EFFECT OF PULP DELIGNIFICATION DEGREE ON FIBER LINE PERFORMANCE AND BLEACHING EFFLUENT LOAD

Jorge L. Colodette*, José L. Gomide, Dalton L. Júnior, and Cristiane Pedrazzi

Industrially made kraft pulps obtained by a modified cooking process may contain 60-75 mmol/kg of hexenuronic acids (HexAs), which represents 6-7.5 kappa units. HexAs do not react with oxygen and very little of it is actually removed across the oxygen delignification stage, causing low efficiencies in the range of 25-35%. In this study, an economical evaluation of the ECF bleaching processes was carried out, having none and double-stage oxygen delignification, when applied to eucalyptus pulps of kappa varying in the range of 14-21. The bleaching processes included sequences containing specific stages for HexAs removal (Z, A/D and D_{HT}). Results indicated that the use of oxygen delignification was not economically attractive, particularly for HexA-rich low-kappa pulps, but processes without oxygen delignification present significant environmental challenges.

Keywords: Kraft pulp, Delignification degree, Bleaching, HexA, Effluent load

Contact information: Pulp and Paper Laboratory, Federal University of Viçosa, Av. Peter H. Rolfs, s/n, Viçosa, MG Brazil 36.570-000; phone:55-31-3899 2086, fax: 55-31-3899 2490, colodett@ufv.br

INTRODUCTION

Eucalyptus kraft pulps produced by kinetically modified pulping processes contain very high amounts of hexenuronic acids (HexAs), in the range of 60-75 mmol/kg pulp (Almeida and Silva Júnior 2004; Lanna et al. 2002; Colodette et al. 2001). This HexA concentration range is roughly equivalent to 6-7.5 kappa units (Vuorinen et al. 1996). Considering that the out-of-digester kappa number varies in the range of 14-18 for eucalyptus pulps and that, purportedly, the HexA contents of the pulps at this kappa number range tend to be rather constant (Almeida and Silva Júnior 2004; Lanna et al. 2002; Chakar et al. 2000), the significance of HexAs in the overall kappa number may vary sharply, depending upon the pulp's initial kappa number. For example, kappa 14 and 18 pulp samples containing equal amounts of HexAs (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 HexAs on overall kappa number is more significant for the kappa 14 pulp.

Oxygen delignification efficiency is rather low for low-kappa pulps containing high HexA concentrations (Colodette et al. 2006; Eiras and Colodette 2003) since oxygen does not react with HexAs (Vuorinen et al. 1996). As a matter of fact, it is doubtful whether or not oxygen delignification is worth implementing at all for HexA-rich eucalyptus kraft pulps having low kappa number.

The objective of this study was to evaluate bleachability of HexA-rich (derived from modified cooking) eucalyptus kraft pulps of kappa number 14, 17.5 and 21, with sequences containing specific stages for removal of hexenuronic acids such as D_{HT}, A/D, and Z. Note that the kraft pulping modifications were made to simulate the Andritz Lo-solids^{TM} cooking process, within the limitations of laboratory equipment available.

EXPERIMENTAL

Materials

Five trees of a 7-years old hybrid *Eucalyptus grandis x Eucalyptus urophylla* clone were used. The trees were obtained from commercial plantations and they derived from progeny of a first generation cross of the aforementioned species. The average characteristics of the five samples were as follows: 532 kg/m^3 density, 42.5% cellulose, 27.3% total lignin, 17.4% hemicelluloses, 5.1% uronic acids, 2.4% acetyl groups, 3.2% ethanol/toluene extractives, and 2.0 lignin syringyl/guayacyl (S/G) ratio.

Methods

Pulping was carried out by a modified kraft pulping method to kappa numbers 14, 17.5 and 21. Conditions were kept constant, except that active alkali charges were varied to achieve the desired kappa number. 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, liquor-to-wood ratio (L/W) = 3.5/1; (2) upper cooking zone: 155°C, 60 minutes, 30% of active alkali, L/W = 3.5/1; (3) lower cooking zone: 156°C, 120 minutes, 25% of total active alkali, L/W = 3.5/1 L/kg. 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, respectively. Bleaching of 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), whereby: O/O refers to a double stage oxygen delignification without inter-stage washing; D_{HT} refers to a long (120 min) and unusually high temperature chlorine dioxide stage (90-95 °C); (PO) refers to a fully pressurized hydrogen peroxide stage in the presence of oxygen; D refers to conventional chlorine dioxide stage; P refers to atmospheric peroxide stage; A/D refers to a hot (90-95 °C) acid hydrolysis (pH 2.5-3) followed by a hot chlorine dioxide stage without inter-stage washing; Z/E refers to a high consistency ozone stage followed by an alkali extraction without inter-stage washing.

General oxygen delignification and bleaching conditions are listed in Table 1. In the O/O stage the alkali charges of 1.7, 1.8, and 1.9 % on o.d. pulp weight were used for the kappa 14, 17.5 and 21 pulps, respectively. These charges were all applied in the first stage and in the form of oxidized white liquor (OWL). The oxygen charge was kept constant and equal to 2.3 % for all three pulps, with 1.8 % being applied in the first O-stage and 0.5% applied in the second O-stage. For the D_{HT}(PO)DP and A/D(PO)DP sequences, a kappa factor of 0.15 was applied to the first chlorine dioxide stage, regardless of pulp kappa number. The balance chlorine dioxide was applied to the second D-stage of the sequence. For the Z/ED(PO) sequence the fixed charge of 1.52% ClO_2 was applied in the single D-stage, regardless of pulp kappa number. The same approach was followed for the O/OD_{HT}(PO)DP, O/OA/D(PO)DP and O/OZ/ED(PO) sequences, except that only 0.57% of ClO_2 was applied in the single D-stage of the latter sequence.

Except where otherwise stated, the following standard analytical procedures were used: viscosity - Tappi T 230, kappa number - Tappi T 236, residual alkali - Tappi T 625, carbohydrates - Tappi T 249, black liquor solids - Tappi T 650, pulp yield and rejects - gravimetric, COD - Paptac H3, color - Paptac H5, AOX - Scan P 69:94, forming handsheets for reflectance testing - Tappi T 272, diffuse brightness of pulp - Tappi T 525 and brightness reversion - Tappi UM 200. The analyses of bleach chemical solutions and residuals were carried out according to Kraft (1967). Pulp hexenuronic acids were measured according to Vuorinen et al. (1996). The pulp cellulose and hemicelluloses (xylans) contents were determined, indirectly, from the carbohydrate analytical data. Bleaching chemical costs were calculated in US$/odt of bleached pulp, using market chemical prices (US$/ton of product 100% pure) as follows: O_2 = 100, ClO_2 = 1000, H_2O_2 = 850, O_3 = 1500, NaOH 500, oxidized white liquor 190, H_2SO_4 = 80, $MgSO_4$ = 270.

Table 1. General oxygen delignification and bleaching conditions

Stage	Consistency %	Time, min	Temp., ºC	Pressure, kPa	End pH
O/O	10/10	15/45	100/105	600/500	12/11.5
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

It was 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 by about 2%, from 16.6 to 18.7% as NaOH (Table 2). 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 HexAs 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 (Almeida and Silva Júnior, 2004). 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 effective 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 the pulp xylan level decreased 3.7%, from 19.4 to 15.7% in spite of the HexAs 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. The question which 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?

Table 2. Pulping Results

Target Kappa No.		**14.0**	**17.5**	**21.0**
Active Alkali, % NaOH		**21.8**	**18.7**	**16.6**
Brown Pulp Characteristics	Measured Kappa **No.**	14.1	17.4	20.9
	Viscosity, mPa.s	40.5	54.7	87.1
	Xylans, %	15.7	17.2	19.4
	Screened Yield, %	49.3	51.4	53.4
	Rejects, %	0.0	0.1	0.3
	HexAs, mmol/kg	68.5	69.7	48.5
Black Liquor	Solids, %	15.8	14.9	14.2
	Active alkali, g/L NaOH	10.9	6.7	4.3
	Final pH	12.5	12.3	11.9

Oxygen Delignification Results

The main factors affecting eucalyptus kraft pulp oxygen delignification efficiency are kappa number, HexAs content, and carryover to the bleach plant. The overall oxygen delignification efficiency, as measured by the kappa drop across the O/O stage, increased with increasing kappa number, but the efficiency based only on the "true lignin kappa number" tended to decrease (Table 3). "True lignin kappa number" is the one derived only from lignin, after subtraction of the kappa number due to hexenuronic acids, considering the ratio 10 mmol/kg HexA equals to 1 kappa number unit. The lignins from higher kappa pulps tend to contain less free phenolic hydroxyl groups (Gellerstedt 1996), which are the main sites for oxygen reactions, and this may explain the slightly lower efficiency based solely on lignin. However, the higher kappa pulps contained, proportionally, more lignin available for reaction than the lower kappa ones because of their similar or lower HexAs contents. Therefore, the higher kappa pulps produced higher overall oxygen delignification efficiency than the lower kappa ones, given that HexAs do not react with oxygen (Vuorinen et al. 1996). In this work, the influence of HexAs on kappa number was calculated assuming that 10 mmol/kg pulp of HexAs is equivalent to 1 kappa unit (Vuorinen et al. 1996). This ratio has been somewhat questioned in a later work by Li and Gellerstedt, 1997 who claim a ratio of 11.6-11.9 mmol/kg pulp of HexAs per kappa unit.

Table 3. Characteristics of the brown and oxygen-delignified pulps of kappa 14, 17.5 and 21

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

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). The eleven bleach plants installed or rebuilt in South America in the last 10 years have chosen among these technologies. These choices stem from the fact that aforementioned sequences contain a first bleaching stage adapted to remove HexAs, which are abundant in eucalyptus pulps produced by modified cooking processes, and a last stage adapted to prevent pulp brightness reversion, which is a common problem for eucalyptus kraft pulps bleached to high brightness (Colodette et al, 2006). 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 under similar operating conditions (Table 1), maintaining a constant 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.

Sequences

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 4) and oxygen-delignified (Table 5) pulps. Note that chemical costs include all oxidants, acid, base and additives used in each bleaching sequence. The D_{HT} stage is highly efficient for bleaching eucalyptus pulps derived from modified cooking. Such pulps contain large amounts of HexAs and the chlorine dioxide stage run at high temperature (D_{HT}) easily removes them by acid hydrolysis while simultaneously oxidizing the lignin. The D_{HT} stage is not effective for bleaching pulps containing no or low HexAs such as Soda/AQ, sulfite, softwood kraft and even hardwood kraft produced by conventional cooking procedures. On the other hand, the sequence containing the ozone stage has one less stage than the others and tends to consume more chemicals. As should be 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 and bleached with the Z/ED(PO) sequence (Table 4). 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 4). 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 has low tolerance for high-kappa pulps, particularly those not treated with oxygen. It is worth noting that the oxygen delignification stage largely reduced the kappa number differences among the various pulps. 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.

In this work bleachability has been defined as the ratio between kappa number entering the bleach plant and total active chlorine (TAC) required for attaining the target brightness of 90% ISO. Total active chlorine was defined by the following equation: TAC = (ClO_2*2.63 + H_2O_2*2.09 + O_3*2.5). The factors 2.63 and 2.09 are simple conversions of ClO_2 and H_2O_2 into active Cl_2 based on their oxidation equivalents. On the other hand, the factor 2.5 is not a simple conversion of O_3 into active Cl_2 based on oxidation equivalents, but rather a result that has been reported in-mill experiences with ozone (Munro and Griffiths, 2000). Based on simple oxidation equivalent conversion this factor would be 4.3 for the ozone case. For the brown pulp, bleachability tended 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. However, for the oxygen-delignified samples bleachability tended to increase with increasing kappa number only for the D_{HT}(PO)DP sequence, while decreasing 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 kappa units/ kg active 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 the 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. Suitable 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. Note that brightness reversion values for eucalyptus pulps may vary from 1-5% ISO (by Tappi UM 200 standard) depending upon the pulping and bleaching procedures. One explanation for the good brightness stability of these pulps is the presence of a final hydrogen peroxide stage in all sequences evaluated. Previous work (Eiras and Colodette 2005) carried out with eucalyptus pulps using the same brightness reversion procedure used in this work (Tappi UM 200) have indicated better brightness stability for pulps bleached with sequences ending with a final peroxide stage in relation to those ending with a final D stage. Final viscosities tended to be acceptable regardless of kappa number and bleaching sequence for both brown and oxygen-delignified pulps, but the A/D(PO)DP sequence delivered the highest viscosities. As expected, pulps cooked to lower kappa numbers and oxygen delignified showed the lowest final viscosities. 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. There was a clear trend towards slightly lower yields for pulps treated with oxygen in relation to the brown ones.

Table 4. 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
OWL for O_2 delig, % NaOH	0	0	0	0	0	0	0	0	0
NaOH for Bleaching, %	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	1,52	1,52	1,52
[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
[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 + O_3*2.5);
[2]Includes yield loss across O/O stage.

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 it 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. Kappa ranges of 25-30 and 17-20 have been considered ideal for softwood and hardwood kraft pulps, respectively. However, with the advent of modified cooking associated with elemental chlorine free and totally chlorine free bleaching, there has been a trend towards lower kappa numbers. 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. The establishment of an ideal kappa number for terminating pulping can be properly done, taking into account bleaching and wood costs.

Table 5. 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 delig, % NaOH	1,7	1,8	1,9	1,7	1,8	1,9	1,7	1,8	1,9
NaOH for Bleaching, %	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	0,57	0,95	1,14
[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
[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 + O_3*2.5);
[2]Includes yield loss across O/O stage.

Table 6 shows the effect of incoming kappa number on overall fiber line economics for brown and oxygen-delignified pulps, respectively. A wood cost of US$45/odt of wood was used for the calculations, since this cost is currently typical for the Brazilian market (spot market). For brown pulp, increasing kappa number results in a prediction of 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, for the oxygen-delignified pulp this trend is somewhat changed, at least for the D_{HT}(PO)DP bleaching technology, due to its high efficiency. The oxygen delignification stage brings the kappa number of the high kappa pulps to values sufficiently low for the efficient operation of the D_{HT}(PO)DP sequence and, consequently, the chemical costs for this sequence is rather low even for the high kappa pulps. Therefore, in this particular case, the yield gains benefit from terminating the cook at a higher kappa number more than offset the slight increase in bleaching chemical costs (Table 6) caused by the high kappa. In other words, the D_{HT}(PO)DP sequence accommodates better the potential bleaching cost increase derived from a high incoming kappa than the other sequences. The lower tolerance of the Z/ED(PO) sequence to high kappa numbers is clearly seen, whereby a sharp increase in wood plus bleaching costs occurs when kappa number is increased above 14 both for brown and oxygen-delignified pulps.

Table 6. 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 and Z/ED(PO), with and without Oxygen Delignification

Operational Costs	**D_{HT}(PO)D**			**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.

Economy of Oxygen Delignification

Oxygen delignification is currently a standard technology for production of bleached eucalyptus kraft pulps. The overall understanding is that such a stage is paramount to decrease operational costs and foremost to improve pulp mill environmental performance. Considering that oxygen delignification is highly inefficient for eucalyptus kraft pulps derived from modified cooking, the need for such a stage has been questioned. Table 6 shows that there is always an 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 to 14 US$/odt pulp, depending upon the bleaching technology and kappa number considered. If one takes into account the D_{HT}(PO)DP sequence, which was the most efficient among all those considered in this study, the operational cost benefits of oxygen delignification are even less significant, 4 to 10 US$/odt pulp, depending upon the incoming kappa number. The most significant operational cost comes from wood, which is not largely affected by oxygen delignification. The price of wood is a major factor influencing operational costs. As an example, for the 14.1 kappa pulp a decrease in wood price from US$45/odt (Table 6) to US$30/odt reduces operational costs from US$127.5/odt to US$ 96.2/odt, for the D_{HT}(PO)DP sequence and from US$123.4/odt to US$ 91.9/odt, for the O/OD_{HT}(PO)DP sequence. This shows that 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$4/odt pulp caused by oxygen delignification is sufficient to adequately remunerate a capital investment of over 20 million US$. Therefore, the justification for installing the O-stage for bleaching eucalyptus kraft pulp is indeed an environmental one. Among the sequences evaluated, the D_{HT}(PO)DP and Z/ED(PO) presented the highest and lowest effluent loads, respectively (Table 7). 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 brown pulp. Oxygen delignification substantially decreased effluent load. 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 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. Further investigations in our research program will focus on effluent treatability and pulp strength properties, considering these two scenarios.

Note that the costs related to increased effluent load and loss in energy (fewer solids to burn) for the processes without oxygen delignification was not taken into account in the economical analyses (Table 6). This matter will be addressed in another publication where a more in depth economical evaluation of the various approaches is presented. For example, the average costs for effluent treatment using aeration stabilization basins or activated sludge systems in Brazilian eucalyptus mills is in the range of 2-3 US$/$m^3$ effluent. Such treatments manage to decrease COD by 60-70% from raw effluents containing 30-40 kg O_2/odt pulp COD. Thus, it is possible to derive an estimate for increased effluent treatment cost based on increased effluent COD. On the other hand, the energy losses due to fewer solids to burn can be easily calculated on the basis of decreased solids to recovery, which in the case of eucalyptus kraft pulp mills vary in the range of 3-4%. It is worth noting that for mills having a bottleneck in the recovery area the decreased solids may result in increased mill throughput. Therefore, the economical analyses must take this matter also into account.

Table 7. Bleaching Effluent Load for Production of 90% ISO Brightness Pulp using Modified Cooking Technology to Kappa No. 14-21 and Bleaching with the D_{HT}(PO)DP, A/D(PO)DP, and Z/ED(PO) Sequences, with and without Oxygen Delignification

Brown Kappa No.	14.1	17.4	20.9	14.1	17.4	20.9	14.1	17.4	20.9
Effluent Load	**D_{HT}(PO)DP**			**A/D(PO)DP**			**Z/ED(PO)**		
Bleaching Filtrate COD, kg O_2/bdt	32,5	42,1	51,1	31,5	37,5	40,4	18,9	23,9	29,3
Bleaching Filtrate Color, kg Pt/bdt	64,0	77,2	85,4	32,3	41,6	50,5	14,1	27,3	41,9
Bleaching Filtrate AOX, kg Cl/bdt	0,45	0,64	0,81	0,47	0,73	1,03	0,17	0,24	0,30
Effluent Load	**O/O D_{HT}(PO)DP**			**O/O A/D(PO)DP**			**O/O Z/ED(PO)**		
Bleaching Filtrate COD, kg O_2/bdt	25,7	29,1	30,8	24,5	25,2	26,9	14,2	17,1	20,0
Bleaching Filtrate Color, kg Pt/bdt	16,6	20,3	25,8	9,1	12,3	14,8	4,9	9,1	13,1
Bleaching Filtrate AOX, kg Cl/bdt	0,16	0,20	0,24	0,19	0,22	0,30	0,09	0,10	0,12

CONCLUSIONS

- Eucalyptus fiberlines already equipped with oxygen delignification will benefit from terminating the cook at higher kappa numbers (17.5-21) and proceeding with the sequence D_{HT}(PO)DP, which gives the lowest operating costs.
- For new fiberlines, the most attractive economy to manufacture bleached eucalyptus kraft pulp is achieved by terminating the cook at kappa number ~14 and bleaching with the D_{HT}(PO)DP sequence, without oxygen delignification. The great economical advantage derives from the significant capital savings. But this approach leads to significant effluent load challenges.

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