are within experimental error.

The results of the four-stage bleaching with and without the final Paa stage are compared in Table 3. The use of peracetic acid in the sequences D(Ep)D/Paa and D_{HT} (Ep)D/Paa sequences, with or without washing after D_1 , result in slightly decreased pulp viscosity and increased bleaching chemical costs as compared to the reference bleaching. The increased chemical costs for the D(Ep)D/Paa and D_{HT} (Ep)D/Paa sequences stems from the fact that 1 kg Paa displaced only 1 kg ClO_2 /odt pulp, and the former is a more expensive chemical. The lowest bleaching cost was achieved with the reference bleaching with the D_{HT} (Ep)DD sequence. For this sequence the relative bleaching cost was assigned to be 100. Thus as compared to this one, the D(Ep)D/Paa and D_{HT} (Ep)D/Paa sequences cost 10-25% more than the minimum (Table 3). Similar trends were also observed for the A/D(Ep)D/Paa sequence (Table 4). An increase of cost due to the Paa stage were similar for the sequences starting with D_0 and D_{HT} stages. For the sequence starting with the D_0 stage the final Paa stage decreased brightness reversion, but this trend was not seen for the sequence starting with the D_{HT} stage. There was no significant effect of the Paa stage on pulp $L^*a^*b^*$ coordinates. Although larger doses of Paa were evaluated, the value of 1.0 kg/odt pulp was the most effective for the sequences starting with both D_0 and D_{HT} stages. The absence of washing between D_1 and Paa stage showed no significant effects on pulp quality but increased chemical cost slightly due to increased NaOH demand. Similar brightness developments and viscosity loss trends were observed when the pulp was washed between the D_1 and the Paa stage. It is apparent that

there is no need for washing between D_1 and Paa stage, considering that the pHs of these stages are similar. Eucalyptus pulps contain very little lignin left to be removed in the D_1 stage, because the pulp brightness is already high after the (Ep) stage ($> 80\%$ ISO) and most of the left over kappa number is related to HexA (Colodette et. al. 2008). Thus, very little colored material is removed in the D_1 , which facilitates omission of the washing stage. This practice can be advantageous to reduce capital costs.

The results presented in Table 4 indicate that the use of peracetic acid as the last stage of the D/Q(PO)Paa sequence resulted in decreased pulp viscosity but increased bleaching chemical costs substantially. To achieve a similar brightness target using a conventional D/Q(PO) sequence, an additional hydrogen peroxide charge of 20 kg/odt was necessary. Therefore, the replacement ratio was 4 kg/odt H_2O_2 per 1 kg/odt Paa. This was the highest replacement ratio achieved in this study. There was no significant effect of the Paa stage on pulp reversion and $L^*a^*b^*$ coordinate. Although lower doses of Paa were evaluated, the value of 5.0 kg/odt pulp proved the most effective. The Paa stage application on the Z/ED/Paa sequence caused a slight decrease in chemical and pulp viscosity. To achieve a similar brightness target using the Z/EDP sequence, an additional hydrogen peroxide charge of 5 kg/odt was necessary. Therefore, the replacement ratio was 1.4 kg/odt H_2O_2 per 1 kg/odt Paa. In spite of the fact that the amount of HexA decreased when using the final Paa stage, the brightness reversion of the pulp bleached with the Z/ED/Paa sequence was slightly higher when compared to the reference. This is explained by the absence of a final hydrogen peroxide stage in the sequence having the Paa stage in relation to the reference one.

Summarizing Tables 3 and 4, one may conclude that the application of Paa in four-stage type sequences such as D(Ep)D/Paa, $D_{HT}(Ep)D/Paa$, and A/D(Ep)DPaa results in very low replacement ratio of Paa for chlorine dioxide and, as consequence, the cost effectiveness of such practice is not favorable. On the other hand, there is no significant pulp quality gain to justify the use of the Paa stage. The Paa application in the D/Q(PO)Paa sequence does reduce cost and permits the use of larger quantities of Paa. Due to the fact that it contains only two stages, this sequence is very uneconomical by nature. The most interesting application of Paa was in the Z/ED/Paa sequence where it replaced a final peroxide stage with some advantages. Besides eliminating one washing device and slightly increasing bleaching chemical costs, it had no significant effect on pulp quality, except for a slight decrease in pulp viscosity and increase on brightness reversion.

Effect of the Paa Stage on Pulp Refinability and Strength

The investigated sequence $D_{HT}(Ep)D/Paa$ had lower chemical cost with the Paa stage. Hence, it was chosen to evaluate the pulp strength properties and refinability. Purportedly, the pH of the last bleaching stage may affect pulp refinability and quality, with alkaline pH values being more favorable than acid ones, particularly in regard to refinability. This explains why a number of eucalyptus pulp mills are converting sequences of the D(Ep)DD type into D(Ep)DP ones. In order to have a full picture of the Paa stage influence on pulp quality, it was evaluated in three different pH values, namely 4.0, 6.5, and 8.5. All the data so far presented relates to the Paa stage being run at a pH around 5.0.

Table 3. Chemical Consumptions, Costs and Pulp Quality for Bleaching with the Sequences D(Ep)DD, D(Ep)DP, D_{HT}(Ep)DD, D_{HT}(Ep)DP, D(Ep)D/Paa, D(Ep)DPaa, D_{HT}(Ep)D/Paa, and D_{HT}(Ep)DPaa

Results	Bleaching sequence reference				Bleaching sequence evaluated			
	D(Ep)DD	D(Ep)DP	D _{HT} (Ep)DD	D _{HT} (Ep)DP	D(Ep)D/Paa	D(Ep)DPaa	D _{HT} (Ep)D/Paa	D _{HT} (Ep)DPaa
Kappa Factor	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16
H ₂ O ₂ , kg/odt	3.0	5.0	3.0	5.0	3	3	3	3
NaOH, kg/odt	9.3	12.3	9.3	12.3	13.7	11.7	14.5	11.5
H ₂ SO ₄ , kg/odt	7.5	7.0	7.5	7.0	7	7	7	7
DTPA, kg/t	-	-	-	-	0	0	0	0
O ₃ , kg/odt	0.0	0.0	0.0	0.0	0	0	0	0
ClO ₂ , kg/odt	10.65	9.65	9.15	8.15	9.65	9.65	8.15	8.15
CH ₃ COOH, kg/odt	-	-	-	-	1	1	1	1
Total Act. Cl, kg/odt	34.3	35.8	30.3	31.9	32.6	32.6	28.6	28.6
Chemical Cost, US\$/odt	108	121	100	112	125	119	119	110
Kappa No.	1.7	2.2	1.0	1.2	1.9	1.8	0.7	0.8
HexA, mmol/kg	12.5	14.7	5.4	6.8	12.3	12.1	5.1	5.0
Brightness, % ISO	89.9	90.0	89.8	90.1	89.8	89.9	89.9	89.7
Reversion, % ISO	3.0	2.0	2.1	1.8	2.5	2.1	2.4	2.1
Viscosity, mPa.s	13.9	14.0	11.6	11.5	13.1	13.2	10.4	11.0
L*	97.9	97.7	97.5	97.7	97.9	97.9	97.9	97.7
a*	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	0	-0.1
b*	2.7	2.9	3.0	3.1	2.7	2.7	2.9	3.2

Table 4. Chemical Consumptions, Costs and Pulp Quality for Bleaching with the Sequences A/D(Ep)DD, A/D(Ep)DP, D_{HT}/Q(PO), Z/EDP, A/D(Ep)D/Paa, D_{HT}/Q(PO)Paa, and Z/ED/Paa

Results	Bleaching sequence reference				Bleaching sequence evaluated		
	A/D(Ep)DD	A/D(Ep)DP	D _{HT} /Q(PO)	Z/ED(PO)	A/D(Ep)D/Paa	D/Q(PO)Paa	Z/ED/Paa
Kappa Factor	0.16	0.16	0.26	-	0.16	0.26	0.05
H ₂ O ₂ , kg/odt	3.0	5.0	35	5.0	3	15	0
NaOH, kg/odt	10.5	13.5	35	16.0	15.5	18	13.5
H ₂ SO ₄ , kg/odt	12.3	12.3	3	13.2	12.3	3	13.2
DTPA, kg/odt	-	-	1.5	-	0	1.5	0
O ₃ , kg/odt	0.0	0.0	0.0	6.0	0	0	6
ClO ₂ , kg/odt	9.65	8.65	9.89	1.90	8.65	9.89	1.9
CH ₃ COOOH, kg/odt	-	-	-	-	1	5	3.5
Total Active Chlorine, kg/t	31.6	33.2	99.2	42.1	30.0	62.0	34.9
Chemical Cost, US\$/odt	110	123	342	154	129	248	158
Final Kappa No.	0.5	0.8	1.9	1.0	0.3	1.6	0.6
HexA, mmol/kg	7.3	8.9	4.9	10.4	6.8	2.3	7.9
Brightness, % ISO	89.9	90.3	90.2	89.7	89.7	90.1	90.0
Reversion, % ISO	2.4	1.8	2.3	2.1	2.3	2.3	2.5
Viscosity, mPa.s	11.3	11.4	10.7	12.2	11.0	7.9	10.0
L*	98.0	97.6	98.1	97.7	97.5	97.7	97.7
a*	0.0	0.0	-0.1	-0.2	-0.1	-0.2	-0.2
b*	3.2	3.1	2.5	2.9	2.9	3.2	3.3

Most of the literature considers a pH around 5.0 ideal to run the Paa stage. The low and high values used here were intended to identify the impact of Paa on pulp quality rather than on bleachability. The results of the Paa bleaching under the three different pH values are shown in Table 5. The pulp bleached with the D_{HT}(Ep)DD sequence was used as reference. The impact of Paa stage bleaching pH on pulp refinability and strength properties is shown in Figs. 19 through 24. It observed that pulp refinability improved when Paa bleaching pH raised from 4 to 8.5 and also in relation to the reference bleaching without the Paa stage (Fig. 19). Tensile strength was also affected positively by raising the end pH of the Paa stage (Fig. 20). The effects of bleaching pH on burst and

tear strength and air resistance were not significant, but there was a slight trend for increasing burst and air resistance and decreasing tear with increasing pH (Figs. 21 through 23). Pulp opacity tended to decrease with increasing Paa bleaching stage pH (Fig. 24).

Table 5. Chemical Consumptions, Costs, and Pulp Quality for Bleaching with the Sequences, D_{HT}(Ep)DD and D(Ep)D/Paa, with the Latter having the Paa Stage Run at pH 4.0, 6.5, and 8.5

Results	D _{HT} (Ep) DD	D _{HT} (Ep) D/Paa	D _{HT} (Ep) D/Paa	D _{HT} (Ep) D/Paa
Paa Stage End pH	-	4.0	6.5	8.5
Kappa Factor	0.16	0.16	0.16	0.16
H ₂ O ₂ , kg/odt	3	3	3	3
NaOH, kg/odt	9.3	12	13	14
H ₂ SO ₄ , kg/odt	7.5	7	7	7
DTPA, kg/t	0	0	0	0
O ₃ , kg/odt	0	0	0	0
ClO ₂ , kg/odt	9.15	8.15	8.15	8.15
CH ₃ COOH, kg/odt	0	1	1	1
Total Act. Cl, kg/odt	30.3	28.6	28.6	28.6
Chemical Cost, US\$/odt	100	112	115	117
Kappa No.	1.0	0.7	1.0	1.1
HexA, mmol/kg	5.4	4.3	5.6	6.2
Brightness, % ISO	89.8	90.3	89.8	89.5
Reversion, % ISO	2.1	2.8	2.8	2.9
Viscosity, mPa.s	11.6	12.2	11.1	10.4
L*	97.5	97.7	97.3	97.2
a*	-0.1	0	0	0
b*	3.0	2.9	3.0	3.1

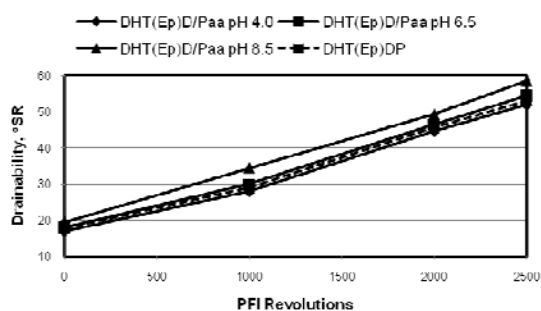


Fig. 19. Effect of Paa bleaching stage pH on pulp drainability

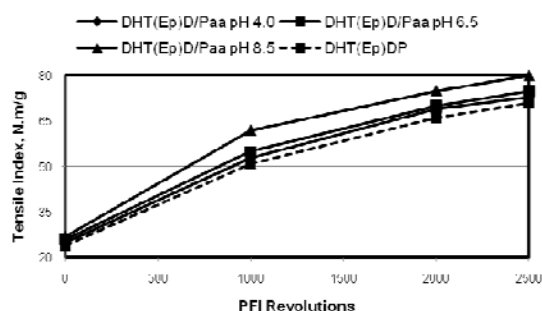


Fig. 20. Effect of Paa bleaching stage pH on pulp tensile strength

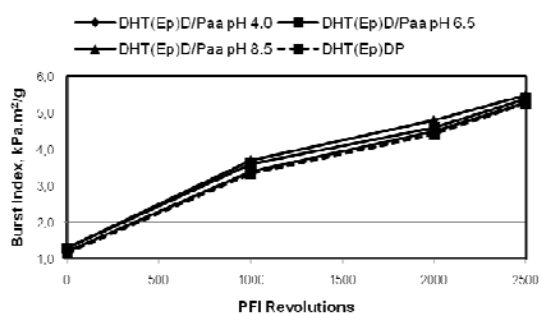


Fig. 21. Effect of Paa bleaching stage pH on pulp tensile burst strength

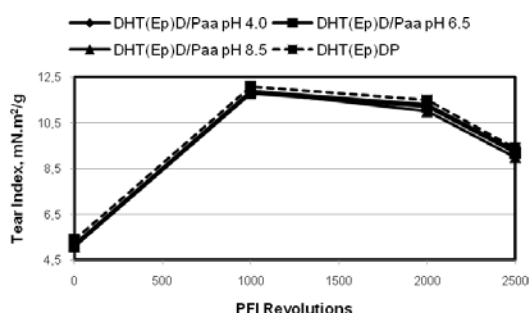


Fig. 22. Effect of Paa bleaching stage pH on pulp tear strength

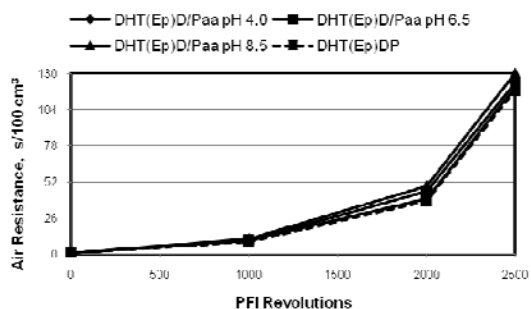


Fig. 23. Effect of Paa bleaching stage pH on pulp air resistance

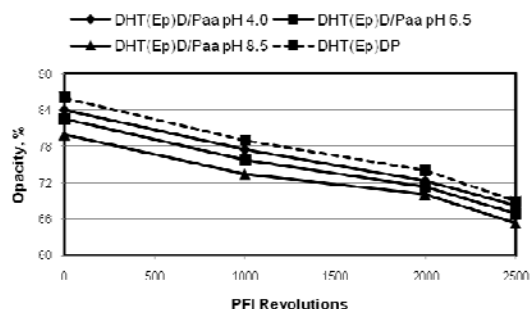


Fig. 24. Effect of Paa bleaching stage pH on pulp opacity

CONCLUSIONS

1. Peracetic acid was consumed relatively fast when applied as the last stage of ECF bleaching sequences. A reaction time of 120 min at 75 °C and pH 5.0 is seemingly adequate, regardless of the Paa dose applied in the range of 1-5 kg/odt pulp.
2. The proper dose of Paa to be applied depends upon the sequence under investigation with four-stage sequences of the D(Ep)D/Paa, $D_{HT}(Ep)D/Paa$, and A/D(Ep)D/Paa

- types requiring very low doses of Paa (1 kg/odt pulp), while short sequences such as D/Q(PO)Paa and Z/ED/Paa demand higher Paa doses (3.5-5 kg/odt).
3. The application of Paa in four-stage type sequences such as D(Ep)D/Paa, D_{HT}(Ep)D/Paa, and A/D(Ep)DPaa result in a low replacement ratio of Paa for chlorine dioxide (1kg ClO₂: 1 kg Paa/odt) without improving pulp properties.
 4. The D(Ep)D/Paa, D_{HT}(Ep)D/Paa and A/D(Ep)DPaa sequences require no washing between D₁ and Paa stage. In practice they need only three washing devices, i.e., one less than their reference counterparts.
 5. The Paa application in the D/Q(PO)Paa sequence decreased bleaching cost significantly and allowed for the use of larger quantities of Paa. For a Paa application of 5 kg/odt, a replacement ratio of 4 kg H₂O₂: 1 kg Paa/odt was achieved.
 6. The D/Q(PO)Paa sequence and its D/Q(PO) reference counterpart are both very expensive to run in comparison to the four-stage type sequences.
 7. The most interesting application of Paa was in the Z/ED/Paa sequence, where it replaced a final peroxide stage of the reference sequence in a cost effective way. A replacement ratio of 1.4 kg H₂O₂: 1 kg Paa/odt was obtained, and the overall bleaching cost of this sequence was only slightly higher than those of the four-stage type sequences. The D(PO) section of the Z/ED(PO) sequence a pressurized tower and two washers would be required, while for D/Paa two non-pressurized vessels and only one washer would be required.
 8. In general, the Paa application as the last bleaching stage caused slight decrease in pulp viscosity, kappa number and HexA content but had no significant effect on pulp reversion and L*a*b* coordinates.
 9. The refinability and bonding strength properties of the pulps bleached with the sequences D_{HT}(Ep)DD and D_{HT}(Ep)D/Paa were quite similar when the pH of the last bleaching stage of both sequences were in the range of 5. These properties improved slightly when Paa bleaching pH was raised to 8.5.

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Article submitted: November 16, 2009; Peer review completed: February 6, 2010;

Revised version received: March 2, 2010; Accepted: March 6, 2010; Published: March 8, 2010.