New Possibilities and Gains with Strong Equilibrium Peracetic Acid for Eucalyptus Pulp

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Sustainability aspects are driving forces for those pulp mills in which production capacity must be harmonized with less amount of water consumption and effluent generation in their fiber lines. Our effort here is focused on demonstrating ECF technologies using PAA as 1st bleaching stage whereby a mill could have a potential to save 50% in the water consumption. Beside, water consumption and effluent generation cutback, it is claim that PAA as 1st strong stage is capable to attend savings in sodium hydroxide make up and decrease steam specific consumption. The main purpose of this work was to develop ECF technologies adapted to partial bleach plant closure for bleaching eucalyptus Kraft pulp aiming at decreasing chemical costs and improving effluent. Results showed that PAA as pre bleaching could displace effectively the A-Z-stages or Z/D0-stage. Furthermore, low charge effluent was produced from the remaining final stages. It was demonstrated that the optimization of currently existing ECF bleaching sequences will result in PAA-ECF sequences with chlorine dioxide specific consumption around 3kg/t. It is also noted that a light ECF (OX ≤ 30 mg/kg) pulp could be achieved by applying PAA-stage displacing the A-Z-stages or Z/D0-stage.

Keywords: Low environmental impact sequence; ClO_2 debottleneck; Light ECF eucalyptus pulp; water consumption; effluent load; peracetic acid (PAA)

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INTRODUCTION

Brazil is the larger eucalyptus bleached Kraft pulp producer in the world market and this raw material is becoming one the most important source of fibres to produce different paper grades. New very large size investments will take place in Soult America during the next coming years. Sustainability standpoint is one of the key driving forces for those giant pulp mills in which production capacity on the state-of-the-art must be harmonized with less amount of water consumption and effluent generation in their Eucalyptus ECF fiber lines. Bleaching technology adapted to partial bleach plant closure is the answer for current and upcoming environmental restrictions for green field side or even for others company strategies in order to reduce investment cost in water and effluent treatment.

Most bleach plants currently in operation in South America utilize ECF technology centered on ClO_2 bleach chemical. Hence, supplementary investments in existing pulp production often lead to shortage of chlorine dioxide from the integrated on-site plant. Since most bleaching sequences used in South American pulp mills are of the D0-(EP)-D1-P type, the old ECF bleaching practices are not fully applicable to eucalypt Kraft pulps because eucalyptus kappa number is comprised mostly of hexenuronic acids (HexA). As a matter of fact, the kappa number due to lignin hardly exceeds 3 kappa units in oxygen delignified eucalypt Kraft pulps. Therefore, the bleaching process is more efficiently done when process conditions are adjusted to pulp brightening rather than pulp delignification.

With current technology, the primary environmental load consists of effluents from D0 and (EP)-stages, which are discarded since they can't be recovered by sending them into evaporation plant/ recovery system due to high Cl^- content. Our paper is focusing on overcoming this dilemma. Numerous attempts have been demonstrated to resolve this problem, mostly the basic idea being of chlorine dioxide in the first stage. Our effort here is focused on demonstrating ECF light technologies using peracetic acid stage (PAA) whereby a mill could redesign their water usage and save 50% in the fresh water consumption. This estimation is based on an evaluation that the PAA and (EP) effluent could be sent to the brown stock washing and evaporation. In addition the condensate form the evaporation plant could be utilized in the (EP) washers instead of oxygen delignification stage. Furthermore, our results imply possibility to eliminate bottleneck in the ClO_2 production.

Environmental performance associated to capital costs are the factors becoming ever more important focus in the last decades by the pulp industry. ECF sequence adapted to partial bleach plant closure was mentioned to align these items in the A_{hot}(EOP)D(PO) sequence, in which the proposal was reuse of A_{hot} and (EOP) filtrates (Costa et al, 2005). Beside improve environmental performance for the bleaching sequence and capital costs in water and effluent treatment this proposal is less flexible to achieve high level pulp brightness 90+ % ISO.

PAA has been evaluated mostly as last stage, called post-bleaching, in order to improve final pulp brightness ceiling (Barros et al 2010, Jäkärä et al 1999, Jäkärä et al 1997). Beside PAA-stage technologies and chemistry has been much required since allows for elimination of bleaching stages through shortening bleaching sequences and/or omission of washing between stages as (D/PAA) or (PAA/P)-stage Barros et al 2010.

In addition, a strong first bleaching stage applied to Kraft-O_2 eucalyptus pulps can eliminate lignin almost completely since more than half of the pulp kappa number is comprised of HexA (Costa et al 2007, Ventorim et al 2006). A pulp containing almost no lignin could in principle be further bleached with only one additional stage, if such stage is well established. Therefore, the bleaching process is more efficiently done when process conditions are adjusted to pulp brightening rather than pulp delignification (Barros et al 2010, Azevedo et al 2011). Note that HexA are colorless leuco-chromophores compounds which could removed by PAA-stage as first bleaching stage in pre-bleaching ECF technology. Since PAA could develop electrophilic and nucleophilic attack significantly enough to activate the residual lignin in the following cleaning stages (Gierer 1986, Jaaskelainen et al 1967). It was demonstrated that PAA improve the lignin solubility by (a) cleavage of lignin-carbohydrate complex, which became easy to removal; (b) increase the amount of phenolic hydroxyl groups and carboxylic acid group and ester group; (c) decrease the residual lignin Mw due to the cleavage of side chains and (d) increase conjugated carbonyl structures, which are reactive sites for nucleophilic attack by the hydroperoxide anion in P-stages (Jaaskelainen et al 1967).

The main objectives of this work include: (1) establishment optimum PAA-stage operating conditions (2) application of a PAA-stage in ECF bleaching of eucalyptus kraft pulps.

EXPERIMENTAL

This paper is based on results from laboratory-scale experiments. The results include the use of PAA as a brightening agent at the bleaching plant. Two eucalyptus pulp samples were collected in the last washer after the oxygen delignification (Kraft-O_2) stage of two different Brazilian bleach plants. These Kraft-O_2 Eucalyptus pulps samples were used as raw material in the laboratory experiments. The main specifications of these two pulp samples are presented in Table I. Strong equilibrium peracetic acid 33 to 35% from Kemira Chemicals Company (Kemirox) was used in the laboratory trials. The optical properties were determined according to SCAN, TAPPI or ISO standards.

Table I: Characterization of the two Kraft-O_2 Eucalyptus pulps samples

Conditions and Results	Samples	
	Sample A	Sample B
Kappa Number	9.5	9.0
Viscosity (dm^3/kg)	799	925
Brightness (% ISO)	54.6	58.6
HexA (mmol/kg)	56.7	44.6
COD carryover (kg/odt)	10	10

The main reaction conditions used are presented in Table II. After each bleaching stage, run in duplicate, the samples were washed with 9 and 3.5 m^3/odt of distilled water each stage, 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 oxidants and residuals were measured according to Pulp & Paper Manufacture (Kraft 1967). Figure 1 shows schematically the experimental flowchart of this work.

Table II: General Bleaching Conditions

Bleaching Conditions	Bleaching Stage						
	Q	A	Z	PAA	PAA*	P	D
Consistency, %				10			
Temperature, °C	65	95	50	65	65	95	85
Time, min	30	120	1	60	60	120	120
Initial pH	6.5	3.0	3.0	7.5	3.0	11.5	6.0
Final pH	6.5	2.5	2.5	5.5-6.0	2.5-3.0	10.5-11.0	4.5-5.0
DTPA, kg/odt	2	-	-	-	-	-	-
H_2SO_4, kg/odt	-	7		-	-	-	-
O_3, kg/odt	-	-	3.4 (sample B) 3.5; 5.0 (sample A)	-	-	-	-
PAA, kg/odt	-	-	-	1.5; 3.0; 4.5	3.0	-	-
H_2O_2, kg/odt	-	-	-	-	-	Variable	-
ClO_2, kg/odt	-	-	-	-	-	-	Variable

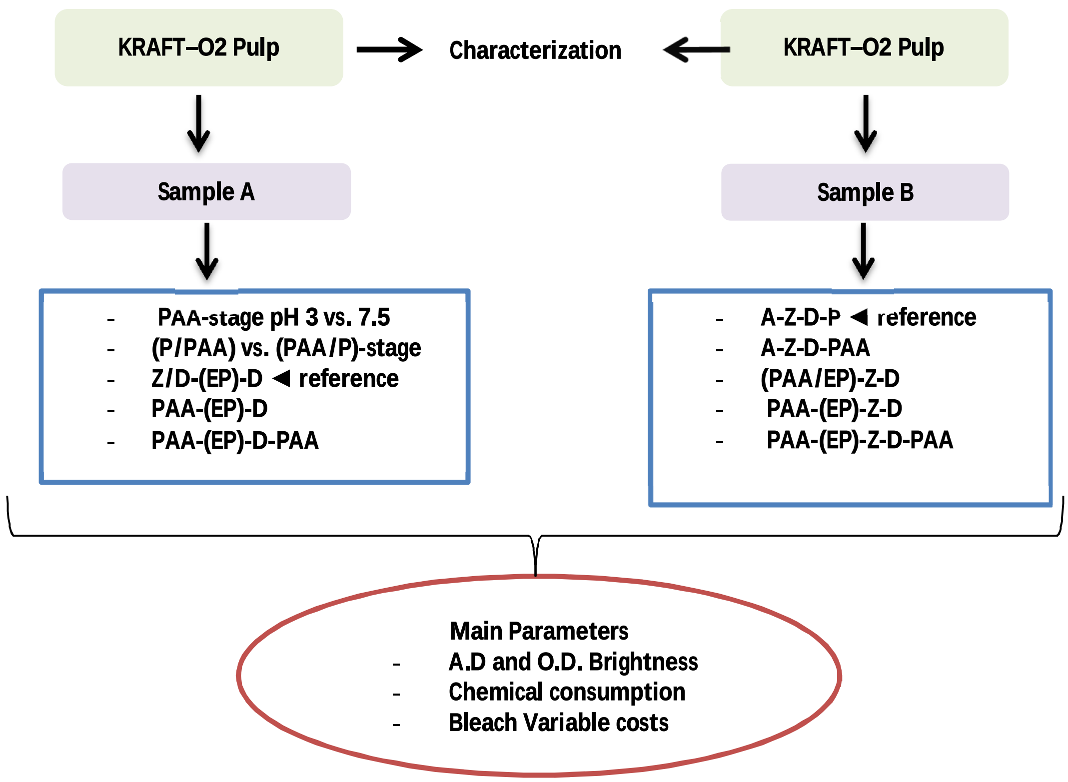

Figure 1: Schematically flowchart of the experimental.

RESULTS AND DISCUSSION

Simultaneous use of PAA-stage and P-stage in different pH

A preliminary test was done with sample A in order to demonstrate the best reaction pH for PAA-stage. Figure 2 shows the contrast between reaction pH, in which PAA*-stage was done in reaction pH of 3.0 and PAA-stage in reaction pH of 7.5. In addition, the location of P-stage was evaluated before and after PAA-stage to achieve the same brightness with final D-stage. It was used a previous Q-stage in order to avoid the metals effect on the results.

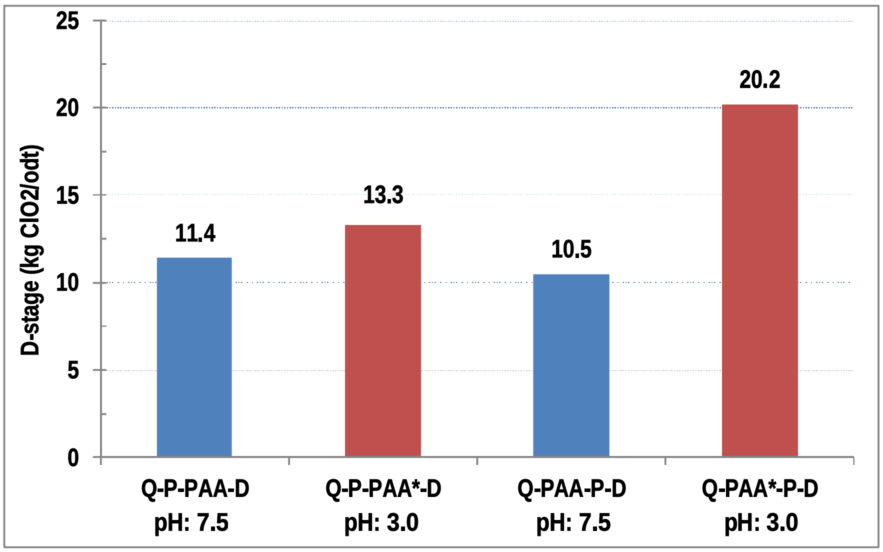

Figure 2: PAA-stage reaction pH effect and location of P-stage on the chlorine dioxide consumption to achieve 88%ISO of A.D. brightness. (Charge in P-stage of 7 kg H_2O_2/odt and PAA-stage of 3 kg PAA/odt)

Figure 2 shows that PAA-stage reaction pH of 7.5 presented lower chlorine dioxide consumption than 3.0. Probably nucleophilic reaction from PAA in neutral pH improve brightness rather than in low pH. Beside slight advantage, i.e. low chlorine dioxide consumption was observed to P-stage after PAA-stage. However, when the washing step was deliberately omitted Figure 3 show s that P-stage before PAA-stage generated lower chlorine dioxide consumption. Consequently (P/PAA)-stage exhibited superior results than (PAA/P)-stage.

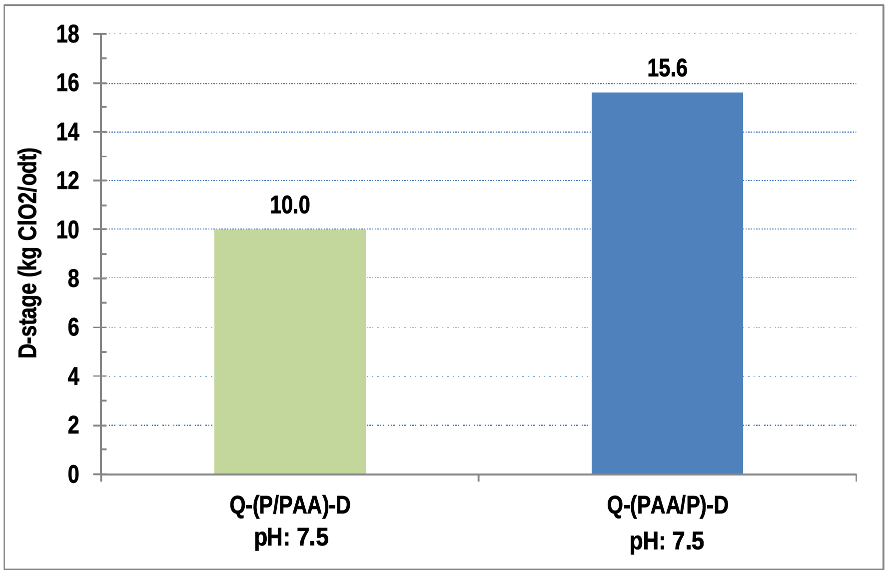

Figure 3: (P/PAA)-stage vs. (PAA/P)-stage on the chlorine dioxide consumption to achieve 88% ISO of A.D. brightness. (Charge in P-stage of 7 kg H_2O_2/odt and PAA-stage of 3 kg PAA/odt).

COD effect on the Brightness

Two different COD load from oxygen delignification stage were tested in different charge of PAA (Figure 4). Kraft-O_2 pulp (48.2 %ISO and kappa number 12, which is the Sample A before the 2nd oxygen stage) was bleached in 4 dosages of PAA (3; 5; 7 and 10 kg PAA/odt pulp) with 6.5 and 15 kg/odt of COD load. The results presented in Figure 4 shows that the additional load of COD did not affect significantly the pulp brightness gain in the PAA stage.

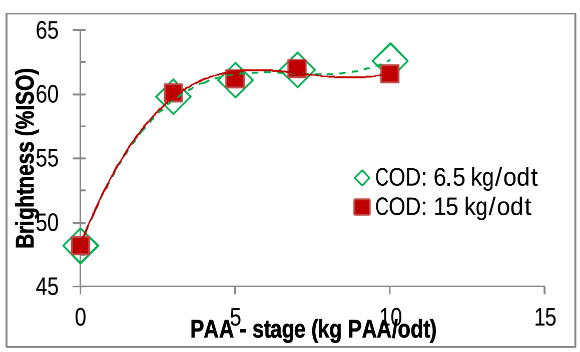

Figure 4: COD effect on the brightness.

Peracetic Acid Application: Pre- and Post-bleaching Technology

Eucalyptus kraft-O_2 pulp – sample B

PAA could be a strong 1st stage in order to displace A-Z stages and win brightness. PAA-stage is ably to active the residual lignin to the further stages by increase the amount of phenolic hydroxyl groups and as well increased the conjugated carbonyl structures which are reactive sites for nucleophilic attack by the hydroperoxide anion, present in P-stage. Figure 5 shows the effect of PAA-stage on the brightness after PAA-P and PAA/P-stages in contrast A-Z in two different charges (3.5 and 5 kg/t of pulp).

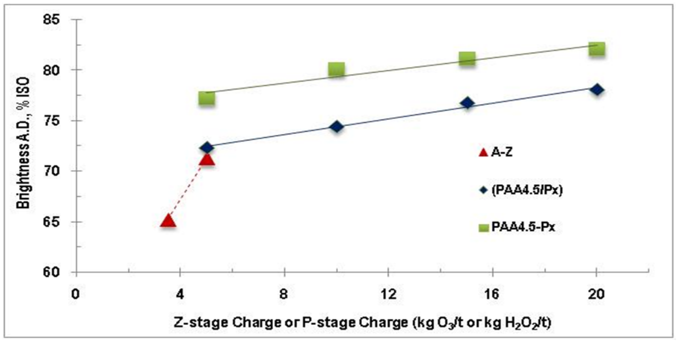

Figure 5: Activation of P-stage with PAA-stage with and without washing.

Beside the possibility to decrease investments in one stage when the washer is omitted between stages (PAA-P vs. PAA/P), these filtrates could be recovered and savings in steam, sodium hydroxide make up and water + effluent treatments was a potential possibility for mill scale operation. Using these savings in account Figure 4 shown the comparison among the reference and PAA-sequences from Kraft-O_2 pulp sample B. From Figure 6 it could be noted for cost view point that PAA-stage could be an alternative economically feasible if it was apply the partial bleach alkaline filtrate closure.

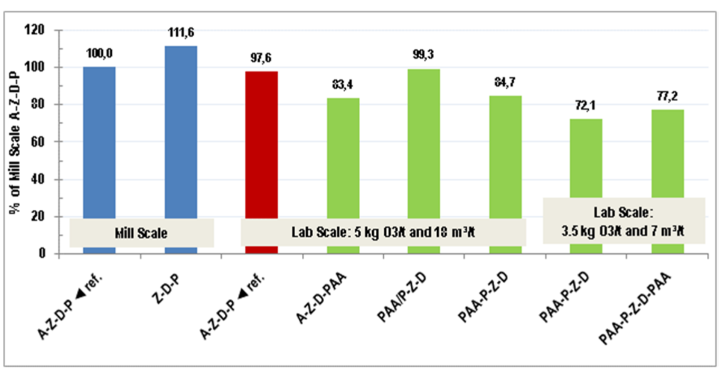

Figure 6: Relative cost evaluation from the Mill scale bleaching sequences and PAA-sequence Lab Scale for 5 and 3.5 kg O3/t and 2 different washing conditions.

Bellow Table III demonstrate the main chemical specific consumption from different alternatives sequences using PAA-stages as pre-bleaching or/and post bleaching stages. It could be noted that ClO_2 is straightforwardly displaced by PAA and Light ECF pulp could be achieved with 3 kg ClO_2/odt. Additionally, this mean that PAA application is an alternative to these fiber lines in order to eliminate ClO_2 production bottleneck, improving pulp production capabilities and/or decrease pulp down grade amount (bellow 88% ISO for example).

Table III-Main chemical specific consumption from different sequences for Kraft-O_2 pulp sample B.

	PAA (kg/t)	ClO_2 (kg/t)	H_2O_2 (kg/t)	Make up + NaOH (kg/t)	H_2SO_4 (kg/t)
A-Z-D-P ◄ ref. (mill scale)	0	10.7	22.5	27.6	11.2
Z-D-P (mill scale)	0	12	22	37	22
Laboratory Scale: 5 kg O_3/t and 18 m³/t					
A-Z-D-P (ref.)	0	9	9.2	32	12.5
A-Z-D-PAA	1.5	5	0	23.7	5
(PAA/EP)-Z-D	4.5	8	5	20.1	7.5
PAA-(EP)-Z-D	4.5	4.3	5	14.7	7.5
Laboratory Scale: 3.5 kg O_3/t and 7 m³/t					
PAA-(EP)-Z-D	3	4.3	10	18.5	7
PAA-(EP)-Z-D-PAA	4.5	3	10	18.4	7

In addition, sodium hydroxide consumption and fiber line global make up decrease due to the alkaline filtrate bleach plant closure since this filtrate can be recovered by sending them into evaporation plant (low Cl^- content). Furthermore, this work is focused on demonstrating ECF light technologies using PAA whereby a mill could redesign their water usage and save 50% in the fresh water consumption. This estimation is based on an evaluation that the PAA and P-stages effluent could be sent to the brown stock washing and evaporation. In addition the condensate form the evaporation plant could be utilized in the P washers instead of oxygen delignification stage. The result from this opportunity to redesign the fiber line water consumption and effluent generation means significantly less investment in water and effluent treatment for extra production in establish fiber lines or in green field sites. It is important to note that much less environmental impact will be expected from these bleach sequence in which PAA and P-stages filtrate was recovered. As mentioned earlier in the literature effluent charge from final two bleaching stages generate much less COD, BOD5 and Color charges, decreasing around 60,4%; 60% and 94%, respectively (Costa 2007). For cost view point Table 3 shows that PAA-P-Z-D proposal sequence is the best alternative among others to the mill sequences listed above (A-Z-D-P and Z-D-P) for Kraft-O_2 pulp sample B.

PAA as post-bleaching technology has been used in integrated pulp and paper production and also in the production of market pulp. In market pulp production the use of PAA post bleaching results in a lower residual kappa number of bleached pulp and in a lower post-colour number. Mill-scale trials have shown that the runnability of the drying machine was also improved. The selectivity of PAA post bleaching has also been utilized to improve pulp strength by reducing the amount of less selective bleaching chemicals at the same final brightness target (Jäkärä et al 1999, Jäkärä 1997). Below Figure 6 demonstrated that PAA as post-bleaching also stabilizes the brightness and inhibits brightness reversion. Brightness stability, i.e. low level of brightness reversion, difference (Δ) between A.D. and O.D. brightness was established for kraft-O_2 pulp A. Figure 7 results shows that PAA-sequence result in Δ = 1.3 %ISO and the reference Δ = 2.8 %ISO. Probably, in integrated pulp and paper production this will result in low demand for optical brighteners agents (OBA/FWA). As mentioned in the literature the OBA consumption was decreased in 20% and the dosage stabilized in mill trial (Hämäläinen, 2008).

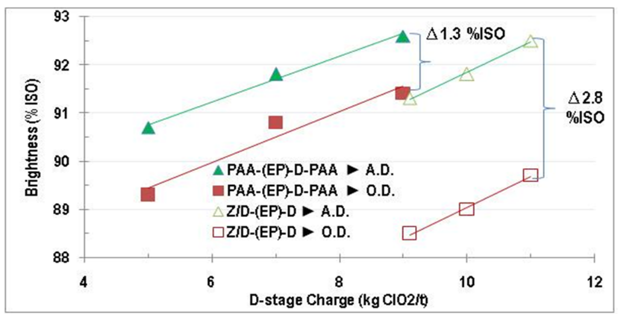

Figure 7: Air Dry Brightness (A.D.) and Over Dry Brightness (O.D.) for the reference sequence; Z/D-(EP)-D and for PAA-sequence; PAA-(EP)-D-PAA.

Below Figure 7 shows the relative cost comparison among reference Z/D-(EP)-D and alternatives with PAA-stage as pre-bleaching with and without PAA-stage as post-bleaching in order to achieve 90%ISO A.D. brightness. In addition, it can be observed in Figure 8 the cost contrast among these sequences to achieve 90%ISO O.D. brightness, i.e. comparison was performed on the equivalent final brightness. When the comparisons are around the A.D. brightness the difference is slight. However, if the comparisons are related to O.D. brightness the difference is much significant, which reflect the tendency demonstrated in Figure 7. Table IV shows the main chemical specific consumption from different sequences for Kraft-O_2 pulp sample A. It could be observed that

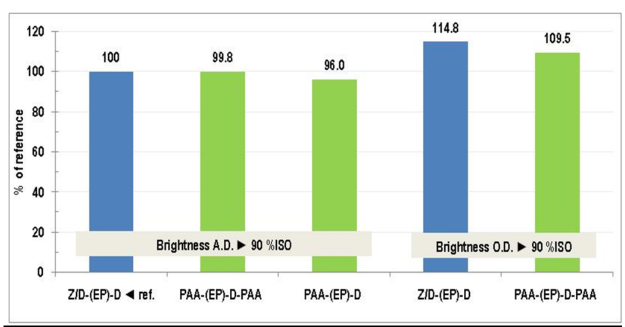

Figure 8: Relative cost evaluation from the lab scale bleaching sequences; Z/D-(EP)-D and PAA-sequence balanced at 90% ISO Air Dry Brightness (A.D.) and 90% ISO Over Dry Brightness (O.D.).

Table IV – Main chemical specific consumption from different sequences for Kraft-O_2 pulp sample A.

Alternative Sequences	PAA (kg/t)	ClO_2 (kg/t)	H_2O_2 (kg/t)	Make up + NaOH (kg/t)	H_2SO_4 (kg/t)	O_3 (kg/t)
			Brightness A.D. ► 90 %ISO			
Z/D-(EP)-D ◄ ref.	**0**	**7.9**	**7**	**27**	**11.2**	**3.4**
PAA-(EP)-D-PAA	**6**	**4.5**	**16**	**13.,2**	**0**	**0**
PAA-(EP)-D	**4.5**	**6.2**	**16**	**12.6**	**0**	**0**
			Brightness O.D. ► 90 %ISO			
Z/D-(EP)-D	**0**	**12.3**	**7**	**27**	**10.5**	**3.4**
PAA-(EP)-D-PAA	**6**	**7**	**16**	**15.2**	**0**	**0**

CONCLUSIONS

The Lab results with PAA-stage data above discussed allows for the following conclusions:

1. PAA application in pre-bleaching saved sodium hydroxide make up, steam and water, thus reducing environmental impact.
2. For pulp and paper mills with limited Water and Effluent treatment capacities, the PAA-stage as pre-bleaching technology can save investments in these plants.
3. PAA application in prost-bleaching increased pulp brightness ceiling and decreased brightness reversion.
4. For pulp mills with limited ClO_2 generation capacity, the PAA-stage application can potentially increase through put since full brightness can be achieved with very low ClO_2 charges (4.5 and 3.0 kg ClO_2/odt for samples A and B, respectively).

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