THE TRUE IMPORTANCE OF OXYGEN DELIGNIFICATION FOR EUCALYPTUS KRAFT PULPS

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ABSTRACT

Eucalyptus wood xylans are very rich in 4-O-methyl-glucuronic acids (MeGUA). In average, values in the range of 2 MeGUA / 10 xyloses have been observed on *Eucalyptus grandis* and *Eucalyptus urophylla* woods. Even considering that these eucalyptus species possess relatively low amounts of xylans, the total amount of MeGUA in the wood is rather significant, varying from 4-5.5% on wood dry weight. The high amounts of MeGUA in the wood associated with the very moderate pulping conditions (low temperature, long retention time) currently practiced for such woods have led to kraft pulps of very high hexenuronic acid contents (HexA´s). Industrially made kraft pulps obtained by modified cooking process may contain 60-75 mmol/kg of HexA´s, which represents about 6-7.5 kappa units. HexA´s do no react with oxygen and very little of it is actually removed across the oxygen delignification stage. Therefore, the oxygen delignification stage is rather inefficient when applied to HexA´s rich pulps. Oxygen delignification efficiency for HexA´s rich eucalyptus pulps have been in the range of 25-35% only. In this study, it is carried out an economical evaluation of ECF bleaching processes having none and double-stage oxygen delignification when applied to eucalyptus pulps of kappa varying in the range of 14-21. The bleaching processes include sequences containing specific stages for HexA´s removal (Z, A/D and D_{HT}). The results are interpreted on the basis of fiber line yield, chemical consumption, operational costs and effluent load. The results indicate that the use of oxygen delignification is not economically attractive, particularly for HexA´s rich low kappa pulps, but processes without oxygen delignification are environmentally challengeable. The most economical processes, considering Brazilian wood prices, includes cooking to lower kappa number, no oxygen delignification and ECF bleaching with the D_{HT}(PO)DP sequence.

INTRODUCTION

Eucalyptus kraft pulps produced by kinetically modified pulping processes contain very high amounts of hexenuronic acids, in the range of 60-75 mmol/kg pulp (1-3). This HexA´s concentration range is roughly equivalent to about 7-7.5 kappa units (4-5). Considering that the out of digester kappa number varies in the range of 14-18 for eucalyptus pulps and that, purportedly, the HexA´s contents of the pulps at this kappa number range tends to be rather constant (1-2, 6), the significance of HexA´s in the overall kappa number may vary sharply depending upon the pulp initial kappa number. For example, kappa 14 and 18 pulp samples containing equal amounts of HexA´s (e.g. 7.5 units kappa) will have 53.4 and 41.2% of their kappa represented by these acids, respectively. Thus, the impact of HexA´s on overall kappa number is more significant for the kappa 14 pulp.

Oxygen does not react with HexA´s and very little impact on the HexA´s derived kappa number is observed during the oxygen delignification stage (5). Therefore, the oxygen delignification efficiency is rather low for low kappa pulps containing high HexA´s concentration (7-8). As a matter of fact is doubtful whether or not oxygen delignification is worth at all for HexA´s rich eucalyptus kraft pulps of low kappa number.

The objective of this study was evaluating bleachability of HexA´s-rich (derived from modified cooking) eucalyptus kraft pulps of kappa number 14, 17.5 and 21 with the sequences D_{HT}(PO)D, A/D(PO)D, Z/ED(PO), O/OD_{HT}(PO)D, O/OA/D(PO)D and O/OZ/ED(PO), which contain specific stages for removal of hexenuronic acids, namely D_{HT}, A/D and Z. The results were interpreted on the basis of fiber line yield, chemical consumption, operational costs and effluent load.

EXPERIMENTAL

Material

Five trees of a 7 year old hybrid *Eucalyptus grandis x Eucalyptus urophylla* clone were collected in the field in the form of logs, debarked, and transported to the UFV Pulp and Paper Laboratory. Five 50 cm long bolts were cut from each tree at different heights (0, 25, 50, 75 and 100%) in order to obtain representative sample of the whole tree. All bolts were debarked and chipped in a laboratory chipper. The chips produced were screened (35x35mm and 8x8mm screens) and air dried to uniform moisture content of about 20%. The chips from each tree were mixed and well homogenized in a rotary 250 liter chip mixer and stored in polyethylene bags to maintain uniform moisture content. Table 1 show the apparent density and the main chemical composition of the five wood samples used. For pulping and bleaching studies, the chips from the 5 samples were mixed at equal proportions.

Table 1. Wood main characteristics

Wood density and chemistry	**Tree N^o**					
	1	**2**	**3**	**4**	**5**	**Avg**
Apparent Density, kg/m^3	528	534	539	519	541	**532**
Cellulose, %	42.9	43.1	42.0	42.5	42.0	**42.5**
Total Lignin, %	27.3	26.9	27.2	27.7	27.6	**27.3**
Hemicelluloses Sugars, %	17.3	17.5	17.4	17.1	17.7	**17.4**
Total Uronic Acids, %	4.9	5.3	5.5	4.8	5.1	**5.1**
Total Acetyl Groups, %	2.3	2.1	2.4	2.7	2.6	**2.4**
Total Extractives, %	3.2	3.1	3.5	2.9	3.2	**3.2**
Lignin S/G	2.1	2.0	2.2	1.9	2.0	**2.0**

Methods

Pulping was carried out by a modified kraft pulping method to kappa number 14, 17.5 and 21. Conditions were kept constant, except that active alkali charges were varied to achieve the desired kappa number. A Continuous Digester Simulation System (Figure 1) was used to simulate the process. The system consists of a seven liter capacity batch digester, equipped with a recirculation pump, heat exchanger, and computer monitored electronic time and temperature controllers. The digester is coupled to a set of electrically heated accumulator vessels individually connected to the digester. The system is heated and pressurized and permits use of different cooking liquors in the accumulator vessels, so that the different cooking zones of a continuous digester can be simulated. The following cooking conditions were used on 500 g (dry weight basis) pre-steamed chips: (1) impregnation zone: 112°C, 60 minutes, 45% of total active alkali, L/W = 3.5/1; (2) upper coking zone: 155°C, 60 minutes, 30% of active alkali, L/W = 3.5/1; (3) lower coking zone: 156°C, 120 minutes, 25% of total active alkali, L/W = 3.5/1. A total sulfidity of 37% and an H-factor of 680 were used in all cases. Total active alkali values of 21.8, 18.7 and 16.6%, expressed as NaOH, were required for kappa number 14, 17.5 and 21, repectively. After completing the cooking cycle of all cooks the chips were removed from the digester by vacuum suction and defibered in a 20 liter capacity laboratory hydrapulper at 0.6% consistency, thoroughly washed with hot water and the pulp produced stored at appropriate conditions.

Bleaching of the 14, 17.5 and 21 kappa pulps was carried out to 90% ISO brightness with the sequences D_{HT}(PO)DP, A/D(PO)DP, Z/ED(PO), O/OD_{HT}(PO)DP, O/OA/D(PO)DP and O/OZ/ED(PO). The O/O, A/D, D_{HT} and (PO) stages were carried out in a Mark V reactor/mixer (Quantum Technologies, OH, USA) using 250-300 g o.d.(oven dried) pulp samples under the conditions listed in Table 2. The pulp was placed in the reactor at the desired consistency and heated to the desired temperature. The pre-established reactant charges were injected under constant mixing. High consistency ozone bleaching (Z/E) was performed in a rotating glass reactor, using 25 g o.d. pulp samples under the conditions listed in Table 2. Sample pH was adjusted by adding sulfuric acid as needed with the pulp at 6% consistency. The mixture was held at this pH for about 15 minutes and then dewatered in a centrifuge. Following, the pulp was fluffed in a stainless steel laboratory fluffer and its consistency determined. The fluffed pulp sample was placed in a 3000 mL glass flask adapted to a rotary evaporator. Ozone flow of known concentration was passed through the sample and the left over ozone was collected in a 5% KI solution. After iodometric titration of residuals, ozone consumption was calculated. Alkaline Extraction (E), conventional chlorine dioxide bleaching (D) and conventional peroxide bleaching (P) were carried out in polyethylene bags with 50-80 g o.d. pulp samples using the conditions listed in Table 2. The bleaching liquor was added to the pulp at room temperature, the bag was manually mixed, heated in a microwave oven to the desired temperature and transferred to a vapor bath where it was kept for the reaction time. All bleaching stages were run in duplicate and residual liquor samples were extracted for analysis at the end of the reaction, and the pulps were washed with the equivalent of 9 m^3 distilled water per o.d. ton of pulp.

The COD, TOC, color and AOX of the combined bleaching effluents were analyzed after filtration of the effluents to remove fibers. The combined effluent comprised of equal parts of filtrates from each bleaching stage of the sequence. For example, for the sequence D_{HT}(PO)D the equivalent to 9 m^3/odt of filtrate was collected for each one of the stages comprising a 27 m^3/odt of effluent. Note that in the sequences having the O/O stage, the filtrates from this stage were not included in the mix since this effluent is usually cycled back to black liquor recovery. The measurements were done in this combined effluent.

The general analytical procedures used in this study were as follows: (1) Pulp pentosans: Tappi T223 cm-84; (2) Pulp sugar composition: HPLC - RID method, after acid hydrolysis according to Tappi Standard T 249; (3) Pulping yield: Gravimetric - Proprietary LCP; (4) Pulping rejects: Gravimetric - Proprietary LCP; (5) Pulp kappa number: Tappi T 236 cm-85; (6) Pulp viscosity: Tappi T230 om-94; (7) Pulp hexenuronic acids content: reference (5): (8) Forming hand sheets for reflectance tests: Tappi T 218 sp-97; Pulp brightness: Tappi T525 om-92; Bleaching yield: Yield loss (%) = 0.0812*TOC(kg C/bdt) + 1.913; Pulp Brightness reversion: Tappi UM 200: Pulp metals: All metals were analyzed by atomic absorption with a CG 7000 spectrophotometer using hollow cathode bulbs after wet washing of the pulp samples according to CPPA G.30P standard; Effluent COD: CPPA H.3; Effluent Color: CPPA H.5; Effluent AOX: Scan - P 69:94; Effluent Total Organic Carbon (TOC): Direct reading in TOC equipment (infrared detection) - Standard Methods for the examination of Water and Wastewater, 1995; Analysis of ClO_2 and H_2O_2 in solutions and residuals: reference (9).

Bleaching chemical costs were calculated in US$/odt of bleached pulp. The following reagent prices (US$/ton of product) were used for the calculation of bleaching chemical costs (all products at 100% wt. basis): ozone = 1500, chlorine dioxide = 1000, hydrogen peroxide = 850, oxygen = 100, sodium hydroxide for bleaching = 500, sodium hydroxide for O_2 delignification = 190, sulfuric acid = 80, anhydrous $MgSO_4$ = 270.

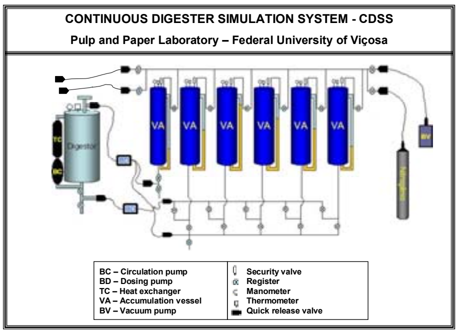

Figure 1. Continuous Digester Simulation System (CDSS).

Table 2. General bleaching conditions

Stage	Const., %	Time, min	Temp., °C	Pres-sure, bar	End pH
O/O	10	15/45	100/105	600/500	11.5
D_{HT}	10	120	95	-	2.8
A/D	11/10	120/10	95/90	-	2.8/3.0
Z/E	40/10	1/30	30/60	-	2.5/10
(PO)	10	120	95	500	10.5
D	10	120	85	-	4.5
P	10	120	85	-	10.5

RESULTS AND DISCUSSION

Pulping results

The pulping results to target kappa number 14, 17.5 and 21 are presented in Table 3. It is observed that extending cooking from kappa number 21 to 17.5 resulted in a screen yield drop of 2%, from 53.4 to 51.4%, and increased active alkali demand of about 2%, from 16.6 to 18.7% as NaOH. Rejects decreased from 0.3 to 0.1%. The pulp viscosity decreased from 87.1 to 54.7 mPa.s and the xylan content dropped from 19.4 to 17.2%. Pulp HexA´s content increased from 48.5 to 69.7 mmol/kg pulp in spite of the fact that xylan content decreased. This trend has been observed in other studies with eucalyptus pulps (1). The residual active alkali increased from 4.3 to 6.7 g/L and the black liquor pH increased from 11.9 to 12.3. Extending cooking even further from kappa number 21 to 14 resulted in a yield drop of 4.1%, from 53.4 to 49.3%, and an increase in active alkali demand of 5.2%, from 16.6 to 21.8%. The pulp viscosity decreased from 87.1 mPa.s to 40.5 mPa.s and pulp xylan level decreased 3.7%, from 19.4 to

15.7% despite of the HexA´s content increase from 48.5 to 68.5 mmol/kg. Thus, it is apparent that a significant part of the yield difference between kappa 21 and 14 derives from xylan losses. The residual active alkali increased from 4.3 to 10.9 g/L and the black liquor pH increased from 11.9 to 12.5. No rejects were observed at kappa 14. The aforementioned results confirmed the very well known concept that higher kappa pulps present higher yield and viscosity because they demand lower active alkali during pulping. The lower demand of active alkali causes a higher retention of the xylans in the pulp, thus increasing overall pulp yield. The question that remains is: Is the wood savings derived from this improved yield sufficient to pay for the additional chemicals cost required to bleach the higher kappa pulps, considering the low cost of eucalyptus wood in Brazil?

Oxygen Delignification Results

The main factors affecting eucalyptus kraft pulp oxygen delignification efficiency are kappa number, HexA´s content and carryover to the bleach plant. Table 4 shows these important characteristics for brown and oxygen delignified pulps. The overall oxygen delignification efficiency as measured by the kappa drop across the O/O stage increases with increasing kappa number, but the efficiency based only on the true lignin kappa number tend to decrease. The lignin from higher kappa pulps tend to contain less free phenolic hydroxyl groups (10), which are the main sites for oxygen reactions, and this explain the slightly lower efficiency based solely on lignin. However, the higher kappa pulps contained more lignin available for reaction than the lower kappa ones because of their similar or lower HexA´s content. Therefore, the higher kappa pulps produced higher overall oxygen delignification efficiency than the lower kappa ones, given that HexA´s do not react with oxygen (5).

Table 3. Pulping results

Target Kappa N°.	Trial Run	Active Alkali, % NaOH	Brown Pulp Characteristics						Black Liquor Characteristics		
			Actual Kappa N°.	Viscosity, mPa.s	Xylans, %	Screen Yield, %	Rejects, %	HexA´s, mmol/kg	Solids, %	Act. alkali, g/L NaOH	Final pH
14	A	21.8	13.9	39.6	15.8	49.0	0.0	68.5	15.7	10.8	12.5
	B	21.8	14.1	40.1	15.6	49.3	0.0	68.9	15.8	10.7	12.5
	C	21,8	14.2	41.9	15.7	49.5	0.0	68.2	15.9	11.2	12.5
	Avg	**21.8**	**14.1**	**40.5**	**15.7**	**49.3**	**0.0**	**68.5**	**15.8**	**10.9**	**12.5**
17.5	A	18.7	17.4	50.5	17.2	51.2	0.0	69.1	15.0	6.9	12.4
	B	18.7	17.3	54.6	17.3	51.3	0.0	69.6	14.9	6.5	12.3
	C	18.7	17.6	58.9	17.0	51.6	0.1	69.3	14.8	6.8	12.3
	Avg	**18.7**	**17.4**	**54.7**	**17.2**	**51.4**	**0.1**	**69.7**	**14.9**	**6.7**	**12.3**
21	A	16.6	21.0	84.0	19.2	53.3	0.2	47.9	14.2	4.4	11.8
	B	16.6	20.7	89.9	19.3	53.4	0.4	48.7	14.3	4.3	11.9
	C	16.6	20.8	87.5	19.6	53.5	0.2	49.0	14.2	4.3	11.9
	Avg	**16.6**	**20.9**	**87.1**	**19.4**	**53.4**	**0.3**	**48.5**	**14.2**	**4.3**	**11.9**

Oxygen delignification has been implemented in single or double stage. For eucalyptus pulps that contain significant amounts of hexenuronic acids (HexA´s), the second stage is rather ineffective. After being treated in the first oxygen stage, the pulp contains very little lignin left, with the remaining kappa number being comprised mostly of hexenuronic acids. The second oxygen stage has little impact on kappa number because the remaining lignin quantity is small and well distributed in the cell wall. However the second stage improves brightness, which is a useful asset ahead in the bleaching sequence. The double stage process is in fact very well fitted for softwoods since the kappa number after the first oxygen stage is still quite high and comprised mostly of lignin. For eucalyptus pulps, the use of a second oxygen stage is always questionable and depends significantly on pulp *true* lignin content as has been demonstrated by Colodette et al. (8). In this study an option was made to compare results considering the double stage oxygen delignification process (O/O) since this has been the mill practice preference for eucalyptus.

Table 4. Characteristics of brown and oxygen delignified[1] pulps of kappa 14, 17.5 and 21

Characteristics		Brown Pulp			Oxygen Delig. Pulp		
Kappa Nº	Total	14.1	17.4	20.9	10.2	11.9	12.8
	Lignin	7.3	10.4	16.1	3.4	5.0	8.0
	HexA´s	6.8	7.0	4.8	6.8	6.9	4.8
Efficiency, %	Total	-	-	-	27.6	31.6	38.7
	"True" Lignin	-	-	-	53.4	51.9	50.3
COD, kgO_2/odt		10	10	10	10	10	10

[1]O/O stage: 10% consistency, 15/45 min, 100/105°C, 600/500 kPa, 1.7-1.9 kg NaOH (from OWL), 1.8% O_2 (plus 0.5% for WL oxidation).

Bleaching Results

Current best available technologies to bleach eucalyptus kraft pulps include sequences such as D_{HT}(PO)DP, A/D(PO)DP and Z/ED(PO). These sequences were compared for kappa 14, 17.5 and 21 pulps untreated or previously treated with double-stage oxygen delignification. For the sake of a fair comparison, all bleaching sequences were carried out at similar operating conditions (Table 2), maintaining constant a kappa factor of 0.15 in the first chlorine dioxide stage and varying chlorine dioxide and peroxide doses in subsequent stages in order to achieve the target brightness of 90% ISO. For the sequence initiating with the Z/E stage a fixed ozone charge of 0.6% on oven dried pulp weight was applied in the ozone treatment. Note that the ideal kappa factor to bleach eucalyptus pulp depends upon the length of the sequence and on the kappa number of the pulp entering the bleach plant. A kappa factor of 0.18-0.22 has been considered ideal for bleaching hardwood pulps in 3-4 stage bleaching sequences beginning with a conventional D_0 stage. For sequences beginning with a hot acid or hot chlorine dioxide stages such as D_{HT}(PO)DP and A/D(PO)DP, lowering the kappa factor to values in the range of 0.15 has shown to decrease bleaching cost even further in mill scale operations. Considering that the D_{HT} and A/D stages have been designed to take care of hexenuronic acids so that chlorine dioxide is not wasted with these compounds, it is apparent that the ideal kappa factor to run these stages should not be exactly the same used for the conventional D_0 stage. A lower kappa factor should be more appropriate for sequences beginning with D_{HT} and A/D technologies in order to leave enough HexA´s left over for hydrolysis during the prolonged hot acid conditions. If the kappa factor is too high in the D_{HT} and A/D stages, the excess chlorine dioxide existing in the system will consume the HexA´s, thereby defeating the purpose of having a hot acid stage.

Sequence

A summary of optimized bleaching results with the sequences D_{HT}(PO)DP, A/D(PO)DP and Z/ED(PO), for the brown and oxygen delignified kappa 14-21 pulps to a target brightness of 90% ISO is presented in Tables 5 and 6, respectively. The lowest and highest bleaching chemical costs were obtained with the sequences D_{HT}(PO)DP and Z/ED(PO), respectively, for both brown (Table 5) and oxygen delignified (Table 6) pulps. The D_{HT} stage is highly efficient for bleaching eucalyptus pulps derived from modified cooking due to their high HexA´s contents. On the other hand, the sequence containing the ozone stage has one stage less than the others and tends to consume more chemicals. As should have been expected, the bleaching cost increased with increasing kappa number of the brown pulp, regardless of the bleaching sequence. The impact was much more significant for the pulps not treated with oxygen delignification (Table 5) and bleached with the Z/ED(PO) sequence. For the brown pulp bleached with the D_{HT}(PO)DP and A/D(PO)DP sequences, an increase of about US$5/odt was observed when the kappa number was increased from 14.1 to 17.4 or from 17.4 to 20.9, whereas for the Z/ED(PO) sequence this increase reached US$7.5/odt when the kappa was raised from 14.1 to 17.4 and US$13.7/odt when it was raised from 17.4 to 20.9 (Table 5). For the oxygen delignified pulps bleached with the D_{HT}(PO)DP sequence, an increase of only about US$2/odt was observed by raising kappa number from 14.1 to 17.4 or from 17.4 to 20.9, while for the Z/ED(PO) sequence an additional US$8/odt was required. Thus, the ozone based sequence is of low tolerance to high kappa pulps, particularly those no treated with oxygen. It is worth noting that the oxygen delignification stage largely reduced the kappa number differences among the various pulps; the 14.1, 17.4 and 20.9 kappa pulps differed by about 3.5 units before oxygen delignification and after such stage they had the kappa reduced to 10.2, 11.9 and 12.8, respectively, differing by only 1-2 kappa units among themselves (Table 4). Hence, the kappa number of the original pulp had a smaller effect on the bleaching cost for the oxygen delignified than for the brown pulps.

For the brown pulp, bleachability tend to increase with increasing kappa number, with the exception of the kappa 20.9 pulp bleached with the sequence Z/ED(PO), which presented an unusually low bleachability in relation to all other samples. This kappa number value is probably excessively high for a three stage bleaching sequence initiating with an ozone stage (limited to 6 kg/odt ozone application). However, for the oxygen delignified samples bleachability tend to increase with increasing kappa number only for the D_{HT}(PO)DP sequence, while decreasing with increasing kappa number for the other two. This result may be explained by the high efficiency of the D_{HT} stage in reducing kappa number, a fact that is reflected by the much higher bleachability values achieved by the D_{HT}(PO)DP sequence (2.19-2.49 K unit/ kg act. Cl), as compared to the other two sequences (1.84-2.10). The only exception to this basic tendency was the unusually high bleachability (2.52) achieved by the Z/ED(PO) sequence with kappa 14.1 pulp previously delignified with oxygen. This is an indication that ozone bleaching with a three stage sequence is well fitted to lower kappa pulps.

Pulp brightness reversion was not significantly affected by pulp kappa number, oxygen delignification or bleaching sequence. Reversion values in the range of 1.6 to 2.4 were obtained in the whole spectrum of treatments and no clear trend was possible to derive. In any case, this reversion amplitude is rather low and all pulps can be considered of high brightness stability. One explanation for the good brightness stability of these pulps is the presence of a final hydrogen peroxide stage in all sequences evaluated. Final peroxide stages tend to minimize reversion rather significantly regardless of the imprint of previous bleaching stages (11). Final viscosity tended to be acceptable regardless of kappa number and bleaching sequence for both brown and oxygen delignified pulps, but the sequence A/D(PO)DP tended to deliver higher viscosities than the other two sequences.

Table 5. Performance of the D_{HT}(PO)DP, A/D(PO)DP and Z/ED(PO) sequences for bleaching kappa 14-21 brown eucalyptus kraft pulps to 90% ISO brightness

Sequence	D_{HT}(PO)DP			A/D(PO)DP			Z/ED(PO)		
Brown Kappa No.	14.1	17.4	20.9	14.1	17.4	20.9	14.1	17.4	20.9
H_2O_2, %	0.5	0.5	0.5	0.5	0.5	0.5	0.8	1.5	2.7
O_2, %	0.5	0.5	0.5	0.5	0.5	0.5	0	0	0
O_3, %	0	0	0	0	0	0	0.6	0.6	0.6
NaOH, %	1.5	1.5	1.6	1.8	1.9	2.0	1.8	2.1	2.8
H_2SO_4, %	0.6	0.6	0.6	0.9	0.9	0.9	1.0	1.0	1.0
$MgSO_4$, %	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
ClO_2, %	2.1	2.6	3.0	2.5	3.0	3.4	1.5	1.5	1.5
[1]Total Active Chlorine (TAC), %	6.45	7.85	9.05	7.65	8.85	9.95	7.17	8.64	11.14
Bleachability, Brown K # / TAC	**2.19**	**2.22**	**2.31**	**1.84**	**1.97**	**2.10**	**1.97**	**2.02**	**1.88**
Chemical Cost, US$/odt	**33.7**	**39.0**	**44.1**	**40.0**	**45.0**	**49.7**	**41.2**	**48.7**	**62.4**
Final Brightness, % ISO	90.2	90.2	90.0	90.1	90.0	90.0	90.1	90.0	90.1
Reversion, % ISO	2.0	1.9	1.9	1.8	2.4	2.1	2.2	2.8	2.1
Final Viscosity, mPa.s	16.5	22.8	28.1	17.8	25.8	30.2	15.9	20.7	26.9
Bleached Pulp HexA´s, mmol/kg	4.0	3.2	2.0	5.9	3.0	2.3	3.8	4.6	5.9
[2]Bleaching Yield, %	97.3	96.7	96.0	97.5	96.9	96.3	97.7	97.1	96.4

[1] Total Active Chlorine (TAC) = (ClO_2*2.63 + H_2O_2*2.09 + 2.5*O_3);

[2] Includes yield loss across O/O stage.

Table 6. Performance of the D_{HT}(PO)DP,), A/D(PO)DP and Z/ED(PO) sequences for bleaching kappa 14-21 oxygen delignified eucalyptus kraft pulps to 90% ISO brightness

Sequence	**O/O D_{HT}(PO)DP**			**O/O A/D(PO)DP**			**O/O Z/ED(PO)**		
Brown Kappa No.	14.1	17.4	20.9	14.1	17.4	20.9	14.1	17.4	20.9
O/O Stage Kappa No.	10.2	11.9	12.8	10.2	11.9	12.8	10.2	11.9	12.8
H_2O_2, %	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.8	1.2
O_2, %	2.8	2.8	2.8	2.8	2.8	2.8	2.5	2.5	2.5
O_3, %	0	0	0	0	0	0	0.6	0.6	0.6
OWL for O_2 Delignification, % NaOH	1.7	1.8	1.9	1.7	1.8	1.9	1.7	1.8	1.9
NaOH, %	1.1	1.1	1.2	1.4	1.5	1.6	1.4	1.7	2.0
H_2SO_4, %	0.6	0.6	0.6	0.9	0.9	0.9	1.0	1.0	1.0
$MgSO_4$, %	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
ClO_2, %	1.2	1.5	1.6	1.4	1.8	2.1	0.6	0.9	1.1
[1]Total Active Chlorine (TAC), %	4.25	4.88	5.15	4.75	5.75	6.55	4.05	5.67	7.01
Bleachability, O/O Stage K #/ TAC	**2.40**	**2.44**	**2.49**	**2.15**	**2.07**	**1.96**	**2.52**	**2.10**	**1.83**
Chemical Cost, US$/odt	**28.8**	**31.4**	**33.1**	**32.5**	**37.0**	**40.7**	**32.9**	**40.9**	**47.9**
Final Brightness, % ISO	90.2	90.2	90.3	90.0	90.0	89.8	90.0	90.1	90.0
Reversion, % ISO	2.0	1.9	2.0	1.6	1.8	1.8	2.0	1.9	1.8
Final Viscosity, mPa.s	14.8	19.4	22.8	16.5	21.3	24.7	13.9	18.1	20.9
Bleached Pulp HexA´s, mmol/kg	5.0	4.4	2.2	7.9	4.8	2.6	5.0	3.3	2.0
[2]Bleaching Yield, %	96.5	96.0	95.4	96.8	96.2	95.6	96.9	96.4	95.8

1 Total Active Chlorine (TAC) = (ClO_2*2.63 + H_2O_2*2.09 + 2.5*O_3);
2 Includes yield loss across O/O stage.

As expected, pulps cooked to lower kappa numbers and pulps oxygen delignified delivered lower final viscosities. It is interesting to note that pulps of high initial viscosities experienced greater losses across bleaching than low viscosity ones.

Bleaching yield tended to be slightly higher for the pulps bleached with the Z/ED(PO) sequence in relation to the other two but differences were small, in the range of 0.3-0.5%. As should be expected, higher kappa pulps presented the lowest bleaching yields. Since yield losses across oxygen delignification were taken into account in the overall bleaching yield, there was a clear trend of slightly lower yields for pulps treated with oxygen in relation to the brown ones.

Incoming Kappa Number

The ideal kappa number to terminate pulping and start bleaching has always been a matter of debate. The controversy is only natural since the ideal kappa number depends on a large number of factors that include not only the type of wood, pulping process, type and number of bleaching stages, presence of oxygen delignification, but foremost on the price of the wood and bleaching chemicals. In the good old times of elemental chlorine bleaching it was common to assume a 25-30 and 17-20 kappa ranges as ideal for softwood and hardwood kraft pulps, respectively. However, with the event of modified cooking associated with elemental chlorine free and totally chlorine free bleaching, there has been a trend towards lower kappa numbers. This has been particularly true for the TCF bleaching case. However there is no basic rule. When oxygen delignification is brought into the picture, the ideal kappa to terminate the cook is very much affected by the efficiency of the oxygen stage installed. Furthermore, the hexenuronic acid content of hardwood pulps is another important factor, and that depends on the wood content of 4-O-methylglucuronic acid and pulping process and conditions. For eucalyptus kraft pulps produced by modern pulping technologies it has been postulated that a kappa number around 17 is ideal (2), but such work was done with pulping and ECF bleaching technologies that are no longer considered best available practices for eucalyptus. The establishment of ideal kappa number for terminating pulping can be properly done taking into account bleaching and wood costs. Figures 2 and 3 show the effect of incoming kappa number on overall fiber line economics for brown and oxygen delignified pulps, respectively, as a function of incoming kappa number. A wood cost of US$45/odt of wood was used for the calculations, since this cost is typical for the Brazilian market currently. It is noticeable that for the brown pulp, increasing kappa number results in increased overall bleaching costs regardless of the bleaching process chosen and that is in line with the fact that the wood cost savings due to increasing kappa number are not sufficiently high to override the large impact of the kappa number on bleaching chemical costs. However, when the pulp is oxygen delignified prior to bleaching this trend is changed at least for the D_{HT}(PO)DP bleaching technology, due to its high efficiency. For the other two sequences this trend was kept the same as observed for the brown pulp. The oxygen delignification stage brings the kappa number to values sufficiently low for the efficient operation of the D_{HT}(PO)DP sequence and, in this case, the yield gains benefits from the higher kappa pulp more than offset the slightly increase in bleaching chemical costs (Table 7). The lower tolerance of the Z/ED(PO) sequence to high kappa numbers is clearly seen in Table 7 whereby a sharp increase in wood plus bleaching costs occur when kappa number is increased above 14 both for brow and oxygen delignified pulps.

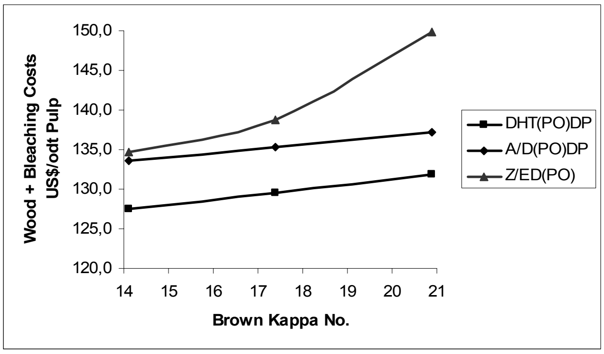

Figure 2. Effect of incoming kappa number on fiber line economics, for brown pulps bleached with the sequences D_{HT}(PO)DP, A/D(PO)DP and Z/ED(PO).

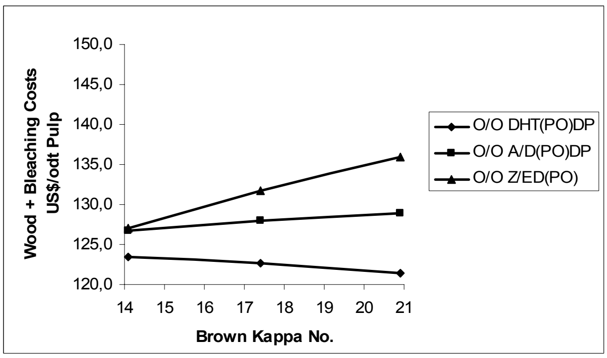

Figure 3. Effect of incoming kappa number on fiber line economics, for oxygen delignified pulps bleached with the sequences D_{HT}(PO)DP, A/D(PO)DP and Z/ED(PO).

Economics of Oxygen Delignification

Oxygen delignification can be considered a standard technology for production of bleached eucalyptus kraft pulps nowadays and any new fiber line will be equipped with this technology. The overall understanding is that such stage is paramount to decrease operational costs and foremost to improve pulp mill environmental performance. However, there are controversies regarding the true economical benefits of installing such stage. It is claimed that the technology requires too high capital, increases recovery load and produces too little operational cost savings. Considering that oxygen delignification is highly inefficient for eucalyptus kraft pulps derived from modified cooking, the need for such stage has been questioned. A comparison of Figures 2 and 3, which show overall cost data for brown and oxygen delignified pulps, respectively, indicate that there is always a operational cost benefit derived from the installation of the oxygen delignification technology, regardless of incoming kappa number and bleaching sequence. However, this benefit is not very large, varying from 4-14 US$/odt pulp depending upon the bleaching technology and kappa number considered (Table 7). If one takes into account the D_{HT}(PO)DP sequence, which was the most efficient among all, the operational cost benefits of the oxygen delignification are even less significant, 4-10 US$/odt pulp depending upon the income kappa number. The most significant operational cost comes from wood, which is not largely affected by oxygen delignification (Table 7). The price of wood is a major factor influencing operational costs. The results shown in Figures 4A-4C takes into account wood costs of 30, 45 and 75 US$/odt, respectively, for pulps bleached with the D_{HT}(PO)DP and O/OD_{HT}(PO)DP sequences. It is observed that oxygen delignification has a slight positive impact on cost, but the major effect comes from wood price.

The capital required to install oxygen delignification is quite high. It is unlikely that an operational cost saving of US$4/odt pulp caused by the oxygen delignification (kappa 14.1 – Sequence D_{HT}(PO)DP, Table 7), or even the US$7/odt (kappa 17.4 – Sequence D_{HT}(PO)DP, Table 7) is sufficient to adequately remunerate a capital investment of over 20 million US$. Therefore, the justification for installing the O-stage for bleaching eucalyptus kraft pulp is indeed an environmental one. Table 8 shows results on environmental performance. Among the sequences evaluated, the D_{HT}(PO)DP and Z/ED(PO) presented the highest and lowest effluent loads, respectively. The D_{HT}(PO)DP sequence is particularly problematic when it comes to effluent color, with the color derived from this sequence being 1.5-2.5 fold higher than that of the A/D(PO)DP and Z/ED(PO) sequences. The lowest AOX values were observed for the Z/ED(PO) sequence followed by the D_{HT}(PO)DP and A/D(PO)DP ones.

Effluent load increased with increasing kappa number as expected. This effect was much more significant with the brown pulp. Oxygen delignification decreased effluent load rather substantially. It decreased COD in the range of 20-40%, with the most significant benefit occurring for the higher kappa pulps. Among the various sequences, no clear trends on COD were observed as far as the impact of oxygen delignification is concerned. The largest impact of the oxygen delignification was on effluent color, causing a reduction of 65-75%. The large influence of the oxygen delignification on color was not significantly affected by pulp incoming kappa number and/or bleaching sequence. The oxygen delignification stage caused a decrease of 50-70% on effluent AOX load with the most significant drops occurring for the D_{HT}(PO)DP sequence and the least significant for the Z/ED(PO) one. The benefits were more significant for the higher kappa pulps.

Table 7. Wood and bleaching chemical costs for production of 90% ISO brightness pulp using modified cooking technology to kappa No. 14-21 and bleaching with the sequences D_{HT}(PO)DP, A/D(PO)DP, Z/ED(PO), with and without oxygen delignification

Operational Costs	**D_{HT}(PO)DP**			**A/D(PO)DP**			**Z/ED(PO)**		
Brown Kappa No.	**14.1**	**17.4**	**20.9**	**14.1**	**17.4**	**20.9**	**14.1**	**17.4**	**20.9**
Bleaching costs, US$/odt pulp	33.7	39.0	44.1	40.0	45.0	49.7	41.2	48.7	62.4
Bleaching Yield, %	97.3	96.7	96.0	97.5	96.9	96.3	97.7	97.1	96.4
Pulping Yield, %	49.3	51.4	53.4	49.3	51.4	53.4	49.3	51.4	53.4
Fiber line Yield, %	48.0	49.7	51.3	48.1	49.8	51.4	48.2	49.9	51.5
Wood Costs, US$/odt pulp	93.8	90.5	87.8	93.6	90.3	87.5	93.4	90.2	87.4
Wood + Bl. costs, US$/odt pulp	**127.5**	**129.5**	**131.8**	**133.6**	**135.4**	**137.2**	**134.6**	**138.8**	**149.8**
Operational Costs	**O/O D_{HT}(PO)DP**			**O/O A/D(PO)DP**			**O/O Z/ED(PO)**		
Bleaching costs, US$/odt pulp	28.8	31.4	33.1	32.5	37.0	40.7	32.9	40.9	47.9
Bleaching Yield, %	96.5	96.0	95.4	96.8	96.2	95.6	96.9	96.4	95.8
Pulping Yield, %	49.3	51.4	53.4	49.3	51.4	53.4	49.3	51.4	53.4
Fiber line Yield, %	47.6	49.3	50.9	47.7	49.4	51.1	47.8	49.5	51.2
[1]Wood Costs, US$/odt pulp	94.6	91.2	88.3	94.3	91.0	88.1	94.2	90.8	88.0
Wood + Bl. costs, US$/odt pulp	**123.4**	**122.6**	**121.5**	**126.8**	**128.0**	**128.8**	**127.1**	**131.7**	**135.9**

[1]At a wood price of US$45/odt

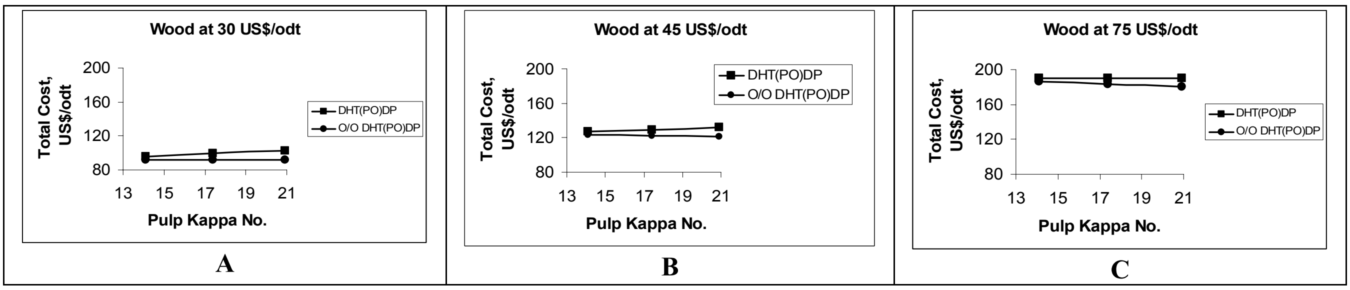

Figure 4. Effect of the oxygen delignification stage on total (wood plus bleaching chemicals) costs as a function of incoming kappa number for three different wood costs. (**A**): 30 US$/odt; (**B**):45US$/odt; (**C**): 75US$/odt.

Table 8. Bleaching Effluent load for production of 90% ISO brightness pulp using modified cooking technology to kappa No. 14-21 and bleaching with the sequences D_{HT}(PO)DP, A/D(PO)DP, Z/ED(PO), with and without oxygen delignification

Results		**Effluent Load of Bleaching Filtrate**		
Bleaching Sequences	**Brown Kappa No.**	**COD, kg O_2/odt**	**Color, kg Pt/odt**	**AOX, kg Cl/odt**
D_{HT}(PO)DP	14.1	32.5	64	0.45
	17.4	42.1	77.2	0.64
	20.9	51.1	85.4	0.81
A/D(PO)DP	14.1	31.5	32.3	0.47
	17.4	37.5	41.6	0.73
	20.9	40.4	50.5	1.03
Z/ED(PO)	14.1	18.9	14.1	0.17
	17.4	23.9	27.3	0.24
	20.9	29.3	41.9	0.3
O/O D_{HT}(PO)DP	14.1	25.7	16.6	0.16
	17.4	29.1	20.3	0.2
	20.9	30.8	25.8	0.24
O/O A/D(PO)DP	14.1	24.5	9.1	0.19
	17.4	25.2	12.3	0.22
	20.9	26.9	14.8	0.3
O/O Z/ED(PO)	14.1	14.2	4.9	0.09
	17.4	17.1	9.1	0.1
	20.9	20	13.1	0.12

State-of-the-art eucalyptus kraft pulp mills tend to install modified cooking to kappa 17-18, double stage oxygen delignification, and ECF bleaching with one of the three sequences aforementioned. Table 9 compares this scenario, considering the D_{HT}(PO)DP sequence, with a scenario of pulping to kappa 14.1, no oxygen delignification and bleaching with the same sequence. It is noticed that the pulp characteristics for the two scenarios are rather similar. The only problems with the kappa 14.1 - no oxygen delignification scenario is indeed an increase of about US$5/odt pulp in operational costs and the significant increase of effluent color and AOX, but it will save about 20 million US$ in capital investment in relation to the kappa 17.4 – O/O stage scenario. Further investigations in our research program will focus on effluent treatability and pulp strength properties, considering these two scenarios.

Table 9. Comparison of optimized fiber lines with and without oxygen delignification

Results	**D_{HT}(PO)DP**	**O/O D_{HT}(PO)DP**
Kappa No	**14.1**	**17.4**
Final Brightness, % ISO	90.2	90.2
Reversion, % ISO	2.0	1.9
Final Viscosity, mPa.s	16.5	19.4
Bleaching costs, US$/odt pulp	33.7	31.4
Bleaching Yield, %	97.3	96.0
Pulping Yield, %	49.3	51.4
Fiber line Yield, %	48.0	49.3
Wood Costs, US$/odt pulp	93.8	91.2
Wood + Bl. costs, US$/odt pulp	**127.5**	**122.6**
Bleaching Filtrate COD, kg O_2/bdt	32.5	29.1
Bleaching Filtrate Color, kg Pt/bdt	64.0	20.3
Bleaching Filtrate AOX, kg Cl/bdt	0.45	0.20

CONCLUSION

The most attractive economics for eucalyptus kraft pulp ECF bleaching is achieved by terminating the cook at kappa No. 14 and bleaching with the D_{HT}(PO)DP sequence, without oxygen delignification, but this approach leads to significant effluent load challenges.

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