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Integrating a Xylanase Treatment into an Industrial-Type Sequence for Eucalyptus Kraft Pulp Bleaching

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ABSTRACT: The influence of a treatment with two commercial xylanases on pulp and effluents obtained after the bleaching stages in the OXAZDP (O, oxygen stage; X, xylanase treatment; A, acid stage; Z, ozone stage; D, chlorine dioxide stage; P, hydrogen peroxide stage) sequence was studied. Also, the potential saving in chlorine dioxide was assessed. The enzyme treatment was performed on pulp containing some black liquor since the operating conditions were close to the conditions used in the storage tower in Fibria, identified as the most suitable point for application. The greatest differences in kappa number and hexenuronic acid content were observed after the X stage. Whereas, in brightness were observed after the Z stage. The effluent properties from the X stage were higher with the enzyme treatments. Also, the enzymes allowed chlorine dioxide consumption in the bleaching stage to be reduced. The control pulp contained twice as much adsorbable organic halides (AOX) and exhibited twice more brightness reversion than did the enzyme-treated samples. However, the tensile index and drainability at an identical degree of refining were lower in the enzyme-treated samples.

1. INTRODUCTION

In the past few years, the paper industry has been able to significantly reduce the specific amount of effluent it produces. The concept of a closed loop mill aims to eliminate discharges to the aquatic environment, recycle and reuse all possible solid and liquid process wastes, and reduce air emissions to the lowest possible quantity and toxicity.

Pulp processed in cellulose mills is washed by passage through a series of filters and presses. However, bleached pulp cannot be exhaustively washed as this would require using vast amounts of water. As a result, pulp subjected to a subsequent bleaching stage contains some residual organic matter and chemicals used in the previous stage. The more closed the water circuit of the process, the higher the chemical oxygen demand (COD) of the black liquor retained by the pulp; as a result, factories with highly closed circuits such as the Jacareí pulp unit of Fibria have to process pulp with high COD levels. On the other hand, current interest in the use of biotechnological processes in the production of pulp and paper has arisen from the high potential of biological treatments for complying with environmental restrictions. The use of such processes for pulp bleaching purposes appears to hold great promise. For example, enzymes such as xylanases have been widely studied in this respect and even used on an industrial scale.[1−4]

The favorable effect of xylanases has been ascribed to their removing xylans; by breaking cellulose-lignin bonds, these enzymes release lignin and facilitate its removal in subsequent bleaching stages. In fact, the use of xylanases has been found to result in increased pulp delignification and brightness,[5−7] save bleaching reagents,[1,6,8−10] and reduce the presence of halogen-containing compounds in the effluents.[10,2] Therefore, by establishing the influence of COD on xylanase bleaching stages, one can assess the efficiency of this type of enzyme in industrial bleaching processes in a more realistic manner.

In a previous study,[11] enzE and enzL were found to be the xylanases most strongly influencing the properties of pulp treated at pH 9.5 at 80 °C, which are close to the operating conditions used in the storage tower of the B fiber line of Fibria—the most suitable point for application of the enzyme during the bleaching sequence employed in the Jacareí unit. The effect of pH and the presence of black liquor on the efficiency of these enzymes were studied.[12]

The main of this paper is to evaluate the influence of an enzE or enzL treatment on pulp and effluent properties after each bleaching stage in the industrial bleaching sequence. An interesting objective is to study the potential saving reagents due to the enzyme application in the sequence. The COD and pH conditions (16 kg $O_2 \cdot t^{-1}$ and pH 9.5, respectively), which were similar to the conditions used at the industrial level, were chosen for the X stage based to the previous results. This study is of great interest since it takes into account a real industrial situation in bleaching processes where the COD levels are high due to the closed circuits.

2. MATERIALS AND METHODS

2.1. Raw Material. The raw material used was eucalyptus pulp produced by the firm Fibria. Samples were collected at a point in the B bleaching line of its Jacareí unit where the pulp had been predelignified with oxygen after standing in the storage tower but before it was acid-washed. The pulp was centrifuged, and the filtrate was collected. The effect of the enzymes on the bleaching sequence was studied on pulp washed with distilled water. The pulp properties were a Kappa number of 11.6, brightness 54.2% ISO, viscosity 1068 $mL \cdot g^{-1}$, and HexA content 65.7 $\mu mol \cdot g^{-1}$; filtrate properties were COD

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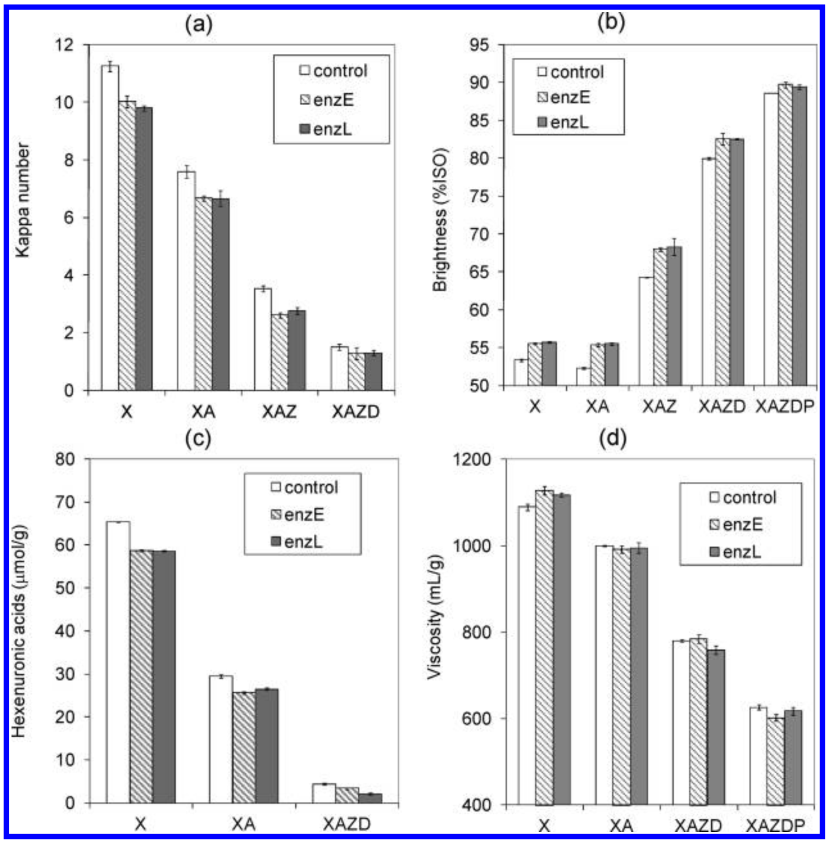

Figure 1. Kappa number (a), brightness (b), hexenuronic acid content (c), and viscosity (d) of the pulp obtained after each bleaching stage in the OXAZDP sequence.

30.8 $kgO_2 \cdot t^{-1}$, pH 11.3, color 6.2 $kgPtCo \cdot t^{-1}$, and turbidity 1.3 $kg_{formazida} \cdot t^{-1}$.

2.2. Bleaching stages. The bleaching sequence was OXAZDP, were O is a delignification stage, X is a xylanase treatment, A is an acidic stage, Z is an ozone stage, D is a chlorine dioxide stage, and P is a hydrogen peroxide stage.

2.2.1. Enzymatic Stage (X Stage). The enzyme treatment was conducted in a Mark V bleaching reactor at an enzyme dose of 0.3 $kg \cdot adt^{-1}$. An amount of 280 g of pulp was supplied with pulp filtrate and water to obtain a black liquor concentration of 16 kg $O_2 \cdot t^{-1}$ and pH 9.5. The sample was loaded into the reactor and stirred at 13.0 Hz for 30 s at 3 min intervals. When the temperature reached 80 °C, the mixture was supplied with enzyme diluted in the volume of water required to obtain 10% odp consistency. Once the reaction time of 60 min was completed, the pulp was filtered and the filtrate collected was for analysis of the final effluent. Finally, the pulp was washed with abundant water, centrifuged, and disintegrated. The control treatment was performed under identical conditions as the X stage, albeit in the absence of the xylanases. Each treatment was done in duplicate.

2.2.2. Acid Stage (A Stage). The acid treatment was performed in a Mark V bleaching reactor at atmospheric pressure, 80 °C and stirred at 13.0 Hz for 30 s at 3 min intervals during 60 min. To this end, an amount of 245 g of pulp from the OX sequence was adjusted to consistency 10% and supplied with sulphuric acid to pH 3.5.

2.2.3. Ozone Stage (Z Stage). The Z stage was conducted with the equipment of the Forest Science Department of ESALQ-USP (University of São Paulo in Piracicaba), using high-consistency pulp.

The amount of ozone produced by the generator was measured prior to each treatment and after each two ozone bleaching treatments. Ozone treatments were done in duplicate on each of the six samples from the OXA sequence at 25 °C. To this end, an amount of 117.5 g of pulp was placed in a 4 L side arm flask and a volume of 1000 mL of KI solution was split between two washing bottles. An ozone stream was passed until a 0.35% odp dose was reached and a volume of 800 mL of distilled water was then added to the pulp, the filtrate being collected for pH and effluent analysis. Also, the bleached pulp was washed and centrifuged to determine its properties. Finally, the KI solution in the washing bottles was collected to determine residual ozone and to calculate the real ozone dose used to bleach.

2.2.4. Chlorine Dioxide Stage (D Stage). The D stage was performed in a pilot bleaching reactor at 80 °C. Duplicate 126 g aliquots of pulp from the Z stage in the OXAZ sequence were adjusted to 10% consistency and supplied with the volume of chlorine dioxide needed to obtain a dose of 18 $kgCl_2 \cdot adt^{-1}$. Then, the pH was adjusted to 4 with 1 N NaOH, the resulting soda dose being about 1.7 $kg \cdot adt^{-1}$. After the treatment time (50 min) was completed, the bags were cooled with water, the pulp was filtered, and the filtrate was collected to determine pH and residual chlorine dioxide. Finally, the pulp was washed with distilled water and centrifuged.

2.2.5. Hydrogen Peroxide Stage (P Stage). The P stage was conducted in polyethylene bags immersed in a water bath at 90 °C. To this end, an amount of 70 g at 10% odp consistency was supplied with the volumes of hydrogen peroxide and magnesium sulfate solutions needed to obtain a dose of 8 and 3 $kg \cdot adt^{-1}$, respectively. Then, the pH was adjusted to 11.5

with 1 N NaOH. Once the treatment time (90 min) was finished, the bags were cooled with water, the pulp filtered and the filtrate analyzed for pH and residual hydrogen peroxide. Finally, the pulp was washed with distilled water and centrifuged.

2.3. Optimization of the Chlorine Dioxide Dose. Pulp from the OXAZ sequence was used to assess the potential saving in chlorine dioxide obtained by using an enzyme treatment in the bleaching sequence relative to a control treatment in the absence of enzyme. The D stage was performed in polyethylene bags that were immersed in a water bath at 80 °C. An amount of 20 g of pulp from the OXAZ sequence at 10% odp consistency at pH 4 adjusted with 1 NaOH was subjected to a D stage during 50 min. The chlorine dioxide doses ranged from 12 to 23 kg Cl_2·adt^{-1}.

2.4. Chemical Pulp Properties. The studied pulp was characterized in terms of kappa number, brightness, and viscosity in accordance with the applicable standards, ISO 3688, ISO 302, and SCAN-CM 15:88. Hexenuronic acid content; determinations were done both on the initial samples and on duplicates obtained after the X and A stages following the method proposed by Chai et al.[13] In addition, pulp from the X stage was used to measure the sugar content by HPLC and to obtain scanning electron micrographs at the Textile and Paper Engineering Department of ETSEIAT (UPC) in Terrassa. The duplicate samples for each treatment (enzE, enzL, and control) obtained from the OXAZDP sequence were mixed and analyzed for adsorbable organic halides (AOX) solubility in 5% soda, brightness reversion, and morphological properties on Fiber Lab V3.5.3 equipment from Kaajani.

2.5. Physical Pulp Properties. The samples for each treatment (enzE, enzL, and control) obtained from the OXAZDP sequence were refined at 1000, 2000, and 3000 revolutions in a laboratory beater (PFI mill type). The resulting refined and unrefined pulps were analyzed for various physical properties in accordance with their respective standards.

The properties measured included bulk, opacity, light scattering coefficient, thickness, air permeability, permeability Bendtsen, tensile index, flexibility, TEA index (tensile energy absorption), tensile stiffness index, breaking length, burst index, tear index, and Klemm capilarity by SCAN methods.

2.6. Effluent Properties. The effluents from the X stage were characterized in terms of COD, total organic carbon (TOC), color, and turbidity in accordance with the applicable standards: SMEWW 5220 D, CETESB NT-07/L5.117, SMEWW 5310, and IPT-ABTCP-E14-1994. Determinations included pH after each bleaching stage and TOC (with a Shimadzu TOC-V CPN analyzer) in order to facilitate subsequent assessment of the process yield. The residual agents (ozone, chlorine dioxide, and hydrogen peroxide) were also calculated.

3. RESULTS AND DISCUSSION

Pulp properties were calculated after each bleaching stage of the OXAZDP sequence to evaluate the evolution of each property with the different bleaching reagents (Figure 1).

3.1.1. Enzymatic Treatment (X Stage). *Pulp Properties.* The use of the enzymes enzE and enzL reduced the kappa number of the X-pulp by one unit with respect to the control treatment (to 10 vs 11.3). A similar decrease was previously obtained by other authors,[8,7,14] albeit at lower pH and temperature values. Xylanase does not react directly with lignin in pulp since it is a nonoxidative enzyme. Xylanase can degrade xylans which are bonded to lignin and the cellulose matrix giving a dissociation of lignin−carbohydrate complexes and reducing the lignin content as a result. On the other hand, the

Table 1. Properties of the Effluents from the X Stage in the OX Sequence

treatment	COD (kg O_2·t^{-1})	TOC (kgC·t^{-1})	color (kgPtCo·t^{-1})	turbidity (kg$_{formzida}$·t^{-1})
control	15.5 ± 0.2	4.9 ± 0.0	7.1 ± 0.3	1.5 ± 0.1
enzE	36.7 ± 0.3	10.9 ± 0.1	12.5 ± 0.4	2.5 ± 0.1
enzL	35.6 ± 0.3	11.1 ± 0.1	11.6 ± 0.4	2.4 ± 0.1

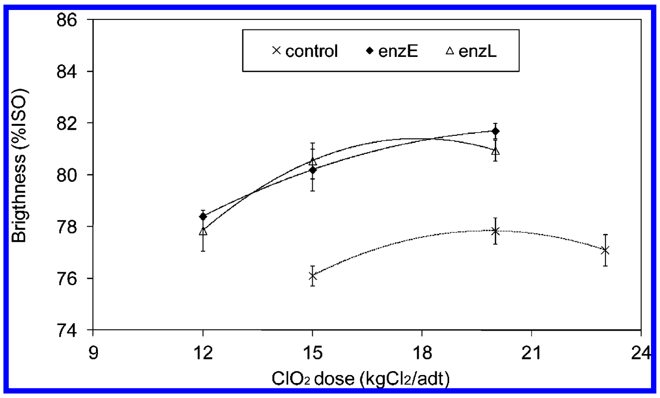

Figure 2. Brightness values of the pulp vs chlorine dioxide doses.

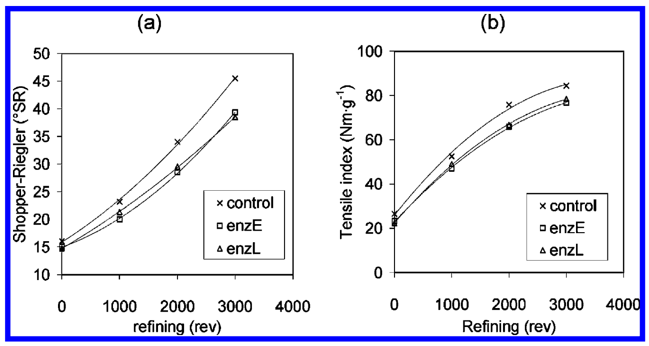

Figure 3. Variation of the Schopper−Riegler grade (a) and tensile index (b) of the pulp as a function of its refining degree.

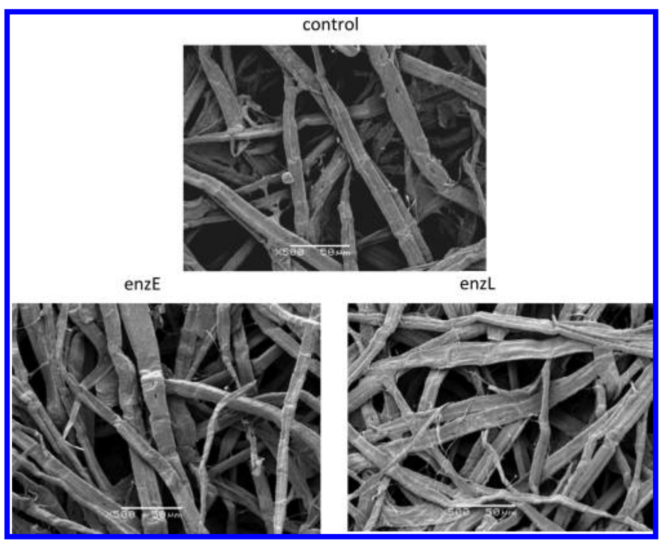

Figure 4. SEM photographs: control pulp and pulps treated with enzE and enzL.

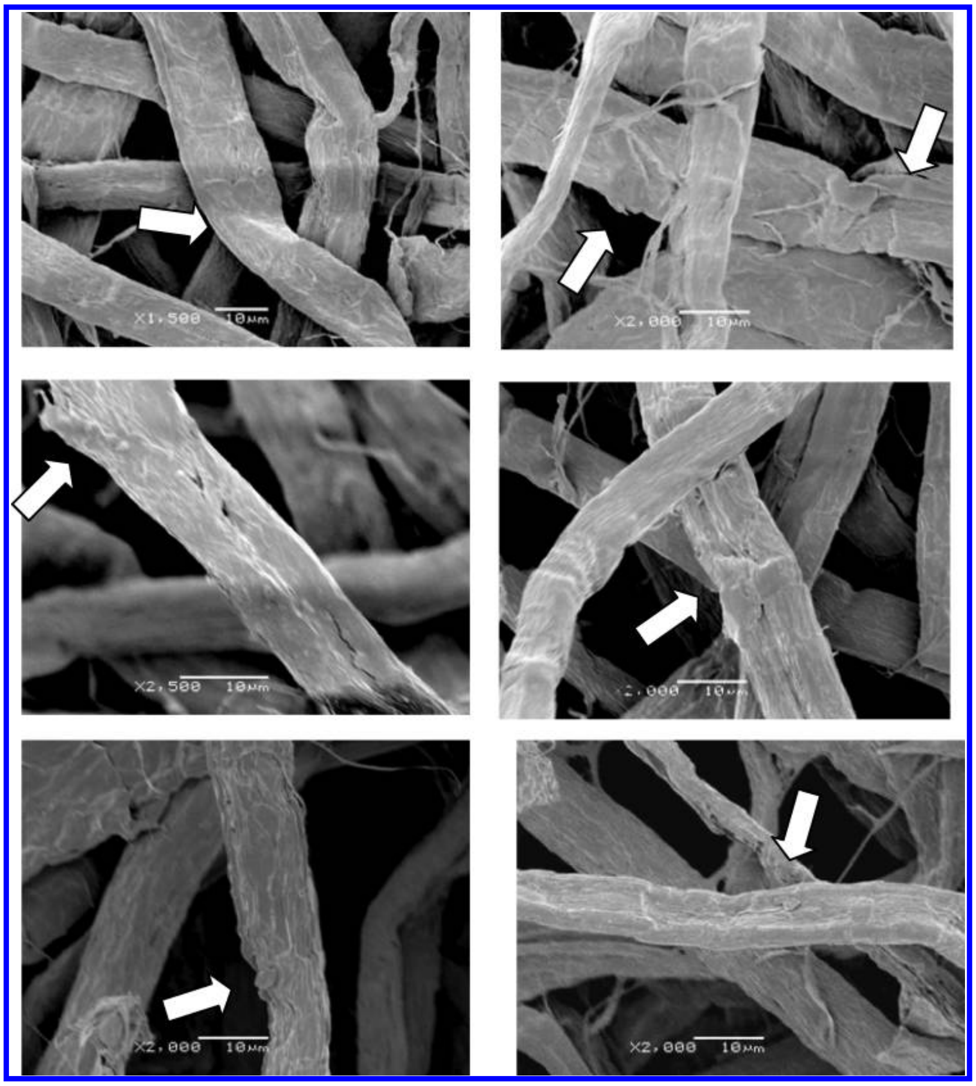

Figure 5. SEM photographs of pulps treated with enzE and enzL (A): effects on fiber surface.

control pulp was found to have an HexA content of 65.4 $\mu mol \cdot g^{-1}$, which was 7 $\mu mol \cdot g^{-1}$ greater than that obtained with the enzyme treatments (58.5 $\mu mol \cdot g^{-1}$). Enzymes reduce the HexA content of pulp,[15] thereby also reducing the amounts of bleaching reagents needed in subsequent stages. Some authors have found the reduction in HexA and kappa number to be correlated; thus, a decrease in HexA content of 10 $\mu mol \cdot g^{-1}$ results in a reduction of 0.86−1.05 in kappa number.[16−18] However, other authors have suggested that enzyme treatments also remove other substances such as carbohydrate degradation products[19,20] or even lignin compounds;[21,19,22] this is consistent with the kappa number decreasing by more than one unit as a result of the HexA content being reduced by 7 $\mu mol \cdot g^{-1}$. Concerning the brightness it is found that the X stage increased brightness by more than two percent points relative to the control treatment (55.5 vs 53.4% ISO). Kraft cooking alters xylose and xylan molecules, which form colored species containing double bonds as a result; a xylanase treatment can also remove such chromophoric species.[19,20,23] Previous studies related the removal of chromophores, hydrophobic substances, and reduced sugars, all present in the effluents from an X stage, to the reduction in kappa number of pulp.[14,24] There were significant differences in the proportions of glucose between control (81.4 ± 1.2%) and enzyme treatment with enzE (82.7 ± 0.9%) and enzL (82.3 ± 0.4%) and, also, in xylose between control (16.2 ± 0.3%) and enzE (15.1 ± 0.3%) and enzL (15.1 ± 0.0%) which confirm that. Previous studies revealed similar changes in the proportion of carbohydrates (viz. an increase in glucose content and a decrease in xylose content) in xylanase-treated pulp.[8,25] Concerning the effluent properties (Table 1) both enzymes had a similar effect, increasing the COD, TOC, color, and turbidity.

3.2. Acid Treatment (A Stage). As can be seen from Figure 1, the A stage reduced the kappa number by more than three units and the HexA content by about 35 $\mu mol \cdot g^{-1}$ with respect to the previous X stage. Also a decrease in pulp viscosity is observed but brightness is maintained. The decrease in kappa number during A stage is associated to the reduction in HexA. The HexA removal with A stage was due to the pulp hydrolysis produced by the low pH and high temperature used in this stage. In addition, the previous enzymatic treatment did not affect the efficiency of A stage. However, it was observed that the enzyme-treated pulp samples required less acid dose (0.3 $kg \cdot adt^{-1}$) than control to obtain an initial pH of 3.5.

3.3. Ozone Treatment (Z Stage). A comparison of the results for the Z stage with those for the previous A stage (Figure 1) reveals that the Z stage reduced the kappa number by four units and increased pulp brightness by 12.0−12.8% ISO

Table 2. Variation of the Physical Properties as a Function of the Tensile Index

physical property	sample	equation	R^2	for a tensile index of 70 N m·g^{-1}
Shopper−Riegler (°SR)	control	$y = 8.21 \times 10^{-3}\cdot x^2 - 4.32 \times 10^{-1}\cdot x + 22.0$	0.98	32.9
	enzE	$y = 9.20 \times 10^{-3}\cdot x^2 - 4.79 \times 10^{-1}\cdot x + 21.4$	0.99	33.0
	enzL	$y = 6.35 \times 10^{-3}\cdot x^2 - 2.23 \times 10^{-1}\cdot x + 16.6$	0.99	32.1
bulk (cm^3·g^{-1})	control	$y = 5.79 \times 10^{-5}\cdot x^2 - 1.31 \times 10^{-2}\cdot x + 2.04$	0.99	1.41
	enzE	$y = 6.64 \times 10^{-5}\cdot x^2$- 1384 $\times 10^{-2}\cdot$x+2.03	1.00	1.39
	enzL	$y = 1.09 \times 10^{-4}\cdot x^2 - 1.87 \times 10^{-2}\cdot x + 2.17$	0.99	1.40
air permeability (s·0.10 mL^{-1})	control	$y = 2.68 \times 10^{-3}\cdot x^2 - 1.95 \times 10^{-1}\cdot x + 3.65$	1.00	3.13
	enzE	$y = 1.49 \times 10^{-3}\cdot x^2 - 6.79 \times 10^{-2}\cdot x + 1.22$	1.00	3.77
	enzL	$y = 2.86 \times 10^{-3}\cdot x^2 - 1.95 \times 10^{-1}\cdot x + 2.64$	1.00	3.00
tear index (mN·g^{-1})	control	$y = -1.65 \times 10^{-3}\cdot x^2 + 2.59 \times 10^{-1}\cdot x - 1.13$	0.99	8.91
	enzE	$y = -1.64 \times 10^{-3}\cdot x^2 + 2.58 \times 10^{-1}\cdot x - 1.02$	0.99	9.02
	enzL	$y = -1.94 \times 10^{-3}\cdot x^2 + 2.88 \times 10^{-1}\cdot x - 1.72$	0.98	8.93
opacity (%)	control	$y = 8.82 \times 10^{-5}\cdot x^2 - 7.88 \times 10^{-2}\cdot x + 78.5$	0.99	73.4
	enzE	$y = 8.38 \times 10^{-4}\cdot x^2 - 1.63 \times 10^{-1}\cdot x + 79.4$	0.98	72.1
	enzL	$y = 1.20 \times 10^{-3}\cdot x^2 - 2.05 \times 10^{-1}\cdot x + 81.1$	0.98	72.6

Table 3. Calculation of the TOC Content Associated with the Effect of the Enzyme Treatment of the Pulp during the X Stage

	TOC (kg C·t^{-1})				
	X stage (initial treatment)		X stage (final treatment)		
sample	experimental	enzyme without COD	experimental	treatment without COD	treatment without COD neitner enzyme
control	5.8		4.9		
enzE	7.4	1.5	10.9	5.9	4.4
enzL	6.9	1.1	11.1	6.2	5.1

with respect to the XA sequence. The difference in brightness amounted to 4% ISO, which exceeds those observed after the X stage and the XA sequence. The XA sequence resulted in differences of one unit in kappa number between the control and enzyme treatments but in comparatively small differences in HexA contents. Because the HexA content of the pulp prior to the ozone treatment was essentially similar between treatments, the brightness increase caused by the Z stage can be ascribed mainly to the xylanase treatments opening up pores in fiber cell walls[7,26] rather than to the differences in HexA content of the pulp prior to ozonization. The X stage altered fiber crystallinity, thereby facilitating diffusion of degraded lignin fragments.[9]

3.4.1. Chlorine Dioxide Treatment. *Optimization of the Chlorine Dioxide Dose.* OXAZ pulp was subjected to the D stage by using variable chlorine dioxide doses from 12 to 23 kg Cl_2·adt^{-1}. On equal chlorine dioxide loads, the NaOH dose needed to adjust the required pH was 0.6 kg·adt^{-1} lower in the enzyme treatments than in the control treatment. The potential saving in chlorine dioxide provided by the D stage in the OXAZDP bleaching sequence was assessed.

Raising the chlorine dioxide dose provided a slight, insubstantial further reduction in Kappa number. No differences in viscosity between chlorine dioxide doses, nor between the control and enzyme treatments, were observed (data not shown).

However, as can be seen from Figure 2, brightness increased with increasing ClO_2 dose. All treatments behaved similarly in this respect; with low doses, an increase by 3 kg Cl_2·adt^{-1} raised brightness substantially relative to higher doses. Increasing the dose over the range 12−15 kg Cl_2·adt^{-1} in the enzyme treatments increased brightness by 3% ISO; similarly, increasing the dose over the range 15−20 kg Cl_2·adt^{-1} in the control treatment raised it by 2% ISO. However, an increase above the previous ranges resulted in an insubstantial increase in brightness in the enzyme treatments or even in a decrease in the control treatment. The control treatment provided 78% ISO brightness with a chlorine dioxide dose of 20 kg Cl_2·adt^{-1}; this brightness level fell short of those obtained with the enzyme treatments (up to 82% ISO). On equal chlorine dioxide doses, the differences in pulp brightness between the control and enzyme treatments were of up to 4% ISO. The enzyme treatments at a low reagent dose (12 kg Cl_2·adt^{-1}) provided a brightness value of 78% ISO, which similar to that obtained at the optimum dose for the control treatment (20 kg Cl_2·adt^{-1}). Therefore, the use of enzymes in the process can help reduce the amount of chlorine dioxide needed to obtain a given brightness level after the D stage in the XAZDP sequence by 8 kg Cl_2·adt^{-1} (or 3 kg Cl_2·adt^{-1}). This saving in reagent is similar to those previously obtained in other studies.[2,6,27]

3.4.2. D Stage in the OXAZDP Sequence. On the basis of the results of the optimization tests, we chose to use a chlorine dioxide dose of 18 kg Cl_2·adt^{-1} in the D stage was used in order to ensure a high enough pulp brightness leading to a level above 88% ISO in the final, P stage. Figure 1 shows the average values of the pulp properties after the D stage in the XAZD sequence. As in the optimization of the chlorine dioxide dose, a comparison of the kappa number obtained after the D stage with that for the prior Z stage reveals that the D stage reduced it by more than 1.5 units. The contents in HexA after the Z and D stages were lower than those obtained after the XA sequence (less than 5 μmol·g^{-1} versus 26−29 μmol·g^{-1}). The D stage

Table 4. TOC Contents of the Effluents from Each Bleaching Stage

	TOC (kgC·t^{-1})					
treatments	X	XA	XAZ	XAZD	XAZDP	mixture
control	4.9 ± 0.1	3.3 ± 0.1	1.3 ± 0.0	1.6 ± 0.1	2.9 ± 0.2	2.8
enzE	10.9 ± 0.2	4.1 ± 0.6	1.4 ± 0.0	1.4 ± 0.1	3.3 ± 0.2	4.3
enzL	11.1 ± 0.1	3.9 ± 0.1	1.3 ± 0.0	1.5 ± 0.1	3.3 ± 0.5	4.2

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increased pulp brightness by about 15% ISO (to 80–82% ISO) relative to Z. The difference between the control and enzyme treatments was 2.5% ISO, which is smaller than that observed after the Z stage. Pulp viscosity was reduced by 200 mL·g^{-1} (to 780 mL·g^{-1}) by the Z and D stages in the XAZD sequence relative to the XA sequence. No significant differences in viscosity between chlorine dioxide doses or the control and enzyme treatments were observed.

3.5. Hydrogen Peroxide Treatment. A hydrogen peroxide dose of 8 kg·adt^{-1} for the P stage was adopted; also, the initial pH was raised to 11.5 in order to increase the low final pH obtained in the tests. The pH at the end of all treatments was 10.9. Figure 1shows the average values of the pulp properties obtained after the P stage in the XAZDP sequence.

The P stage increased brightness by about 8% ISO (to more than 88.5% ISO) with respect to D. The difference between the control and enzyme treatments (which provided brightness values in the region of 89.6% ISO) was 1% ISO. The P stage reduced pulp viscosity by about 160 mL·g^{-1} (to 620 mL·g^{-1}) relative to the prior, D stage. There were no significant differences in this respect between the control and enzyme treatments.

3.6. Chemical Properties of the Final Pulp. The content in adsorbable organic halides (AOX) of the control pulp was 1.25 g·adt^{-1}, which is more than double that of the enzyme-treated pulp samples (0.6 g·adt^{-1}). Therefore, the enzyme treatment resulted in a substantially reduced amount of AOX in the final pulp. Recently, xylanases were found to decrease the OX content of pulp.[6] Reducing the content in AOX of pulp can help lessen their environmental toxicity and meet the stringent requirements of some clients.

Concerning brightness reversion, it is known that eucalyptus pulp bleached under certain conditions can exhibit unstable brightness. In fact, the interactions of environmental factors such as UV light, temperature, and moisture with carbohydrates can cause brightness reversion due in part to the uronic and hexenuronic acids present in xylans. Our experiments show that brightness reversion was more marked with the control treatment (1.2% ISO) than with the enzyme treatments (0.7% ISO). Therefore, the enzyme treatments resulted in less brightness reversion.

The solubility in 5% NaOH was also studied. The pulp bleached with the OXAZDP sequence without enzyme shown a solubility of 7.9%. The enzyme treatments resulted in slightly lower solubility than the control treatment; the differences, however, were insubstantial.

3.7. Fiber Morphology and Scanning Electron Microscopy (SEM) Evaluation. There were no significant differences in fiber morphology between the control and enzyme-treated pulp samples (data not shown). Figures 4 and 5 show SEM photographs of pulps after xylanase treatment. Pulps treated with enzymes and control pulp does not exhibit differences in fiber fibrillation. Although, it can be seen in enzymatic pulps in some points fiber flakes are detached. It can be hemicellulose and glucose agglomerations that precipitated in kraft cooking and enzymatic treatment can detach. This effect has been observed before in previous studies.[8,9,26]

3.8. Physical Properties of the Paper. As can be seen from Figure 3, on equal degree of refining, the paper from enzyme-treated pulp had lower drainability (Schopper–Riegler) and tensile index than that from control pulp. This resulted in differences in the other studied properties. The enzymatic pulps were harder to refine than the control pulp, due to the less xylan content in the pulp. This effect of xylanases on pulp refining efficiency was previously observed by other authors,[28,10,29−31] who ascribed it to a reduction in hemicellulose content. We derived equations relating the physical properties of the pulp to the tensile index and used them to interpolate the values corresponding to an index of 70 N m·g^{-1}. A plot of physical properties as a function of tensile index revealed that all pulp samples shared the same characteristics. Therefore, the enzyme treatment had no effect on the physical properties at the same tensile index (see Table 2).

3.8.1. Total Organic Carbon Content in the Effluents from the OXAZDP Sequence. *X Stage.* As can be seen from Table 3, the effluents from X already exhibited high total organic carbon (TOC) levels at the beginning of the treatment. The high TOC content of the control pulp, 5.8 kg C·t^{-1}, was a result of the presence of black liquor of COD = 16 kg O_2·t^{-1}, whereas those of the enzyme-treated samples (7.4 kg C·t^{-1} with enzE and 6.9 kg C·t^{-1} with enzL) arose from both the presence of black liquor and the enzymes themselves. The initial TOC content in the X stage, which was due to the presence of the enzymes in the effluents, was calculated as the difference from the control TOC; in this way, the amount of TOC associated to the enzymes was found to be 1.5 kg C·t^{-1} with enzE and 1.1 kg C·t^{-1} with enzL.

The TOC of the effluents from X was due to the presence of black liquor and enzyme, and also to the effect of the treatment on the pulp. As noted earlier, the TOC content for the treatment involving no COD was calculated as the difference between the final TOC content for the enzyme and control treatments; this provided an estimated value of 6 kg C·t^{-1}. Similarly, the TOC content associated to the effect of the enzyme treatments was calculated as the difference between the final TOC for the enzyme and control treatments and the previously calculated TOC value associated to the enzymes. The estimated TOC content associated to the enzyme treatment was 4.4 kg C·t^{-1} for enzE and 5.5 kg C·t^{-1} for enzL.

3.8.2. OXAZDP Sequence. Table 4 shows the average TOC contents of pulp from each bleaching stage in the OXAZDP sequence. As can be seen, the TOC contents of the effluents from A, Z, D, and P stages were virtually identical in the control and enzyme treatments.

3.8.3. Relationship between TOC and Pulp Yield. As a rule, the loss of pulp yield resulting from a bleaching stage increases the organic load in the effluents. This has led some authors to calculate pulp yield in each bleaching sequence from TOC measurements of the effluents.[32,33] Each xylan solubilized by a xylanase treatment diminishes pulp yield. Although the loss has an adverse on the process, it can be offset by using lower reagent doses in subsequent bleaching stages.

The TOC content of the effluents from the A, Z, D, and P stages was virtually identical in the control and enzyme treatments, and so was the yield, whether or not an enzyme was used, as a result. The TOC content after X was higher in the effluents from the enzyme treatments; therefore, some yield loss was to be expected. In this work, we assumed 4 kg C·t^{-1} to correspond to a loss of ca. 1% in pulp yield.[34] The yield loss was calculated from this relation and the previously calculated TOC content associated to the enzyme treatments. Such treatments decreased pulp yield by slightly more than 1% relative to the control treatment.

4. CONCLUSIONS

Both studied enzymes, enzE and enzL, had a similar influence on pulp properties. Their use in the OXAZDP sequence resulted in differences from the control pulp; their favorable effects, however, were more apparent in the early bleaching stages. Thus, the most substantial differences in kappa number and HexA content from the control treatment were obtained after the X stage. By contrast, the greatest differences as regards brightness were observed after the Z (oxidative) stage. No significance differences in viscosity after Z between the control and enzyme treatments were observed, however. The proportion of carbohydrates in the control and enzyme-treated pulp samples was slightly different; thus, the xylanases increased the proportion of glucose and decreased that of xylose. Finally, the COD, TOC, color, and turbidity of the effluents from X were greater with the enzyme treatments than with the control treatment.

Tests conducted with a view to optimizing the chlorine dioxide dose to be used on OXAZ pulp at low brightness values revealed that, on an identical dose, the enzyme treatments increased brightness relative to the control treatment. Therefore, a chlorine dioxide saving of 43% could be obtained to certain brightness if this xylanase treatment is used in this ECF sequence

As regards the pulp properties after the OXAZDP sequence, the enzyme treatments provided a 1% ISO higher brightness than the control treatment. On the other hand, the amount of AOX present in the xylanase-treated samples was 50% lower than in the control samples and its reversion was also lower in the treated pulps. Enzyme treated pulps were harder to refine due to the less xylan content. This resulted in lower drainability and tensile index than the control treatment. However, physical properties of treated and untreated pulps, exhibited no significant differences at a certain tensile index.

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