Eucalyptus kraft pulp bleaching: state-of-the-art and new developments

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ABSTRACT: Chemical demand, yield, water consumption, effluent load and treatability, pulp organic chlorine compounds (OX), brightness stability, refinability, and strength are drivers for choosing bleaching technology. This work critically reviews the state-of-the-art processes for oxygen delignification, first stage, second stage, and final bleaching of eucalyptus kraft pulp in light of those drivers. Emerging technologies, such as the P_{Mo} stage and formaldehyde assisted bleaching, are discussed. Implementation of single- or double-stage oxygen delignification is determined by the pulp "true" lignin content. High pulp HexAs content and poor selectivity limits dropping kappa number under 9-10 in single or double O-stage. Mo-catalyzed acid peroxide delignification after O-stage allows further reduction of kappa number to 3-4. Efficient post-oxygen washing is the key for low cost bleaching, with a kilogram of COD/o.d. ton consuming the equivalent to 0.085% active chlorine. A/D-(EP)-D type three-stage sequence suffices for bleaching eucalyptus kraft pulps. The inclusion of a fourth stage is desirable for high brightness/low reversion pulps. Chemical consumption is strongly influenced by brown pulp origin, with variations of 3.2% to 7.7% active Cl_2 demand, depending upon the pulp type. The type of elemental chlorine free (ECF) bleaching technology, based on chlorine dioxide, affects chemical consumption only slightly. Hot acid/hot chlorine dioxide bleaching technology saves small amounts of active chlorine for high bleachability pulps, but none for low bleachability ones. Atmospheric extraction (EP) suffices for eucalyptus kraft pulp bleaching. Formaldehyde saves more chlorine dioxide when used in D_1 than in D_0/D_{HT} stages. A final peroxide stage improves pulp brightness stability. The production of organically bound chlorine decreases by 30% with hot chlorine dioxide bleaching, but this gain disappears after effluent biological treatment.

Application: This paper will help pulp mill engineers better understand the phenomena involved in hardwood pulp bleaching, including process best practices and their effects on product quality and effluent load. It summarizes recent developments in hardwood pulp bleaching. This information will allow readers, particularly bleach plant operators, to better optimize their processes when dealing with hardwood fibers.

Eucalyptus wood has become the most important source of bleached market pulp in the world. The demand for market pulp from eucalyptus reached 8 million tons in 2003 and is projected to reach 14 million tons in 2015 [1]. Fibers derived from single species are currently the world's preferred market pulps. Unlike mixed species pulps, single species offer specific benefits and well-defined attributes. In this regard, eucalyptus pulp fibers produced from cloned plantations have emerged as the most desired fibers in the market.

Bleached eucalyptus kraft pulps are largely used to manufacture tissue and printing and writing (P&W) paper grades. Particularly for P&W grades, final brightness and brightness stability are rigorous parameters that affect optical brightener demand during paper manufacture. The pulp bleaching technology for tissue grades is quite well established, with a three-stage sequence of the D-(EPO)-D type being sufficient (88%-90% ISO brightness). For P&W grades, however, the best bleaching technology is still a matter of debate. Four-stage bleaching sequences of the D-(EPO)-D-D and D-(EPO)-D-P types are recommended to guarantee brightness of at least 92% ISO, with reversion lower than 2% ISO.

Bleaching chemical demand, bleaching yield, water consumption, effluent load and treatability, and pulp organic chlorine compounds (OX), brightness stability, refinability, and strength are drivers that decide bleaching technology. Issues such as first stage bleaching with D_0 vs. A_{HT}/D vs. D_{HT} vs. Z_{HC}/E vs. Z/D, fully pressurized (PO) vs. partially pressurized (EPO) vs. atmospheric (EP) second stage and final bleaching with D vs. D_N/D vs. DD vs. DP stages are not yet settled. In addition, emerging bleaching technologies such as the molybdenum (Mo) catalyzed acid peroxide delignification (P_{Mo} stage) and the use of formaldehyde in D-stages are currently a matter of discussion in regard to eucalyptus kraft pulp bleaching.

This paper addresses such issues using data collected at Federal University of Viçosa (Brazil) Pulp and Paper Laboratory and the pertinent literature. The main purpose of the work is to present a progress on eucalyptus kraft pulp bleaching through a critical review of the state-of-the-art and emerging technologies.

EXPERIMENTAL

Two brown pulp samples of about kappa 17 and various oxygen delignified eucalyptus kraft pulps (industrial and laboratory made) of kappa number in the range of 9-11 were used throughout this study. Single/double stage oxygen delignifica-

tion (O), ozone bleaching (Z/E and Z/D), pressurized peroxide bleaching (EPO and PO), hot chlorine dioxide (D_{HT}) and hot acid hydrolysis followed by chlorine dioxide (A_{HT}/D) stages were performed with 280-300 g oven dried pulp samples in a Teflon-lined mixer/reactor (Quantum Technologies, model Mark V). The charges of chemicals were added to the reactor after the desired pulp temperature was reached and the reaction pressure was adjusted with oxygen when necessary. After the pre-established reaction time elapsed, the reactor pressure was released, the pulp was discharged into a 150-mesh screening box and 300 mL of liquor were squeezed from the pulp for analysis. Chlorine dioxide/chlorine (DC), chorine dioxide (D), atmospheric alkali extraction (E, EP) and hydrogen peroxide (P) bleaching stages were performed in polyethylene bags. In all cases, the required amounts of water and reagents were mixed with the pulp at room temperature and the mixtures heated to the desired temperature in a microwave oven. The samples were than placed in a heating bath for the desired reaction time. All bleaching stages were carried out in duplicate and inter-stage washings simulated a vacuum filter operating at a dilution factor of two (inlet and outlet consistencies of 2% and 12.5%, respectively).

After bleaching, pulp was diluted to 0.3% consistency, pH was adjusted to 5.5-6 with SO_2/H_2SO_4 or SO_2/NaOH, and handsheets were formed and dried for 12 h to 9%-10% humidity in an environmentally controlled room (50±2% relative humidity and 23±1°C). Brightness reversion tests were performed in conformity with TAPPI Method T 200 (Laboratory processing of pulp) using 10 repetitions (4 h, 105±3°C, 0% relative humidity). Reversion results were expressed as percent brightness loss across the accelerated reversion test or as post color number (PCN), in conformity with TAPPI TIS 0606-18 (The Kubelka and Munk relationship between absorption/scattering coefficients and reflectance). Pulp metal content was measured according to the SCAN-CM 38:96 procedure. Pulp kappa number, brightness, viscosity, and xylan contents were determined according to TAPPI T 236 cm-85 (Kappa number of pulp), T 525 om-92 (Diffuse brightness of pulp), T 230 om-94 (Viscosity of pulp), and T 249 cm-85 (Carbohydrate composition of extractive-free wood and wood pulp by gas-liquid chromatography) standard methods, respectively. Pulp contents of hexenuronic acids and bound chlorine (OX) were measured according to the HUT [2] and PTS-RH: 012/90 [3] methods, respectively. Bleaching yields were determined indirectly *via* analysis of bleaching filtrate TOC values. Effluent AOX, BOD, COD, and TOC were measured according to ISO procedures.

RESULTS AND DISCUSSION

Modern eucalyptus kraft pulp bleach plants are usually equipped with:

1) single (O) or double (O/O) oxygen delignification;

2) a first bleaching stage comprised of a conventional chlorine dioxide stage (D_0) or chlorine dioxide bleaching at high temperature (D_{HT}) or a sequential treatment with hot acid hydrolysis and chlorine dioxide (A_{HT}/D) or a sequential treatment with ozone and alkali (Z/E) or a sequential treatment with ozone and chlorine dioxide (Z/D);

3) a second bleaching stage comprised of oxidative extraction with hydrogen peroxide (EP), oxidative extraction with oxygen and peroxide (EPO) or peroxide pressurized extraction (PO);

4) a third bleaching stage with one chlorine dioxide reactor (D_1) or with two reactors, without inter-stage washing (D_N/D);

5) a fourth bleaching stage with chlorine dioxide (D_2) or hydrogen peroxide (P).

The fourth stage is optional and required only when brightness of more than 92% ISO are needed. There are some variations of these basic strategies, but the large majority of the pulp mills that bleach eucalyptus use them.

Oxygen delignification

Oxygen delignification has been used in single or double stages. For eucalyptus pulps that contain significant amounts of hexenuronic acids (HexAs), 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. Oxygen does not react with hexenuronic acids [4]. The second oxygen stage has little effect 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 results shown in **Table I** for samples A (high HexAs) and B (low

Pulp characteristics before and after oxygen delignification	Sample A			Sample B		
	Brown	O	O/O	Brown	O	O/O
Total kappa N°.	17.2	11.7	11.2	17.4	10.8	9.5
Lignin kappa N°.	9.9	4.6	4.0	15.1	8.8	7.5
HexAs kappa N°.	7.3	7.1	7.2	2.3	2.0	2.0
Viscosity, mPa.s	55.0	35.8	27.3	39.7	27.8	23.8
Brightness, % ISO	36.4	51.4	53.4	29.8	48.8	52.5
Kappa drop across O-stage, %	-	32.0	34.9		37.9	45.4
Viscosity drop across O-stage, %	-	34.9	50.4	-	30.0	40.1
Brightness gain, % ISO	-	15.0	17.0	-	19.0	22.7
O-stage yield loss, %	-	1.8	2.0	-	2.0	2.2
O: 10% consistency, 100°C, 45 min, 1.8% O_2, 1.8% NaOH, 500 kPa. O/O: 10% consistency, 100/100°C, 45/45 min, 1.8/0.9%O_2, 1.8/0% NaOH, 500/600 kPa.						

I. Single (O) vs. double (O/O) stage oxygen delignification for two well-washed and DCM extracted eucalyptus kraft pulp samples containing different amounts of hexenuronic acids.

HexAs), respectively, illustrate the point. Sample B has low HexAs content and does benefit from a second oxygen stage, but sample A has very high HexAs content and benefits little from a second stage. 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 hardwoods, the use of a second oxygen stage is always questionable and depends significantly on pulp *actual* lignin content.

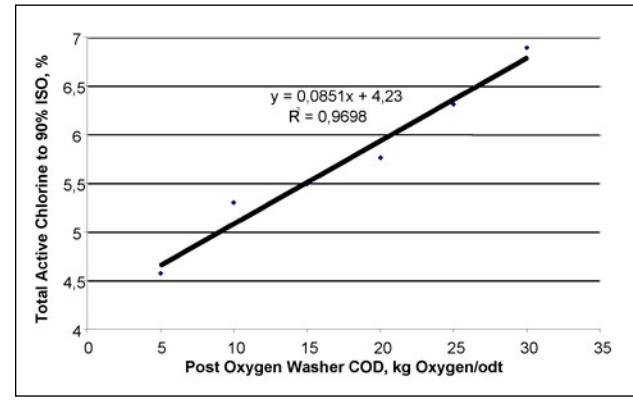
The development of oxygen delignification technology for eucalyptus kraft pulp has centered on the evolution of two-stage systems for increased degrees of delignification. One of the drivers for this is the desire to increase pulp yield by terminating the kraft cook at a higher than normal kappa number and using the more selective oxygen stage to complete the delignification to kappa numbers at which other bleaching agents can take over. This is exemplified by the work of Colodette et al. [5] that illustrates the superior selectivity of oxygen delignification relative to that of kraft pulping. The yield benefit of stopping the cook at kappa 19 instead of 15.5 and following the delignification with oxygen was 2%-2.5%. Furthermore, the study clearly demonstrated that the kappa number entering the bleach plant is not greatly affected by the out of digester kappa number since oxygen delignification efficiency is much higher for the higher kappa pulps [5]. Similar trends have been observed by other workers in connection with softwood pulps [6].

Washing efficiency

Modern eucalyptus kraft pulp bleach plants are usually equipped with state-of-the-art washing equipments, which deliver pulp to the bleach plant with COD values as low as 5 kg O_2/ o.d. ton pulp. However, the brown stock and post-oxygen washing of older mills are usually overloaded and it is not uncommon to find bleach plants with carry over COD to the bleach plant in the range of 20-30 kg O_2/o.d. ton pulp. Carry over COD can be very harmful to the bleaching operation. Evaluations done in our laboratory indicated an increase in active consumption in the order of 0.085% for each unit COD carried over with the oxygen delignified pulp. For example, a well washed pulp having a COD of 5 kg O_2/o.d. ton pulp consumed 1.7% lesser active chlorine than a poorly washed pulp having a COD of 25 kg O_2/ o.d. ton pulp (**Fig. 1**). This result emphasizes the great importance of good washing prior to the bleaching operation. Similar numbers have been reported in other reviews [7, 8].

Further delignification after oxygen stage

Oxygen delignification of eucalyptus kraft pulp has been limited to kappa numbers in the range of 9-10 for selectivity reasons. Thus, lowering the kappa number before ECF bleaching requires the use of other techniques and other chemicals. Enzyme bleaching is becoming increasingly popular in the United States. Currently there are more than 20 U.S. mills using xylanases [9] and many others in other parts of the world. For



1. Impact of post oxygen washer COD carryover on total active chlorine consumption with the sequence D(EP)D to achieve 90.00% ISO brightness. Industrial oxygen delignified kraft pulp (kappa 10.3, HexAs 59.4 mmol/kg, COD adjustments done with industrial spent liquor).
D_0 = 10% consistency, 70°C, 30 min, pH 3.0, kappa factor 0.26; (EP): 10% consistency, 80°C, 120 min, pH 10.5, 0.3% H_2O_2 ; D_1: 10% consistency, 80°C, 120 min, pH 4.5.

eucalyptus kraft pulp, there has not been much interest toward implementation of xylanase bleaching. Xylanases are usually applied in the high density chest after oxygen delignification, thus requiring low capital investment. A slight kappa number reduction is achieved but chemical savings in subsequent ECF bleaching can reach 20% active chlorine [9].

Acid peroxide catalyzed with molybdenum salts (P_{Mo} stage) also show good potential for further reducing kappa number [10]. **Table II** shows that a treatment of an oxygen delignified eucalyptus pulp of kappa 11 with the P_{Mo} stage resulted in kappa reduction up to 3.2, depending upon Mo dose and reaction time. Pulp viscosity also decreased, but ended at acceptable values for bleached grade eucalyptus pulps. Further optimization studies in our lab have led to significant viscosity improvements. A recent mill trial with such a treatment in a bleached eucalyptus kraft pulp mill has reproduced the lab results and showed potential of this technology to decrease bleaching costs.

ECF bleaching

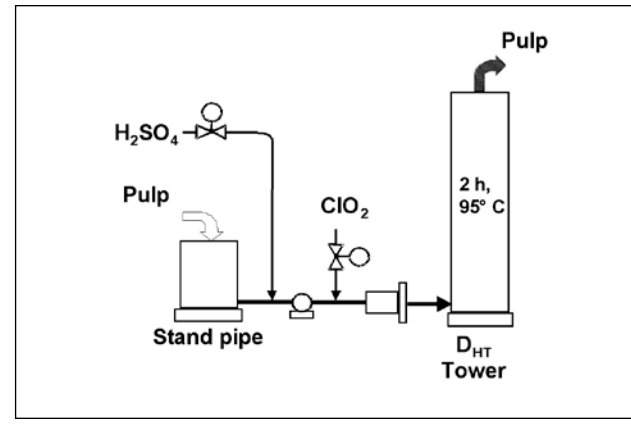
ECF bleaching is dominant, but there are considerable variations in the way ECF bleaching is practiced for eucalyptus kraft pulp. Oxygen delignification plus a core sequence of the D(EPO)DD type seems to predominate, but there are varia-

Reaction time, h	2	2	3	3	4	4
Mo, %	**0.01**	**0.02**	**0.01**	**0.02**	**0.01**	**0.02**
Brightness, % ISO	64.1	64.1	63.4	62.9	63.2	62.3
Kappa N°	4.4	3.6	3.7	3.3	3.4	3.2
Viscosity, mPa.s	23.7	23.0	21.0	20.9	20.8	20.6
HexAs, mmol/kg	15.0	10.3	10.9	7.9	5.3	4.9
Yield loss, %	1.9	1.9	2.0	2.0	2.0	2.1

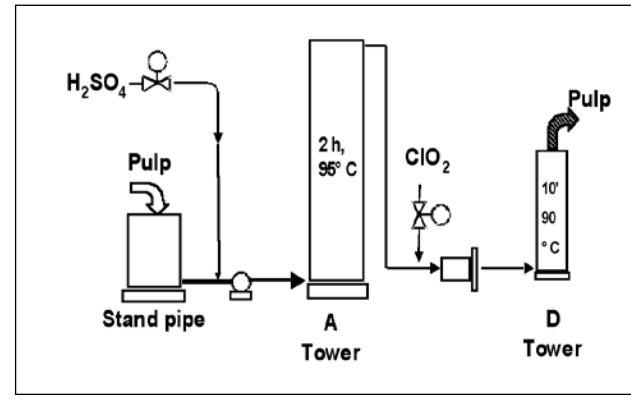
II. Results of P_{Mo} stage (10% consistency, 90°C, 1.0% H_2O_2, pH 3.1-3.3) performance applied to an oxygen delignified eucalyptus kraft pulp (kappa 11, HexAs 58.4 mmol/kg, viscosity 35.7 mPa.s, brightness 51.5% ISO).

tions, particularly in the modes of chlorine dioxide application in the first stage and hydrogen peroxide application in the second stage. In older bleach plants the first chlorine stage has been replaced by chlorine dioxide or ozone. In the case of ozone the replacement has been total (Z/E) or partial (Z/D). In some cases the D_2 stage has been replaced by a final P-stage. Newer bleach plants already come with hot acid/chlorine dioxide in the first stage (D_{HT} or A_{HT}/D technologies) instead of a conventional 30-min D_0 stage. Only a limited number of mills, which are interested in minimizing water consumption, resort to using ozone as the first bleaching stage. In this case, the choice has been the OZ/EDP and OZ/(EP)DP sequences with ozone being implemented at high consistency.

Some alternate bleaching sequences have been recently proposed for eucalyptus kraft pulp, motivated mainly by two major forces: (1) decreasing capital costs and (2) facilitating mill closure. To minimize capital costs, sequences comprised of only two bleaching stages such as D/Q(PO), D_{HT}/Q(PO) and Z/ED have been proposed. Although these sequences allow for the achievement of full pulp brightness, their chemical requirements are considerably higher than those required for bleaching with a conventional four-stage sequence and the pulps produced show low brightness stability. To facilitate mill closure a few sequences that do not contain the first chlorine dioxide bleaching stage (D_0) have been proposed. These include the A_{HT}(EOP)DP, Z/(EO)DD and Z/(EO)DP ones. In all three cases, the filtrates from both the first and second bleaching stages can be cycled back to recovery, thus minimizing water consumption and effluent treatment volume.



2. D_{HT} technology for the first bleaching stage of a modern ECF bleach plant.



3. A_{HT}/D technology for the first bleaching stage of a modern ECF bleach plant.

First bleaching stage

The preferred technology for ECF bleaching of eucalyptus kraft pulp is a core sequence of the D(EPO)DD type. There are many nuances to this sequence. The D_0 stage may be conventional (30 min, 50°C-70°C) or at high temperature (120 min, 90°C-95°C) to extend removal of pulp hexenuronic acid. When operated at high temperature, it can be done in two different ways, namely: the D_{HT} (also designated D* or D/A_{HT}) and the A_{HT}/D technologies. Although they are similar, in principle, there are differences in the application (**Figs. 2** and **3**). While the first concept requires a slightly lower capital investment and less sulfuric/hydrochloric acid to operate, the performance of the two concepts has been a matter of much debate.

A recent study [11] indicated that the D_{HT} technology is more effective than the A_{HT}/D in decreasing chemicals, yield loss and effluent AOX and increasing brightness stability. The sequences D(EPO)D, A_{HT}/D(EPO)D and D_{HT}(EPO)D were compared and showed total active chlorine consumptions (including H_2O_2) of 4.34%, 4.14%, and 3.74%, respectively. According to this data, the A_{HT}/D stage saves about 4.6% while the D_{HT} saves 13.8% of the total active chlorine used in the sequence. The creators of the A_{HT}/D technology claim active chlorine savings in the order of 45% in the ECF bleaching of birch kraft pulp when the A_{HT} stage is optimally performed [4]. They also claim [12] that a South American pulp mill reported savings of >30% active chlorine at their new eucalyptus fiberline that uses the A_{HT}/D-prebleaching stage.

It has been postulated that the large differences in results between the two technologies as applied to eucalyptus kraft pulp can be traced to differences in raw materials, with the type of eucalyptus pulp used in lab trials and industrial operation being the major cause of differences reported [13]. The results shown in **Table III** indicate that the type of eucalyptus pulps indeed affects bleaching performance, a fact quite well established in the specialized literature. However, the differences occur regardless the ECF bleaching technology being used. The differences in bleaching chemical consumptions among D_0, A_{HT}/D, and D_{HT} technologies showed a similar trend for all pulps (samples A-G), with the benefits due to the hot acid/chlorine dioxide bleaching technologies being slightly significant for the pulps easier to bleach only (samples A-D). Another important point to mention is that in none of the cases did the active chlorine savings due to hot acid/hot chlorine dioxide bleaching technologies (A_{HT}/D or D_{HT}) exceed 14%, in disagreement to the >30% reported industrially for eucalyptus [14].

Active chlorine savings due to hot chlorine dioxide bleaching technology seem to disappear for pulps that are very difficult to bleach (samples E-G). In fact, hot stages can make

III. Total active chlorine demand (%)* for bleaching various oxygen delignified eucalyptus pulp samples to reach 90.0% ISO brightness, with various sequences.

Bleaching Technology	*E.globulus Lab.*	*E.grandis Lab.*	*E.urograndis Lab.*	*E.spp. Inds.*	*E.spp. Inds.*	*E.spp. Inds.*	*E.spp. Inds.*
Sample charact.	A	B	C	D	E	F	G
Kappa N°.	10.2	10.4	10.2	10.5	10.3	10.1	10.3
HexAs mmol/kg	55.8	54.3	57.1	67.2	59.4	63.1	52.8
COD, kg O_2/odt	4.5	4.2	4.6	8.7	9.3	8.8	22.4
Act. Cl_2 demand, %	A	B	C	D	E	F	G
D(EP)D[1]	3.20	3.43	3.57	3.89	5.57	6.56	7.74
D(EP)D[2]	2.83	3.05	3.23	3.59	5.19	6.12	7.19
A_{HT}/D(EP)D[3]	2.82	3.04	3.25	3.61	5.38	6.59	7.98
D_{HT}(EP)D[4]	2.75	2.98	3.16	3.51	5.31	6.42	7.91
Z/D(EP)D[5]	-	-	-	4.31	-	-	-
Z/(EP)DP[6]	-	-	-	5.62	-	-	-

***Total active Cl_2** = ClO_2*2.63 + H_2O_2*2.09 + O_3*2.63

[1]**D_0** = 10% consistency, 70°C, 30 min, pH 3.0, **kappa factor 0.20**; (EP): 10% consistency, 80°C, 120 min, pH 10.5, 0.3% H_2O_2 ; **D_1**: 10% consistency, 80°C, 120 min, pH 4.5.

[2]**D_0** = 10% consistency, 70°C, 30 min, pH 3.0, **kappa factor 0.26; (EP)**: 10% consistency, 80°C, 120 min, pH 10.5, 0.3% H_2O_2 ; **D_1**: 10% consist., 80°C, 120 min, pH 4.5.

[3]**A_{HT}/D** = 10% consistency, (95/90°C), (110/10) min, pH 3.0, **kappa factor 0.20; (EP)**: 10% consistency, 80°C, 120 min, pH 10.5, 0.3% H_2O_2; **D_1**: 10% consistency, 80°C, 120 min, pH 4.5.

[4]**D_{HT}** = 10% consistency, 95°C, 120 min, pH 3.0, **kappa factor 0.20; (EP)**: 10% consistency, 80°C, 120 min, pH 10.5, 0.3% H_2O_2 ; **D_1**: 10% consistency, 80°C, 120 min, pH 4.5.

[5]**Z/D** = 10% consistency, 45°C, 1 min, pH 3.0, 0.4% O_3, 0.6% ClO_2 ; **(EP)**: 10% consistency, 80°C, 120 min, pH 10.5, 0.3% H_2O_2 ; **D_1**: 10% consistency, 80°C, 120 min, pH 4.5, 0.4% ClO_2.

[6]**Z/(EP)** = 40/10% consistency, 40/70°C, 2/30 min, pH 3.0/10.0, 0.6% O_3/ 0.6% NaOH, 0.3% H_2O_2; **D**: 10% consistency, 80°C, 120 min, pH 4.5, 0.9% ClO_2; **P**: 10% consistency, 80°C, 120 min, pH 10.0, 0.5% H_2O_2.

bleaching more difficult (sample G). Increasing kappa factor in the D_0 stage from 0.20 to 0.26 has the same benefit as hot acid stage (A_{HT}/D) for easy to bleach pulps (samples A-D). The benefit of using a high kappa factor maintains regardless of the pulp being easy or difficult to bleach (samples A-G). The benefit of increasing kappa factor has been shown by other workers in connection with eucalyptus kraft pulp bleaching to high brightness [15, 16]. The order of efficiency for the easy to bleach pulps (samples A-D) is D_{HT}>A_{HT}/D=D_{HKF}>D_{LKF} (HKF and LKF designate high and low kappa factors, respectively). For the difficult to bleach samples (E-G) the best approach seems to be conventional D_0 stage run at high kappa factor.

The results in Table III show that pulps having similar kappa numbers and HexA contents have very different bleachabilities, depending upon their origin. Laboratory cooked pulps are apparently easier to bleach than industrial cooked ones. Lignin nature is the major factor affecting chemical demand in eucalyptus kraft pulp bleaching, with hexenuronic acids being of little importance. That explains why hot stages do not significantly affect bleaching chemical consumption, particularly for pulp samples of low bleachability. In those cases where hot stages have more effect it is not very unlikely that acid soluble lignins are removed from the pulp by hot acid hydrolysis. Studies with *Eucalyptus globulus* kraft pulps have also indicated the low importance of HexAs in ECF bleaching [17].

The large bleachability differences among the various pulps is rather intriguing but real. The differences were seen in the lab, but they are also true in the mills the samples were extracted from. Since kappa number and HexAs content of the various pulps did not vary significantly and that hot acid stages had very little impact on bleachability, the only options left to explain these facts is indeed the residual lignin structure. Therefore, wood origin and pulping technology are the only possible explanations for such large differences, a matter that still remains to be investigated. The large bleachability differences among various hardwood pulps has also been observed by other researchers [18], which also claim that hot chlorine dioxide bleaching efficiency depends very much on the type of hardwood fibers under investigation.

In regard to chemical consumption, the sequences beginning with the Z/D technology are far more effective than those beginning with the Z/E one (Table III). However, the latter is more interesting in regard to water consumption and effluent discharge. The choice between the two approaches relies upon environmental regulations and water availability constraints. The pulp bleached with the Z/(EP)DP sequence

showed high brightness stability. This trend has been also observed in commercial applications, particularly when the final peroxide stage is carefully optimized [19, 20].

A limited number of pulp mills have implemented ozone in the first bleaching stage, with total (Z/E mode) or partial (Z/D mode) substitution of chlorine dioxide, in sequences such as Z/(EP)DP or Z/D(EPO)D. Some variants of these sequences may include addition of a hot acid stage (A_{HT}) before the ozone treatment. Although the acid hydrolysis decreases the efficiency of the subsequent ozone stage, it has been commercially proven that the introduction of the A_{HT} stage can reduce bleaching costs of the Z/(EP)DP sequence [21]. The main motivations to include ozone in the bleaching of eucalyptus pulps have been the possibility of partially reusing the effluent from the first and second bleaching stages and the low pulp OX content and brightness reversion of ozone-based sequences.

Impact of formaldehyde on chlorine dioxide bleaching

It has been suggested that use of formaldehyde as additive in the chorine dioxide stage may convert some byproducts formed in side reactions back to chlorine dioxide, thereby increasing the efficiency of this reagent [22]. The positive effect of formaldehyde has been attributed [22] to its capacity to regenerate chlorine dioxide from chlorite, according to reaction (1). Note that the products of reaction (1) are acidic in nature and will drop the reaction pH if sufficient NaOH is not previously added to the system. In this study, the results were compared at equal pH values so as to avoid that potential problem.

$$HCHO + 3HClO_2 \rightarrow 2\ ClO_2 + HCO_2H + HCl + H_2O \qquad (1)$$

The results shown in **Table IV** indicate that formaldehyde is more effective when applied to the final D stage of the sequences D(EP)D and D_{HT}(EP)D. The chemical savings due to formaldehyde were also more visible for the D(EP)D sequence in relation to the D_{HT}(EP)D one. Considering that both D_0 and D_{HT} stages were run at pH 3.0 and that the final D stage (D_1) was run at pH 4.5, it is reasonable to assume that formaldehyde better performance in D_1 is due to a larger formation of chlorite in such stage. In the stages run at pH 3.0, formation of chlorite is minimal, leaving very small room for formaldehyde to function.

The reason why formaldehyde is less effective when the dioxide stage is performed at high time/temperature (D_{HT}) is not clear. Likely, less chlorite is formed in the D_{HT} treatment in relation to the D_0 one since chlorine dioxide is consumed rather quickly in the former case.

Second bleaching stage

The second bleaching stage of most eucalyptus bleach plants is comprised of an extraction reinforced with oxygen (EO), with peroxide (EP) or with low pressure (EPO) and high pressure (PO) oxygen/peroxide. The (EO) stage is rather ineffective for bleaching eucalyptus pulps but the use of (EP) stages is growing rather significantly, particularly for bleaching processes that requires only 0.3%-0.5% H_2O_2. In such cases, it is possible to consume almost all peroxide dosed under atmospheric conditions, and the (EP) technology is the most recommended (**Table V**). However, bleach plants that are short in chlorine dioxide generation capacity require use of high peroxide doses in the extraction (0.8%-1.0%), which requires more severe conditions to consume the peroxide. In these cases, pressurized systems are suggested and the (PO) stage is better, for it allows temperatures of 95°C under pressure all along the reaction time.

For bleaching sequences starting with hot chlorine dioxide stages (A_{HT}/D or D_{HT}) it is interesting to run the extraction stage at higher temperatures to take advantage of the hot pulp. Thus, the choice of temperature in the extraction is no longer limited by steam demand but rather by the stage performance. Therefore, the extraction temperature must be carefully optimized, taking into account peroxide dose and especially the content of transition metals existing in the pulp. Too high temperatures can be harmful, for it accelerates peroxide losses through decomposition. When the (PO) stage was run at 90°C the overall chemical con-

IV. Effect of adding formaldehyde in the D_0/D_{HT} and D_1 stages of the D(EP)D and D_{HT}(EP)D bleaching sequences to reach 90.0% ISO brightness with an oxygen delignified eucalyptus pulp*.

Bleaching	Bleaching parameter	No Formaldehyde	1% Formaldehyde Applied in D_0 or D_{HT}	1% Formaldehyde Applied in D_1
D(EP)D[1]	Tot. act. Cl_2, %**	3.89	3.53	3.22
	Viscosity, mPa.s	16.3	16.0	16.4
	Reversion,% ISO	2.5	2.6	2.7
	Yield loss, %	1.9	2.0	2.0
D_{HT}(EP)D[2]	Tot. act. Cl_2, %	3.51	3.48	3.18
	Viscosity, mPa.s	14.8	14.5	15.1
	Reversion,% ISO	2.0	1.9	1.9
	Yield loss, %	2.2	2.3	2.3

*Kappa 10.5, HexAs 67.2 mmol/kg, brightness 53.5% ISO and viscosity 36.8 mPa.s.

**Total active Cl_2 = ClO_2*2.63 + H_2O_2*2.09

[1]**D_0** = 10% consistency, 70°C, 30 min, pH 3.0, kappa factor 0.20; **(EP)**: 10% consistency, 80°C, 120 min, pH 10.5, 0.3% H_2O_2; **D_1**: 10% consistency, 80°C, 120 min, pH 4.5.

[2]**D_{HT}** = 10% consistency, 95°C, 120 min, pH 3.0, kappa factor 0.20; **(EP)**: 10% consistency, 80°C, 120 min, pH 10.5, 0.3% H_2O_2 ; **D_1**: 10% consistency, 80°C, 120 min, pH 4.5.

V. Bleaching results of an oxygen delignified eucalyptus kraft pulp* to 90.0% ISO, with the D_{HT}(EO)D, D_{HT}(EP)D, D_{HT}(EPO)D, and D_{HT}(PO)D sequences.

Bleaching Performance	D_{HT}(EO)D	D_{HT}(EP)D	D_{HT}(EPO)D	D_{HT}(PO)D	D_{HT}(PO)D	D_{HT}(PO)D
	(EO) w/o Mg, 80°C	(EP) w/o Mg, 80°C	(EPO) w/o Mg, 80°C	(PO) w/o Mg, 80°C	(PO) with Mg, 80°C	(PO) w/o Mg, 90°C
Total act. Cl_2, %**	4.53	3.51	3.55	3.55	3.38	3.64
Viscosity, mPa.s	15.7	14.8	15.4	15.6	17.6	13.5
Reversion, % ISO	1.8	2.0	2.1	2.0	1.8	2.3
Residual H_2O_2, %	-	7	2	3	20	0
Yield loss, %	2.1	2.2	2.2	2.3	2.2	2.4

*Kappa 10,5, HexAs 67.2 mmol/kg, brightness 53.5% ISO, and viscosity 36.8 mPa.s.

**Total active Cl_2 = ClO_2*2.63 + H_2O_2*2.09.

D_{HT} = 10% consistency, 95°C, 120 min, pH 3.0, kappa factor 0.20; **(EO)**: 10% consistency, 80°C, 120 min, pH 10.5; **(EP)**: 10% consistency, 80°C, 120 min, pH 10.5, 0.3% H_2O_2 ; **(EPO)**: 10% consistency, 80°C, 120 min, pH 10.5, 0.3% H_2O_2; **(PO)**: 10% consistency, 80°C and 90°C, 120 min, pH 10.5, 0.3% H_2O_2, 0 and 0.15% $MgSO_4$; **D_1**: 10% consistency, 80°C, 120 min, pH 4.5.

sumption of the sequence increased, no peroxide residual was found, and a higher yield loss was observed (Table V). Although the increase in yield loss was rather small, the data are quite reliable since they were obtained by a very precise technique, namely by determination of the total organic carbon (TOC) present in the bleaching filtrates. A detailed report about this technique is given in reference [23]. Another technique that can be used to quantify yield loss is through quantification of the chemical oxygen demand (COD) present in the bleaching filtrates, and indirectly relating it to yield losses [24].

The use of oxygen in the extraction is unnecessary for pulps treated with hot chlorine dioxide (A_{HT}/D or D_{HT}) in the first stage (Table V). Oxygen is a very helpful delignifying agent when applied in the extraction stages of softwood bleaching lines. Softwood pulp contains a sizeable kappa number (4-6 units), largely comprised of lignin, when it reaches the first extraction stage. On the other hand, eucalyptus pulp enters the first extraction stage with very low kappa numbers (1.5-3.0), which are largely comprised of hexenuronic acids. Since oxygen does not react with hexenuronic acids [4], it has very little role when applied in the first extraction stage. Oxygen may actually impair peroxide reinforced extraction efficiency in pulps containing large quantities of manganese. Wekeza and Ni's [25] propose that oxygen accelerates peroxide decomposition through the redox mechanism shown below (reactions 2-4). The production of Mn^{3+} by oxygen complicates peroxide stabilization by Mg^{2+}, which is more effective in stabilizing peroxide against Mn^{2+} but not so effective against Mn^{3+}.

$$4\,Mn^{2+} + O_2 + 2\,H_2O \longrightarrow 4\,Mn^{3+} + 4\,HO^- \quad [2]$$

$$2\,Mn^{2+} + H_2O_2 \longrightarrow 2\,Mn^{+3} + 2\,HO^- \quad [3]$$

$$2\,Mn^{+3} + H_2O_2 + 2HO^- \longrightarrow 2\,Mn^{+2} + O_2 + 2\,H_2O \quad [4]$$

The use of magnesium sulfate in the (PO) stage improved its performance (Table V). According to Lidén and Öhman [26] this should be expected given that magnesium precipitates (hydroxides, carbonates) are effective in counteracting the negative impact on peroxide stability of manganese presents in the pulp, particularly in the form of Mn^{2+}. Magnesium present in precipitates formed under the alkaline conditions of peroxide bleaching is replaced isomorphically by Mn^{2+}. In fact, higher peroxide residuals were observed in the experiment having magnesium as an additive (Table V).

For sequences having ozone as the first stage, the use of peroxide in the extraction has not been widespread. For example, the world's largest bleach plant containing ozone stage bleaches with the sequence Z/EDP. A recent study [27] has indicated, however, that the use of peroxide in the extraction of such sequence, converting it into the Z/(EP)DP, reduces overall bleaching chemicals demand and costs, and decreases bleached pulp OX content.

Final bleaching

Final bleaching of eucalyptus kraft pulps can be done in several different ways, namely: D, D_N/D, DD, D_ND, DP and DED. Although the three and two-stage approaches were popular in the past, the trend nowadays is for the one stage approach to minimize capital investment. The D and D_N/D are both one-stage approaches since they require only one washing system. The one-stage approaches are the lowest capital costs although they show low flexibility and higher operating costs. Kappa number excursions in the digester may complicate brightness target achievement since there are few opportunities to correct the problem along the sequence. Also, pulps bleached with only one final bleaching stage tend to present low brightness stability. Among the two-stage approaches (DD and DP), the DP one has been considered the most interesting since it warrants high final brightness and good brightness stability [28, 29]. Purportedly, the DP final bleaching also produces bleached pulp of better refinability and tensile strength as compared for example with the DD approach [30]. For improved brightness stability, it is suggested the use of high temperature in D_2 and P stages, and high peroxide charge and high peroxide residual in the P stage [31].

Table VI shows a comparison among various final bleaching alternatives in regard to overall bleaching chemical consumption, relative chemical costs, and pulp yield, viscosity, and brightness stability. It is apparent that the lowest relative bleaching cost sequence is the one ending with a single final chlorine dioxide stage. The use of final peroxide stage increases overall bleaching cost because peroxide bleaching does not require only peroxide but also sodium hydroxide.

Brightness stability

Eucalyptus kraft pulps bleached to high brightness under certain conditions may show poor brightness stability [29, 31-33]. The causes of such problem have not been identified in most cases and therefore implementation of definitive solutions has not been possible. The interaction of environmental factors such as UV light, temperature, and humidity with pulp residual lignin, uronic acids, and oxidized carbohydrates have been postulated as the main cause of reversion [34]. Therefore, the chemical nature of the bleached pulp may significantly affect pulp brightness stability.

Brightness stability was evaluated in oxygen-delignified eucalyptus kraft pulps, fully bleached (90-90.5% ISO) by the sequences (DC)(PO)DD, (DC)(PO)DP, D(PO)DD, D(PO)DP, D_{HT}(PO)DD, D_{HT}(PO)DP, A_{HT}/D(PO)DD and A_{HT}/D(PO)DP by running heat reversion tests with 20 repetitions for each sequence (**Table VII**). Details about this study are presented in reference [35]. A final P stage improves brightness stability. Some reducing groups present in the fully bleached pulps are likely the major cause of reversion. Pulp bleached with the sequence (DC)(PO)DD had low brightness stability despite containing only trace amounts of hexenuronic acids and lignin. Hot acid/hot chorine dioxide stages improved pulp brightness stability, but only in sequences without a final P stage.

Table VII lists bleached pulp reversion values (PCN) and chemistry measured by kappa number and contents of hexenuronic acids (HexAs), reducing groups (expressed as copper number), carboxyl

VI. Bleaching performance of an oxygen delignified eucalyptus kraft pulp* to 90.0% ISO, with the D_{HT}(EP)D, D_{HT}(EP)D_N/D, D_{HT}(EP)DD, and D_{HT}(EP)DP sequences.

Bleaching Performance	D_{HT}(EP)D	D_{HT}(EP)D_N/D	D_{HT}(EP)DD	D_{HT}(EP)DP
Total act. Cl_2, %**	3.51	3.30	3.10	3.32
Relative Bleaching cost, %	100	102.5	103.0	103.8
Viscosity, mPa.s	14.8	15.6	16.0	14.5
Reversion, % ISO	2.0	2.0	1.7	1.4
Yield loss, %	2.2	2.1	2.2	2.5

*Kappa 10,5, HexAs 67.2 mmol/kg, brightness 53.5% ISO and viscosity 36.8 mPa.s.

**Total active Cl_2 = ClO_2*2.63 + H_2O_2*2.09.

D_{HT} = 10% consistency, 95°C, 120 min, pH 3.0, kappa factor 0.20; **(EP)**: 10% consistency, 80°C, 120 min, pH 10.5, 0.3% H_2O_2; **D_1**: 10% consistency, 80°C, 120 min, pH 4.5; D_N/D: 10% consistency, 80°C, 60→5/60 min, pH 4.0→9.0/4.5; **D_2**: 10% consistency, 80°C, 120 min, pH 4.5; **P**: 10% consistency, 80°C, 120 min, pH 4.5, 0.2% H_2O_2.

VII. Brightness reversion (PCN) and chemistry of oxygen-delignified eucalyptus kraft pulps bleached to 90±0.5% ISO with different sequences.

Sequences*	Kappa Number	HexAs mmol/kg pulp	Copper Number, g Cu_2O/100g pulp	COOH meq/ 100g pulp	Xylans, %	OX, mgCl^-/kg pulp	PCN±SD
(DC)(PO)DD	0.2	0.08	0.36	5.5	13.6	310	**0.54± 0.032**
(DC)(PO)DP	0.5	0.42	0.24	5.9	13.0	284	**0.17± 0.006**
D(PO)DD	0.9	5.10	0.28	5.1	13.0	182	**0.52± 0.036**
D(PO)DP	1.7	15.9	0.16	7.0	12.9	136	**0.18± 0.009**
D_{HT}(PO)DD	0.5	2.76	0.28	5.5	12.8	165	**0.37± 0.020**
D_{HT}(PO)DP	1.3	12.2	0.20	6.1	12.7	81	**0.22± 0.007**
A_{HT}/D(PO)DD	1.0	6.40	0.26	5.3	13.2	139	**0.27± 0.019**
A_{HT}/D(PO)DP	1.6	15.4	0.19	6.6	13.2	86	**0.22± 0.015**

*The operating conditions for each bleaching stage of the sequence as well as the pulp sample used for the reversion studies are described in reference [35] .

groups, chlorinated organics (OX) and xylans. Pulp residual kappa number did not correlate to any extent with reversion. Bleaching sequences ending with a final P stage showed the highest values for kappa number and yet the lowest PCN values. Also, no clear relationship exists between brightness stability and pulp hexenuronic acid (HexAs) content. In fact, the sequences ending with a final P stage tended to produce pulps of higher HexAs contents and higher brightness stabilities than sequences ending with a final D stage. For example, the pulp bleached with the (DC)(PO)DD sequence presented very low kappa number and HexAs levels and very high brightness reversion, while the opposite occurred for the pulp bleached by the D(PO)DP sequence.

The results of this work with eucalyptus wood pulp do not corroborate the strong evidence reported in the recent literature [36, 37] that HexAs play a very important role in pulp brightness stability of various northern wood pulps. Wood pulp differences may explain the contradictory results since wood itself is an important factor affecting reversion [38]. Furthermore, the type of bleaching process (ECF, TCF, etc.) under comparison may impact the conclusions of HexAs effect on reversion. For example, if one compares only the D(PO)DD and D_{HT}(PO)DD sequences in Table VII it is possible to conclude that HexAs play some role in reversion. The pulp bleached by the latter sequence had a 29% lower PCN value and 46% lower HexAs content than the former, apparently indicating a role for HexAs in reversion. However, when comparing the sequences D(PO)DD with D(PO)DP it is impossible to rationalize the effect of HexAs since the latter sequence showed 40% lower PCN and three folds higher content of HexAs. It is apparent that the final P stage removes reducing groups derived from carbohydrates and lignins such as oxidized cellulose and xylans, and o- and p-quinoid structures generated and incompletely removed in the chlorine dioxide stage that would otherwise interact with pulp HexAs, thus enhancing reversion. In other words, HexAs are troublesome to reversion only if there are enough reducing groups in the pulp. Significantly more p-quinoid structures have been detected [39] in chlorine dioxide bleached pulp compared with peroxide treated ones.

There is some positive correlation between bleached pulp reducing groups content and brightness reversion. Systematically, sequences having a final P stage produced pulps of lower reversion and lower reducing groups content than those ending with a D stage (Table VII). This trend is consistent with the reported effectiveness of alkaline peroxide stages in destroying reducing groups [40-41]. Proof that peroxide reacted with some reducing groups is the observed decrease in these groups and increase in carboxyl content when pulp was treated with a final P stage (Table VII). However, the negative impact of reducing groups on reversion may be counterbalanced by other factors. For example, the (DC)(PO)DD bleached pulp showed only 4% higher PCN than the D(PO)DD bleached one despite the fact that the latter contained 38% less reducing groups than the former. In another example, the D_{HT}(PO)DD bleached pulp showed much lower brightness reversion than the D(PO)DD pulp and yet both contained similar reducing group contents.

Pulp xylan content was not significantly affected by the bleaching sequence, except for a slight drop in those sequences containing hot chlorine dioxide stages. No correlation was observed between xylan content and pulp brightness stability, within the small range of variation observed (12.7%-13.6%). The content of chlorinated organics in the pulp bleached with the various sequences changed according to their active chlorine requirement. A quick look at the numbers in Table VII gives the impression that pulps containing low OX values tend to present lower reversion. However, the pulp bleached with the (DC)(PO)DP sequence also showed very low reversion despite having a very high OX content (284 mg Cl^-/kg of pulp). This matter is being further investigated in our laboratories.

According to Süss and Leporini [36] the brighter the pulp, the more stable the brightness becomes, and the bleaching process has only a limited impact on reversion. Neither ozone, nor hot acid hydrolysis negatively affect brightness stability. If compared at the same brightness level sequences with hot D stages do not revert differently from sequences with an ozone stage. There is, however, a big impact of the final bleaching stage. A pulp bleached in its final stage with chlorine dioxide (D_2) more likely loses brightness in aging than pulp bleached with a final P stage. The reason is the improved extraction of any kind of "impurities" under alkaline conditions. The effectiveness of the final washing stage is the most important factor for obtaining good brightness stability.

Organically bound chlorine

The pulp content of organically bound chlorine has been a matter of concern for ECF bleached market pulp manufacturers. Although a limiting value for pulp OX is not clearly established in the market, some especial clients may show preference for pulps having lower OX contents. For example, there is limited demand for the so-called ECF-light pulps, which should contain less than 30 mg Cl^-/kg pulp. Regular ECF pulps contain between 120 and 200 mg Cl^-/kg pulp. Although no premium is paid to low OX ECF pulps, this may become criteria in the future. Thus, there is always some interest in decreasing the OX content of ECF bleached pulps.

There are several ways to minimize the content of OX in ECF bleached pulps. Süss et al. (42) presented several alternatives that include minimization of chlorine dioxide use by partial replacement with hydrogen peroxide but also more simple alternatives such as strong alkaline extractions after chlorine dioxide stages and very thorough pulp washing.

Organically bound chlorine measured in the bleaching filtrates (AOX) and pulp (OX) is affected not only by the amount of active chlorine used but also by the bleaching process and chemical composition of the pulp. For example, effluent AOX of bleached eucalyptus kraft pulp mills originates largely from hexenuronic acids, whereas pulp OX derives sig-

VIII. Effect of time/temperature on chlorine dioxide performance and filtrate in bleaching of kraft-O_2 pulp* (details about this study can be found in reference [43]).

Results	DE treatment		$D_{HT}E$ treatment	
	D	E	D_{HT}	E
ClO_2 applied, kg/ton	7.6 (3997 g Cl^-/ton)	–	7.6 (3997 g Cl^-/ton)	–
Temperature, °C	60	70	95	70
Time, min	30	60	120	60
Kappa number	4.7	4.1	2.8	2.2
Brightness, % ISO	72.0	73.5	66.5	71.0
Yield loss, %	1.20	0.88	1.70	0.95
Pulp OX, g Cl^-/ton	281**	114	185**	104
Filtrate TOC, kg C/ton	4.8	3.5	6.8	3.8
Filtrate AOX, g Cl^-/ton	350	60	180	40
Filtrate chloride, g Cl^-/ton	1665	288	2295	225
Filtrate chlorate, g Cl^-/ton	842	65	780	61
Filtrate chlorite, g Cl^-/ton	not detected	not detected	not detected	not detected
Total chlorine compounds, g Cl^-/ton	**2857**	**527**	**3255**	**430**

*Kraft-O_2 pulp: kappa 10 and brightness 49.8 % ISO;
** Not included in total chlorine compounds calculation;
D and D_{HT}: 10% consistency, pH 3.0, kappa factor 0.20; **E**: 10% consistency, pH 11.5-11.8, 12 kg/ton NaOH.

nificantly from pulp lignin [44, 45]. A recent study [46] indicated that a significant fraction of the effluent AOX derived from eucalyptus kraft pulp bleaching is unstable and can be removed during storage of the effluent (10 days, pH 7, 35°C). Furthermore, it was postulated that the easily removed AOX likely originates from the chlorination of hexenuronic acids while the stable AOX originates from lignin [46].

Table VIII, extracted from reference [43] shows that the quantity of AOX present in the $D_{HT}E$ filtrate is about 50% lower than that found in the DE filtrate for a given kappa factor. The lower AOX values in $D_{HT}E$ filtrates is apparently due to two factors: 1) slightly lower chlorinated organics generation and 2) conversion of organically bound chlorine into chloride. The slightly lower generation of chlorinated organics under conditions of higher time/temperature is explained by the partial acid hydrolysis of HexAs, which are important sources of AOX [44, 45]. Evidence for the second hypothesis, the most significant one, is the reduction of AOX levels and simultaneous increase in filtrate chloride levels, with the increase in reaction time at 95°C (Table VIII). At the end of the reaction, a 22.5% higher level of chloride was found in $D_{HT}E$ filtrates. This additional chloride probably arose from degradation of chlorinated organic compounds under the condition of high time/temperature of the D_{HT} stage. The conversion of chlorine dioxide into chlorate was not significantly influenced by reaction time/temperature and was only 7% lower in the $D_{HT}E$ process, while chlorite was not detected in either case.

The amount of OX bound to the pulp after the extraction stage was slightly influenced by the high reaction time/temperature condition. The pulp OX value after $D_{HT}E$ was only 9% lower than after DE (Table VIII). It should be noted that the pulp OX content was 34% lower after D_{HT} than after D. Apparently, a significant fraction of the pulp OX generated in the chlorine dioxide stage is destroyed in the alkaline extraction stage. It has been shown that pulp OX content is directly related to the residual lignin content [44]. Therefore, it is reasonable to assume that the lignin content in the pulps after DE and $D_{HT}E$ did not differ significantly. The difference between pulp kappa number values in the two cases was probably due to differences in their HexAs contents.

A possible link between organically bound chlorine and pulp brightness stability has been established in recent work, and this matter is being further investigated [47].

Effluent load and treatability

Typical effluent load and treatability of modern eucalyptus ECF bleach plants are given in **Table IX** for the D(EP)DD, D_{HT}(EP)DD, A_{HT}/D(EP)DD and A_{HT}D(EP)DD sequences. Details about this study can be obtained in reference [48]. The pulp used in this study was of very low bleachability, partially because of its unusually high COD carryover value (25.5 kg O2/o.d. ton pulp) entering the bleach plant. The bleaching difficulty has also been observed at the pulp mill from where it was extracted. Total active chlorine consumptions were 7.1%, 8.4%, 8.4%, and 5.9%, respectively, for the aforementioned sequences. These results exemplify a case where hot acid/hot chlorine dioxide stages are deleterious to overall bleaching performance.

An evaluation of effluent organic load (BOD, TOC, COD, and color) until the second stage, D(EP) vs D_{HT}(EP), indicate that the D_{HT}(EP) treatment produces slightly higher values in relation to the D(EP) one, which should be expected since it decreases pulp kappa number to a larger extent. After biological treatment, with exception of COD, the organic load differences remained practically unaltered, which suggests no difference in organic load biodegradability between D(EP) and D_{HT}(EP) effluents (Table IX). However, the AOX generation by the D_{HT}(EP) treatment was about 36% lower than that of the D(EP) one (Table IX).

The destruction of AOX in the D_{HT} stage has been shown

IX. Load and treatability* with activated sludge of combined effluents from various sequences produced during bleaching of an oxygen delignified eucalyptus kraft pulp** to 90.00% ISO brightness. (details about this study can be found in reference [48])

Results	COD, kg O_2/o.d. ton		BOD_5, kg O_2/o.d. ton		AOX, kg Cl^-/o.d. ton		TOC, kg C/o.d. ton		Color, kg Pt/o.d. ton	
Act. sludge*	Before	After	Before	After	Before	After	Before	After	Before	After
D(EP)	32.5	9.9	15.4	0.78	0.475	0.170	12.6	5.55	37.8	34.7
D_{HT}(EP)	34.8	11.1	18.2	0.93	0.304	0.179	14.6	4.92	40.6	38.2
D(EP)DD[1]	41.1	14.3	17.7	1.19	0.566	0.203	15.8	5.46	39.6	44.6
D_{HT}(EP)DD[2]	44.0	13.8	18.5	1.44	0.510	0.204	17.2	6.09	42.1	39.5
A_{HT}/D(EP)DD[3]	43.7	14.3	16.9	2.25	0.530	0.200	13.8	3.8	30.4	39.7
A_{HT}D(EP)DD[4]	50.9	17.9	18.1	1.13	0.410	0.160	17.6	5.8	46.2	52.2

*Batch activated sludge biological treatment (10 cycles of 24 h - 2 h sedimentation, DBO:N:P = 100:5:1, 28°C, pH 6.8-7.2, dissolved O_2 2-5 mg/L.

**Kappa 11.9, HexAs 45 mmol/kg, viscosity 33.3 mPa.s, brightness 36.7% ISO, COD 25.5 kg O_2/o.d. ton pulp.

[1]**D_0:** 30 min, 60°C, 10% consistency, pH 3.0, KF 0.28; **(EP)**: 120 min, 90°C, 10% consistency, pH 11, 0.5% H_2O_2; **D_1**: 120 min, 70°C, 10% consistency, pH 3.5, 0.95% ClO_2; **D_2**: 120 min, 70°C, 10% consistency, pH 4.0, 0.08% ClO_2.

[2]**D_{HT}** : 120 min, 95°C, 10% consistency, pH 3.0, KF 0.28; **(EP)**: 120 min, 90°C, 10% cst, pH 11, 0.5% H_2O_2; **D_1**: 120 min, 70°C, 10% consistency, pH 3.5, 0.95% ClO_2; **D_2** : 120 min, 70°C, 10% consistency, pH 4.0, 0.57% ClO_2.

[3]**A_{HT}/D** : 110/10 min, 95/90°C, 10% consistency, pH 3.0/3.0, KF 0.28; **(EP)**: 120 min, 90°C, 10% consistency, pH 11, 0.5% H_2O_2; **D_1**: 120 min, 70°C, 10% consistency, pH 3.5, 0.95% ClO_2; **D_2** : 120 min, 70°C, 10% consistency, pH 4.0, 0.57% ClO_2.

[4]**A_{HT}** : 120 min, 95°C, 10% consistency, pH 3.0; **D_0**: 30 min, 60°C, 10% cst, pH 3.0, KF 0.28; **(EP)**: 120 min, 90°C, 10% consistency, pH 11, 0.5% H_2O_2; **D_1**: 120 min, 70°C, 10% consistency, pH 3.5, 0.95% ClO_2; **D_2** : 120 min, 70°C, 10% consistency, pH 4.0, 0.57% ClO_2.

by other workers [43] and has been explained by the conversion of organically bound chlorine into inorganic chloride due to the harsh conditions of this stage (high temperature, long retention time). It is worth noting that after biological treatment the AOX content of the effluents from D(EP) and D_{HT}(EP) had virtually the same amount of AOX (Table IX). In other words, the efficiency of AOX removal from the D(EP) effluent was much higher than that of the D_{HT}(EP) effluent. It is apparent that the amount of AOX destroyed during the hot chorine dioxide stage would be destroyed during the activated sludge treatment anyway. This leads to the conclusion that chlorine dioxide bleaching of eucalyptus pulps generates a large quantity of phony bound chlorine compounds, which are quite easily removed by a hot treatment or biodegraded in the effluent treatment station. This phony AOX likely originates from reactions of chlorine dioxide and its derivatives with pulp hexenuronic acids [46].

An evaluation of the combined effluents of the whole bleaching sequence for the D(EP)DD, D_{HT}(EP)DD, A_{HT}/D(EP)DD, and A_{HT}D(EP)DD bleaching technologies (Table IX) shows that, with exception of the parameter color, slightly higher organic loads are produced by the sequences having a hot chlorine dioxide or hot acid stages, but such differences tend to become less significant after the biological treatment. On the other hand, the sequences having a hot chlorine dioxide or hot acid stages produce less organically bound chlorine but after biological treatment this benefit tend do disappear. The data in Table IX suggest that hot acid or hot chorine dioxide bleaching has little impact on biological effluent treatment station.

CONCLUSIONS

- The choice between single and double-stage oxygen delignification depends upon the true pulp lignin content (discounted the HexAs).
- Application of Mo-catalyzed acid peroxide delignification after O-stage allows reduction of kappa number from 9-10 to 3-4.
- Efficient post-oxygen washing is the key for low cost bleaching, with a kg of COD/o.d. ton pulp consuming the equivalent to 0.085% active chlorine.
- Three-stage bleaching of the D-(EP)-D type suffices for eucalyptus kraft pulps. The inclusion of a fourth stage is desirable for production of very high brightness/low reversion pulps.
- Bleaching chemical consumption is strongly influenced by brown pulp origin, with variations of 3.2% to 7.7% active Cl_2 demand depending upon the pulp type.
- The type of ECF Bleaching technology, based on chlorine dioxide, affects chemical consumption only slightly. Hot acid/hot chlorine dioxide bleaching technology saves only small amounts of active chlorine for high bleachability pulps but none for the low bleachability ones.
- Atmospheric extraction (EP) suffices for eucalyptus kraft pulp bleaching.
- Formaldehyde saves more chlorine dioxide when used in D_1 than in D_0/D_{HT} stages.
- A final peroxide stage significantly improves pulp brightness stability.
- The production of organically bound chlorine decreases by 30% with hot chlorine dioxide bleaching but this gain disappears after effluent biological treatment. **TJ**

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LITERATURE CITED

1. Jaakko Poyry. Available at www.poyry.com/en/. Cited November 29, 2004.

2. Tenkanen, M., Gellerstedt, G., Vuorinen, T., et. al., *J. Pulp Paper Sci.* 25(9): 306(1999).

3. Papiertechnische Stiftung (pTS), PTS-rH 012/90: determination of the total halogenated organics, PTS, Munich, Germany, 1990.

4. Vuorinen, T., Buchert, J., Teleman, A., et al., *Proceedings of the 1996 International Pulp Bleaching Conference*, Tappi Press, Atlanta, Georgia, USA, pp. 43-51.

5. Colodette, J.L., Gomide, J.L., and Brito, A.C., *Proceedings of the 1995 TAPPI Pulping Conference*, Tappi Press, Atlanta, Georgia, USA, pp. 404-413.

6. Bökstrom, M. and Nordén, S., "extended oxygen delignification," International Pulp Bleaching Conference, Helsinki, Finland, 1998, Proceedings, Book 1, pp. 23-31.

7. Souza, J.R.S., "impactos do fator de diluição na lavagem da polpa marrom na polpação kraft," Monografia do programa de Pós-Graduação *Lato Sensu* em Tecnologia de Celulose e papel, UFV, Viçosa, Brazil, 2003.

8. Trindade, H.S., "A importância da lavagem da polpa nos estágios de branqueamento," Monografia do programa de Pós-Graduação *Lato Sensu* em Tecnologia de Celulose e UFV, Viçosa, Brazil, 2003.

9. Burgt, T.V.D., Tlan, J., and Thibault, L.C., "U.S. kraft mills lead in xylanase implementation," *Proceedings of the 2002 TAPPI Fall Technical Conference and Trade Fair*, Tappii Press, Atlanta, Georgia, USA.

10. Mounteer, J.L., Colodette, J.L., Gomide, J.L., et. al., "Bleaching of eucalypt kraft pulp to 90%iSO in short sequences without molecular chlorine," *Proceedings of the International Pulp Bleaching Conference*, Stockholm, Sweden, 1991, Book 3, pp. 83-102.

11. Ragnar, M. and Lindstrom, M.E. *Paperi Puu* 86(1): 39(2004).

12. Vuorinen, T., *Paperi Ja Puu* 86(2): 112(2004).

13. Ragnar, M. and Lindstrom, M.E., *Paperi Puu* 86(3): 174(2004).

14. Da Silva, E.C., Success in industrial application of hexenuronic acid removal technology, The Marcus Wallenberg Prize Symposium, Stockholm, Sweden, October 10, 2003.

15. Süss, H.U. and Filho, C.L., "Bleaching of eucalyptus kraft pulp to very high brightness," *Proceedings of the 33rd Congresso Anual da ABTCP*, São Brazil, 2000.

16. Costa, M.M., Oliveira, M.J., Santos, C.A., et. al., *International Colloquium on Eucalyptus Kraft Pulp*, Viçosa, Brazil, 2003, pp. 349-365.

17. Daniel, A.I.D., Pascoal Neto, C., Evtuguin, D.V., et al., *TAPPI J.* 2(5): 3(2003).

18. Ragnar, M., *Appita J.* 56(6): 471(2003).

19. Silva, M.R., Filho, C.L., Bertolucci, L.et. al., "Otimização do estágio (PO) na seqüência de branqueamento da vCp - Jacareí," *Proceedings of the 33rd Congresso Anual de Celulose e Papel da ABTCP*, São Paulo, Brazil, 2000.

20. Silva, M.R.., Filho, C.L., Bertolucci, L.et. al., *Proceedings of the 35th Congresso e Exposição Anual de Celulose e Papel*, São Paulo, Brazil, 2002, pp. 14-17.

21. Silva, M.R., Peixoto, M.A.L., and Colodette, J.L., "Mill experience using a hot acid stage for eucalyptus kraft pulp bleaching," *Proceedings of the 2002 International Pulp Bleaching Conference*, Tappi Press, Atlanta, Georgia, USA.

22. Jiang, Z.; Lierop, B., and Berry, R., *Proceedings of the 2002 International Pulp Bleaching Conference*, Tappi, Atlanta, Georgia, USA, pp. 225-235.

23. Longue Jr., D.; Colodette, J.L. and Gomide, J.L., "Uma nova técnica para avaliação de perda de rendimento em plantas modernas de branqueamento," *II International Colloquium on Eucalyptus Pulps, Concepcion*, Chile, 2005, CD-ROM.

24. Suess, H.U. and Kronis, J., "The correlation of COD and yield in chemical pulp bleaching," *Proceedings of the 1998 TAPPI Breaking Yield Barrier Symposium*, TAppi Atlanta, Georgia, USA.

25. Wekesa, M. and Ni, Y., *Canadian J. Chem. Eng.* 81(10): 1(2003).

26. Lidén, J. and Öhman, L.O., *J. Pulp Paper Sci.* 23(50): J193(1997).

27. Filho, C.L., Suess, H.U., Silva, M.R., et. al., "Adição de peróxido de hidrogênio no estágio de ozônio para melhorar a branqueabilidade da polpa," *36th Congresso e Exposição Internacional de Celulose e Papel*, São Paulo, Brazil, 2003, CD-ROM.

28. Suess, H.U., Filho, C.I., Schmidt. K., et. al., Proceedings of the 32nd Congresso Anual de Celulose e papel, São paulo, Brazil, 1999, pp. 485-492.

29. Suess, H.U., Schmidt, K., Grosso, d., et. al., "peroxide application of ECF sequences – a description of the state-of-art;" *Proceedings of the 53rd Appita annual conference*, Rotorua, New Zeland, 1999.

30. Henrique, P.M., Costa, M.M., Correia, F.M., et. al., "Hydrogen peroxide in eCF bleaching plant: Cenibra's industrial experience," *Proceedings of the 2001 TAPPI Pulping Conference*, Tappi Press, Atlanta, Georgia, USA.

31. Suess, H.U. and Filho, C.L., *35th Congresso e Exposição Anual de Celulose e Papel*, São Brazil, 2002, CD-ROM, p. 1-13.

32. Suess, H.U. and Leporini, C., *Proceedings of the 37th Congresso Anual de Celulose e Papel*, ABTCP; São Brazil, 2004, pp. 1-10.

33. Suess, H.U. and Filho, C.L., "progress in bleaching to top brightness with low reversion," *37th Congresso e Exposição Anual de Celulose e Papel*, São Paulo, Brazil, 2004, Cd-

34. Forsskåhl, I. in *Forest Products Chemistry* (J. Gullichsen and H. Paulapuro, eds.), 1st edn., Papermaking Science and Technology Series; Tappi Press, Atlanta, Georgia, USA, 2000, pp. 277-350

35. Eiras, K.M.M. and Colodette, J.L., *J. Pulp Paper Sci.* 31(1): 11(2005).

36. Buchert, J., Bergnor, e., Lindblad, G., et al., *TAPPI J.* 80(6): 165(1997).

37. Vuorinen, T., Buchert, J., Teleman, A., et. al., *J. Pulp Paper Sci.* 25(5): 155(1999).

38. Colodette J.L., Eiras, K.M.M., Oliveira, R., et al., *Appita J.* 11: 481(2004).

39. Jääskeläinen, A.S., Saariaho, A.M., Matousek, p., et. al., *12th International Symposium on Wood and Pulping Chemistry*, University of wisconsin, Madison, USA, pp. 139-142.

40. Anderson, J.R. and Amini, B. in *Pulp Bleaching–Principles and Practices* (C.W. Dence and D. Reeve, eds.), Tappi Press, Atlanta, Georgia, USA, 1996, pp. 411-442.

41. Lachenal, and Nguyen-Thi, N.B., *Proceedings of the 1993 Tappi Pulping Conference*, Tappi, Atlanta, Georgia, USA, pp. 799-804.

42. Suess, H.U and Leporini Filho, C.L., "How to improve brightness stability of eucalyptus kraft pulp," *36th Congresso e Exposição Internacional de Celulose e Papel*, São Brazil, 2003, CD-ROM.

43. Ventorim G., Colodette J.L., Eiras, K.M.M., *Nordic Pulp Paper Res. J.* 20(1): 7(2005).

44. Costa, M.M. and Colodette, J.L., *International Pulp Bleaching Conference Proceedings*, Tappi, Atlanta, Georgia, USA, 2002, pp. 195-213.

45. Freire, C.S.R.; Silvestre, A.J.D..; Neto, C.P., et. al., *Appita J.* 57(1): 40(2004).

46. Bjorklund, M., Germgard, U., and Basta, J., *TAPPI J.* 3(8): 7(2004).

47. Eiras K.M.M., Colodette J.L., and Francis R.C., "Main causes of brightness instability of kraft eucalyptus pulps," 121st ESPRA Research Conference, Syracuse, New York, USA, 2004, p. 1-10.

48. Gomes, C.M., Mounteer, A.H., Colodette, J.L., et. al., "Characterization and biodegradability of effluents derived from hot acid hydrolysis and hot chlorine dioxide bleaching," *59th Appita Annual General Conference*, Auckland, New Zealand, 2005, CD-ROM.

INSIGHTS FROM THE AUTHORS

We decided to carry out this work to clarify some controversial information regarding eucalyptus kraft pulp bleaching and to present the state-of-the-art technologies recommended for this important hardwood fiber resource.

The work complements our previous work in the areas of bleaching effluent characterization and treatability and novel bleaching technologies, including molybdenum-activated peroxide bleaching and formaldehyde-assisted chlorine dioxide bleaching.

The most difficult aspect was gathering the various pulp samples. We needed pulp samples of different origins, but with similar kappa numbers. In the laboratory, it was not too difficult because we did the cooking ourselves; however, the collection of pulps from different mills having similar kappa numbers was quite challenging.

The most surprising result we found was the great variability in pulp bleachability among the pulp samples collected at the mill sites. Bleaching chemical consumptions varied from 32 kg to 77 kg active chlorine per ton of pulp, depending upon pulp origin, for a fixed kappa number of about 10. The most interesting result was the rather high effectiveness of molybdenum activated peroxide bleaching (P_{Mo} stage) to remove pulp hexenuronic acids.

Hardwood pulp mills can benefit from this work by applying the proper bleaching sequences and optimized bleaching conditions developed in this study to run their process, which will result in chemical savings. Also, they will be able to clarify certain misconceptions regarding hardwood pulp bleaching and better understand their process.

Our next step is to focus on determining the true importance of oxygen delignification for bleaching hardwood pulps that are rich in hexenuronic acids. Also, the development of methods for stabilizing rather than removing hexenuronic acids during ECF bleaching of eucalyptus pulps.

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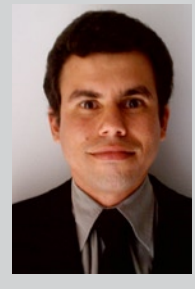

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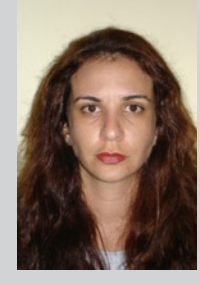

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