

# Enzymatic treatment applied as a final stage in *E. globulus* kraft pulp bleaching

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## Abstract

**BACKGROUND:** Brightness stability of bleached chemical pulps is often associated with the final bleaching stages that should provide the removal of chromogenic species responsible for brightness reversion without compromising the papermaking potential. Aiming at promoting higher brightness stability, a partially bleached *Eucalyptus globulus* pulp (DED) of c. 88% ISO brightness was involved in a study of a final enzymatic stage (X) alternative to conventional chlorine dioxide (D) and hydrogen peroxide (P) bleaching stages (DEDX vs. DEDD and DEDX vs. DEDP). X stage was also applied before and after the final P or D stages (DEDDX/DEDXD and DEDPX/DEDXP) to produce high brightness pulps (c. 91%).

**RESULTS:** X stage with xylanase Pulpzyme HC allowed an increase of c. 1.5% in pulp brightness while decreasing the brightness reversion and a concomitant pulp yield loss of only 0.5%. Significant chemical savings were obtained in the final D (70%) or P (45%) stages to achieve targeted final brightness of c. 91%. DEDXD or DEDXP sequences had advantage over DEDDX and DEDPX, respectively, in terms of brightness stability of fully bleached pulps.

**CONCLUSIONS:** Xylanase interferes with structures responsible for the brightness reversion. X stage allows production of pulp with extra brightness in sequences with a final P stage.

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**Keywords:** eucalyptus kraft pulp; brightness reversion; hydrogen peroxide; chlorine dioxide; xylanase

## INTRODUCTION

Bleaching chemicals contribute significantly to the overall costs of bleached pulp production. Research in this field and mills revamping have been focused on the minimization of environmental impacts, the optimization of energetic efficiency, improvement of product quality and optimization of capital and operating costs.<sup>1,2</sup> Pulp bleaching is a multi-stage process aiming to increase the visible light reflectance of the cellulosic pulp. This is achieved by removing or modifying chromophore groups which are assigned to residual lignin and its degradation products, as well as to some carbohydrates, extractives and metal ions complexed with pulp components. The distinction among chromophores structures differs mainly in the type of presenting functional groups and conjugated double bonds: (i) quinones; (ii) muconic acid derivatives; (iii) stilbenes; and (iv) conjugated double bonds with carbonyl groups (aldehydes or cetones).<sup>3</sup> Furan derivatives and hydroxybenzoquinone structures derived from carbohydrates have been proposed as the major chromophores in bleached pulps.<sup>4–6</sup>

The technology used in pulp bleaching is of paramount importance for the quality standards of the bleached pulp (e.g. strength and optical properties). Moreover, it must be carried out with minimal consumption of chemical reagents, environmental impact and loss of pulp yield. During bleaching, polysaccharides (cellulose and hemicelluloses) should not be extensively degraded to preserve the strength of paper produced from pulp.<sup>3,7</sup> The final bleaching stages required to attain high pulp brightness (90% ISO brightness or higher) are of low efficiency and nonspecific

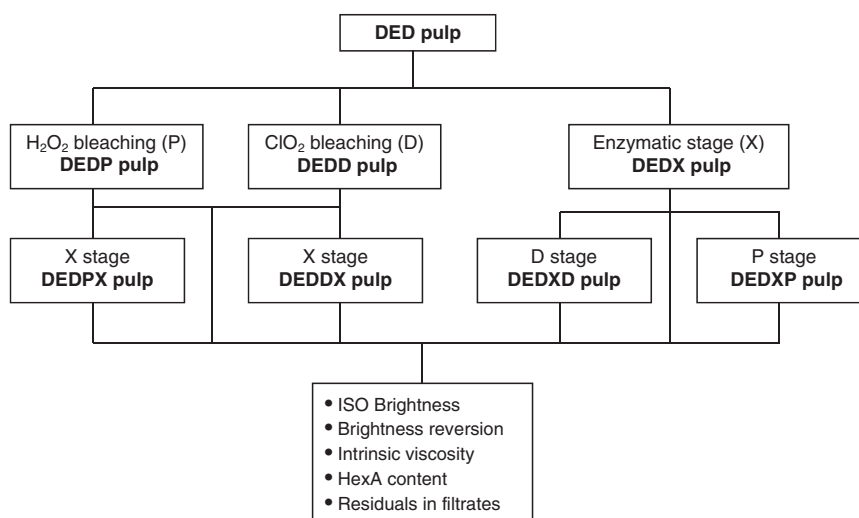
reactions occur, resulting in the production of undesired compounds which are difficult to eliminate. Carbohydrates are prone to oxidation which negatively affects the brightness stability of cellulosic pulps. It is well documented that the utilization of alkaline hydrogen peroxide (P) in a final stage gives much higher brightness stability when compared with pulps bleached with a conventional chlorine dioxide (D) stage.<sup>4,8–11</sup>

Recently it was found that a final D stage in the DEDD sequence caused new unsaturated structures in xylan, which were much less abundant in pulp bleached by a final P stage in the DEDP sequence.<sup>12</sup> The important role of xylan as a source of chromophores and their effect on brightness development and stability of bleached eucalypt pulps have been evidenced.<sup>8,12,13</sup> Xylan in eucalypt kraft pulp is structurally associated with residual lignin, which is the main source of chromophore structures.<sup>14,15</sup> In addition, xylan contains hexenuronic acid residues (HexA) derived from native uronic acid moieties, produced during the harsh alkaline conditions of kraft cooking. Being chromogenic

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**Figure 1.** Schematic representation of the experimental methodology used.

structures, HexA residues do not deteriorate pulp brightness, but can affect the brightness reversion of bleached pulps.<sup>16,17</sup> Taking into consideration the structural association between xylan and chromogenic/chromophoric structures, the highly selective removal of this hemicellulose from the fibre surface promotes pulp brightness thus saving bleaching chemicals and reducing environmental impacts.<sup>18–24</sup> On the other hand, some negative consequences for refining energy and pulp strength can be anticipated as the hydrophilic character and the amorphous state of xylan facilitate fibre swelling and improve interfibre bonding during papersheet formation.<sup>25</sup>

Specific removal of xylan from cellulosic pulp is possible while applying an enzymatic treatment step using xylanases belonging to the hydrolases class.<sup>26</sup> Endo-xylanases (EC 3.2.1.8) catalyze the random hydrolysis of beta-1,4- $\beta$ -D-xylosidic linkages in the xylan backbone.<sup>27</sup> The idea of using hemicellulolytic enzymes in pulp bleaching was first published in the late 1980s by Viikari and co-authors with the aim to reduce the consumption of chlorine and the amount of AOX (adsorbable organic halogen) in effluents.<sup>28–30</sup> Xylanases can be applied at different stages of the bleaching process, but most applications occur at the brownstock storage tower before or after oxygen delignification.<sup>26,30</sup> The application of xylanases at the end of the bleaching sequence is scarce and not systematically investigated.<sup>18,21</sup>

Different mechanisms have been proposed to describe the effect of xylanase on the enhancement of pulp bleachability and brightness stability: (i) enzymatic cleavage of glycosidic bonds in xylan between the regions containing xylan–lignin linkages thus facilitating lignin removal; (ii) selective hydrolysis of xylan precipitated on the fibre surface thus increasing further access of bleaching agents to residual lignin; (iii) hydrolysis of glycosidic bonds near xylopyranose containing HexA groups or chromophoric structures.<sup>19,31–36</sup>

Besides the pulp origin and the residual lignin content, other factors affect xylanase performance in the enzymatic stage: pH, temperature, enzyme dosage, consistency and reaction time. The optimal pH depends on the enzyme origin: xylanases produced by bacteria have usually optimal pH between 6 and 9, whereas xylanases produced by fungi have an optimal pH between 4 and 6.

The main goal of this work was to evaluate the performance of an enzymatic treatment with xylanase as a final stage alternative

to conventional chlorine dioxide or hydrogen peroxide bleaching stages applied to DED pre-bleached *Eucalyptus globulus* kraft pulp in order to promote higher brightness stability of fully bleached pulp. To produce extra bleached pulps (c. 91% ISO brightness) the most suitable position of the X stage in the bleaching sequence was also analyzed (DEDXD or DEDDX and DEDXP or DEDPX).

## EXPERIMENTAL

### Mimicking the final pulp bleaching stage under laboratory conditions

Industrially DED pre-bleached eucalypt kraft pulp (*E. globulus*) of 87.8% ISO brightness, a post color (PC) number of 0.38, a viscosity of 993 mL g<sup>-1</sup> and a hexenuronic acid content of 2.2 mmol kg<sup>-1</sup>, was treated by chlorine dioxide (DEDD), hydrogen peroxide (DEDP) or by xylanase Pulpzyme<sup>®</sup> HC (supplied by Novozymes, Denmark) (DEDX). According to the supplier, the xylanase activity expressed in Active Xylanase Units was 1000 AXU g<sup>-1</sup>. All bleaching experiments were carried out in sealed polyethylene bags heated in a thermostated water bath, under mechanical stirring. A pulp consistency of c. 10% was used in all experiments. After the bleaching stages, liquors/filtrates were collected to measure the residual chemicals and their final pH (>11 after P stage; 5.5 to 6 after D stage). The pulp obtained was washed three times with distilled water and then kept at +4 °C in the fridge for further analyses. Figure 1 shows a schematic representation of the experimental methodology used.

The ranges of bleaching conditions performed on the original DED pulp are summarized in Table 1. Trials employing xylanase were carried out to select pulp treatment conditions for X stage including a 2<sup>3</sup> factorial experimental design (eight trials with three additional replications at the central point) shown in Table 2. These trials were also used for comparison purposes of the subsequent study with D and P stages. ISO brightness levels higher than 90% (from 90.5 to 91%) are usually the mill target due to a brightness loss of c. 1% during pulp drying and storage.

After selection of X stage treatment conditions, DED pulps were bleached with chlorine dioxide or hydrogen peroxide before and after the xylanase stage, as shown in Table 3. In the study 1, different charges of hydrogen peroxide or chlorine dioxide were applied after the enzymatic stage (DEDXD or DEDXP sequences) to

**Table 1.** Ranges of experimental bleaching conditions with chlorine dioxide, hydrogen peroxide and xylanase all applied to the original DED pulp

Bleaching variable	Final D* (DEDD)	Final P (DEDP)	Final X† (DEX)
Temperature (°C)	70	70	55–60
Time (min)	150	60	30–240
D, P or X charge (% odp)	0.15–0.6	0.3–0.9	0.005–0.15
NaOH charge (% odp)	–	0.55	–
MgSO <sub>4</sub> ·7H <sub>2</sub> O (% odp)	–	0.2	–

\*Calculated as active Cl<sub>2</sub> (= 2.63 × ClO<sub>2</sub> charge); †X charges (% odp) correspond to 0.05–1.5 AXU g<sup>-1</sup> odp; odp – oven-dry-pulp.

**Table 2.** Experimental 2<sup>3</sup> factorial design of bleaching trials employing xylanase stage

Trial	pH	T (°C)	Xylanase charge (AXU g <sup>-1</sup> odp)
1	7	55	0.5
2	8	55	0.5
3	7	60	0.5
4	8	60	0.5
5	7	55	1.5
6	8	55	1.5
7	7	60	1.5
8	8	60	1.5
9	7.5	57.5	1.0
10	7.5	57.5	1.0
11	7.5	57.5	1.0

**Table 3.** Operating conditions used in the three studies (bleaching with chlorine dioxide or hydrogen peroxide before or after the xylanase stage)

Study	Pulp*	Final stage§	ClO <sub>2</sub> † (% odp)	H <sub>2</sub> O <sub>2</sub> ‡ (% odp)	Xylanase (AXU g <sup>-1</sup> odp)
1	DEX	P	–	0.5; 0.7	–
	DEX	D	0.15; 0.20; 0.35	–	–
2	DEX	P	–	0.5	–
	DEX	D	0.15	–	–
3	DEDD	X	–	–	1.5
	DEDP	X	–	–	1.5

\*X: 57.5 °C; pH = 7.5, 2 h, 1.0 AXU g<sup>-1</sup> odp for study 1; X: 60 °C, pH = 8, 2 h, 1.5 AXU g<sup>-1</sup> odp for study 2; D: 70 °C, 150 min, 0.15% odp as Cl<sub>2</sub>; P: 70 °C, 60 min, 0.5% odp for study 3.

§D: 70 °C, 150 min, P: 70 °C, 60 min; X: 60 °C, pH = 8, 2 h.

†as active Cl<sub>2</sub>; ‡NaOH = 0.65% odp; MgSO<sub>4</sub>·7H<sub>2</sub>O = 0.2% odp.

obtain final brightness levels similar to any of the performed tests in the original pulp (DEDD or DEDP). The conditions of the final P and D stages used in DEDXP and DEDPX or DEDXD and DEDDX sequences (studies 2 and 3) were selected from study 1. Then, it was possible to compare the savings that could be obtained on chlorine dioxide and hydrogen peroxide consumption with pulps pretreated with enzyme, and also to determine the most suitable position for an enzymatic stage (before or after P or D stage), i.e. comparison between the results of studies 2 and 3.

## Pulp analysis

Intrinsic viscosity was measured in cupriethylenediamine (CED) solution according to ISO Standard 5351. Handsheets for optical properties determination were prepared using ISO 3688 standard procedure. Brightness and brightness reversion were measured according to ISO 2470 and T280 respectively. Brightness reversion was expressed in terms of PC number knowing absorption of pulps at 457 nm, expressed as  $k/s$  values, before and after the artificial ageing (Equation (1)):

$$PC \text{ number} = 100 \times [(k/s)_{\text{after aging}} - (k/s)_{\text{before aging}}] \quad (1)$$

where  $k$  is the specific absorption coefficient and  $s$  is the specific scattering coefficient;  $k/s$  relates to the reflectance ( $R_{\infty}$ ) of the opaque sample according to the Kubelka–Munk equation ( $k/s = (1 - R_{\infty})^2 / (2R_{\infty})$ ). In a subgroup of pulps, hexenuronic acid (HexA) and monosaccharide contents were determined, respectively, according to TAPPI T 282 procedure and Saeman hydrolysis.<sup>37</sup> For the latter the pulp samples were treated with H<sub>2</sub>SO<sub>4</sub> 72% for 3 h at 25 °C, followed by hydrolysis with H<sub>2</sub>SO<sub>4</sub> 1 mol L<sup>-1</sup> for 2.5 h at 100 °C. The corresponding alditol acetate derivatives were analysed by gas chromatography (Varian 3350 gas chromatograph equipped with a FID detector, 260 °C, and with a DB-225 JandW column), under the following conditions: initial temperature 220 °C (5 min); temperature gradient of 10 °C min<sup>-1</sup>; final temperature 240 °C (6 min).

## RESULTS AND DISCUSSION

### Pulp bleaching by DEDP and DEDD sequences

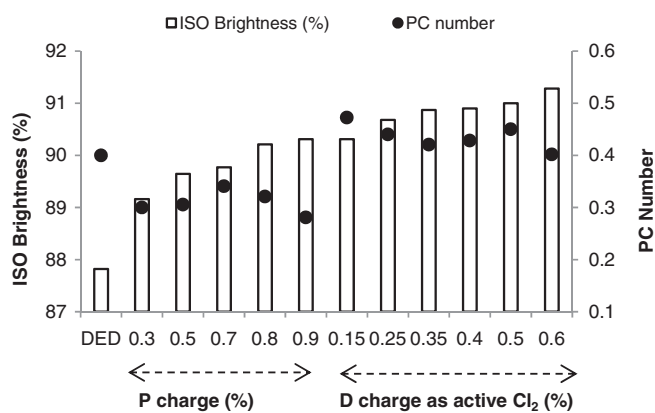
The conventional final stages with peroxide and chlorine dioxide were applied to the DED pulp having in mind two main objectives: (i) to monitor the reference brightness and brightness reversion of pulps while applying the conventional reagents; and (ii) to compare these values with those obtained after enzymatic treatments.

When comparing the values of brightness achieved with hydrogen peroxide (P) and chlorine dioxide (D) (Fig. 2), it can be observed that there is a more efficient performance with the final D stage. The final P stage requires higher reagent charge to get the same brightness as achieved in the D stage (the conversion factor from H<sub>2</sub>O<sub>2</sub> charge to active Cl<sub>2</sub> is 2.09). Although an increase in the charge of both reagents leads to an increase in brightness, the final P stage is more efficient regarding brightness stability. These results confirm the general rule that the amount of chromogens affecting brightness reversion is greater after the final D than after the final P stage.<sup>8</sup> Since most of these chromogenic structures are associated with the xylan located on the fibre surface, an alternative stage with xylanase was applied to DED pulp aiming at reducing the brightness reversion of fully bleached pulp.

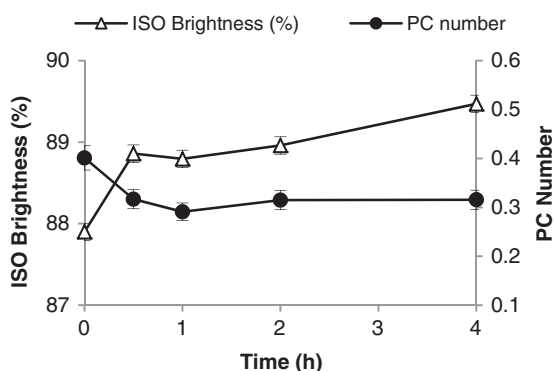
### Bleaching stage with xylanase

#### Effect of reaction time

The operating conditions of the enzymatic stage applied to DED bleached pulp (DEX) were chosen according to supplier recommendations (pH = 8, T = 60 °C, enzyme dosage of 0.5 AXU g<sup>-1</sup> odp) for 30 min, 1, 2 and 4 h. Pulp brightness increased with time, faster during the first 30 min (Fig. 3). This fact could be explained by the higher accessibility of xylan to the fiber surface than in the bulk, which needed longer hydrolysis time.<sup>38</sup> In fact, the kinetics of xylose release studied by enzymatic peeling revealed preferential xylan hydrolysis from the outer layers of cellulosic fibers of DED pulp.<sup>38</sup>



**Figure 2.** Brightness and brightness reversion (PC number) values obtained in final hydrogen peroxide (P) and chlorine dioxide (D) bleaching stages applied to the original pulp (DED).

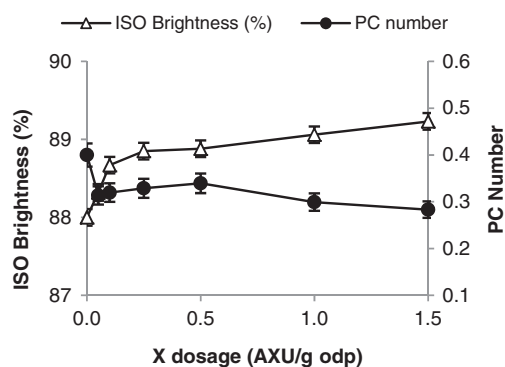


**Figure 3.** Effect of reaction time in enzymatic treatment on the pulp brightness and PC number (60 °C, pH = 8, 0.5 AXU g<sup>-1</sup> odp).

Simultaneously to brightness gain, the brightness reversion was diminished. Brightness gain can be ascribed to enzymatic attack of xylan linked to lignin-carbohydrate complexes with consequent removal of lignin fragments. In fact, the UV absorbance at 280 nm of the filtrate after xylanase treatment was much higher than after the control trial without enzyme (data not shown). The removal of chromophores and chromogens associated with xylan (e.g. residual lignin, hexenuronic acids and other oxidizable structures of carbohydrate origin) and the dissolution of xylooligosaccharide fractions also contribute to brightness gain and brightness stability.<sup>17,22–24</sup> In addition, a slight increase in intrinsic viscosity was observed in pulps treated with xylanase (from c. 990 to c. 1030 mL g<sup>-1</sup> after 4 h) and could be explained by the removal of low molecular weight polysaccharide fraction (xylan). This behaviour was observed previously upon xylanase treatment.<sup>23,24</sup> The treatment period of 2 h was maintained in all following bleaching trials.

#### Xylanase loads

A study on the effect of xylanase load in the range from 0.05 to 1.5 AXU g<sup>-1</sup> odp was carried out during pulp enzymatic treatment at 60 °C, pH = 8 and 2 h (Fig. 4). The pulp brightness sharply increased with xylanase dosage up to 0.25 AXU g<sup>-1</sup> odp followed by a less accentuated increase for higher amounts of enzyme. At the same time, a sharp drop in brightness reversion occurred with the lowest enzyme dosage followed by a slight decrease with loads higher than 0.50 AXU g<sup>-1</sup> odp. Although the viscosity of treated pulps was



**Figure 4.** Effect of xylanase dosage on brightness and PC number (60 °C, pH = 8, 2 h).

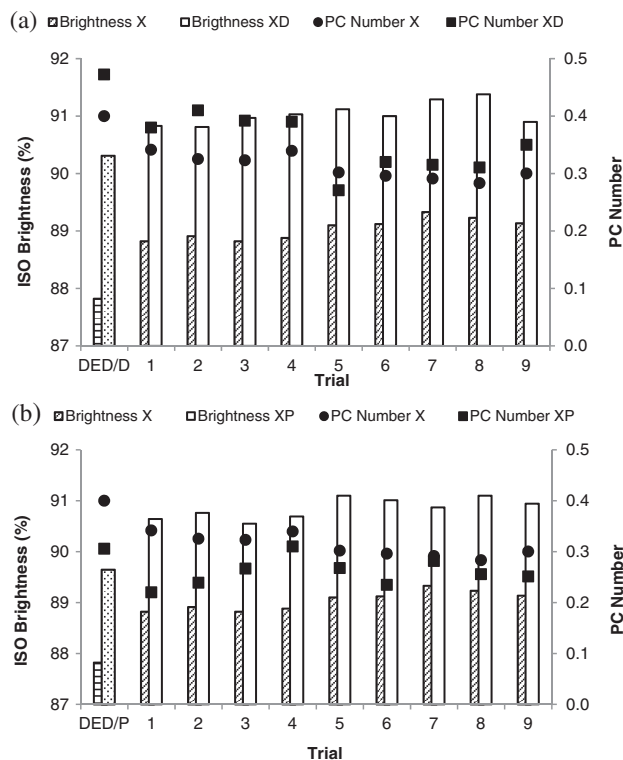
always superior to that of initial pulp, and a tendency to decrease has been detected (1016 to 998 mL g<sup>-1</sup>) with increasing xylanase dosage, the range of these values was within the experimental error.

#### Pulp bleaching by advanced sequences DEDXD and DEDXP

The original DED pulp was treated in an X stage following the full 2<sup>3</sup> factorial experimental design presented in Table 2 (three factors at two levels). In the range studied, enzyme dosage was the main factor with statistical significance affecting both brightness and PC number (positive and negative effect, respectively). The application of enzymatic stage under the conditions of the central point (T = 57.5 °C, pH = 7.5, 1 AXU g<sup>-1</sup> odp, 2 h) did not reveal a significant loss of pulp yield (about 0.5%). The corresponding DEDX pulps were subjected to a final bleaching stage with either chlorine dioxide (DEDXD) or hydrogen peroxide (DEDXP) using the same reagent load in the D stage (0.15% odp as active Cl<sub>2</sub>) or in the P stage (0.5% odp). All bleaching sequences were compared in terms of efficiency towards brightness gain and brightness reversion. The results are presented in Fig. 5. For the highest level of xylanase dosage (1.5 AXU g<sup>-1</sup> odp) minimal differences were observed between PC number before and after the last stage (X vs XD or X vs XP pulps) regardless of both pH and temperature levels applied.

All DEDX<sub>n</sub>D pulps (n = 1–9) showed higher brightness reversion than DEDX pulps. However, when compared with DEDD pulp with the same ClO<sub>2</sub> load, DEDXD pulps showed a clearly significant increase in brightness (≥90.8% ISO vs 90.3% ISO) and a much lower brightness reversion. Hence, eventual ClO<sub>2</sub> savings for the same final pulp brightness may be suggested. For instance, to achieve an ISO brightness of c. 91% a ClO<sub>2</sub> charge of c. 0.5% is needed to bleach the original DED pulp (Fig. 2) whereas for X<sub>4</sub>D pulp of Fig. 5(a) a charge of 0.15% was used. The corresponding saving of bleaching reagent was about 70%.

The positive effect of the X stage on brightness and brightness reversion is also observed in Fig. 5(b) for DEDX<sub>n</sub>P pulps when compared with DEDP pulps (Fig. 2). Nevertheless, the P stage always reduces brightness reversion even if a pre-treatment with xylanase is performed. In contrast to the final D stage discussed above, the final P stage in DEDXP sequence reduces the brightness reversion of DEDX pulps. It must be highlighted that in Fig. 2 the highest ISO brightness value of 90.3% was achieved with a H<sub>2</sub>O<sub>2</sub> charge of 0.9% odp. On the other hand, all DEDXP pulps of Fig. 5(b) showed higher brightness with a H<sub>2</sub>O<sub>2</sub> charge of 0.5% odp, thus giving rise to 45% reagent savings (or higher). This study



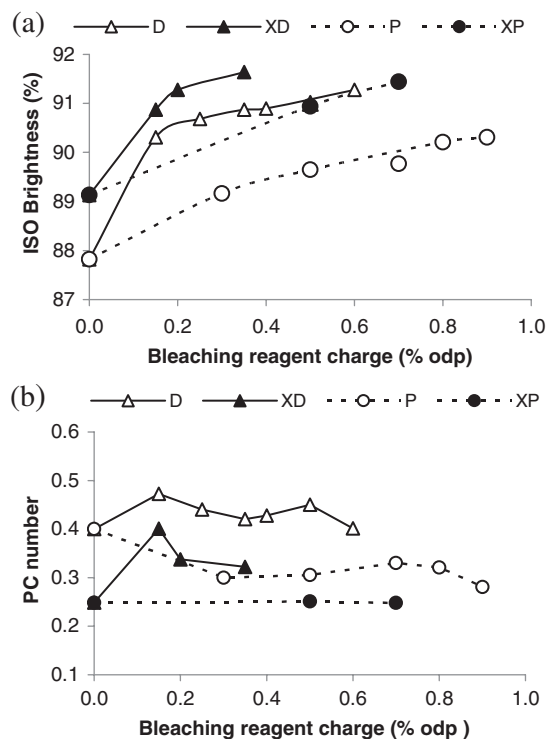
**Figure 5.** Brightness and PC number values of (a) DED, DEDD, DEDX and DEDXD pulps; (b) DED, DEDP, DEDX and DEDXP pulps. Trials 1–9 correspond to the experimental design in Table 2 (X series); fixed  $\text{ClO}_2$  load of 0.15% odp was used in the final D stage (XD series); fixed  $\text{H}_2\text{O}_2$  load of 0.5% odp was used in the final P stage (XP series).

demonstrates that the application of an enzymatic treatment before the hydrogen peroxide stage is worthwhile if the enzyme costs are offset.

To further study the effect of xylanase on DEDXD or DEDXP bleaching sequences, the original DED pulp was treated by enzyme under the conditions of the central point ( $T = 57.5^\circ\text{C}$ ,  $\text{pH} = 7.5$ ,  $1 \text{ AXU g}^{-1} \text{ odp}$ , 2 h) followed by a D stage or a P stage at varied bleaching reagent loads. The results are shown in Fig. 6. Typically, DEDXP pulps had lower pulp brightness but higher brightness stability than DEDXD pulps.

An ISO brightness of *c.* 89% was reached for the DED pulp treated by xylanase (DEDX - zero charge in Fig. 6(a)), which is below the value usually achieved by applying a final dioxide stage (DEDD). However, in the DEDXD sequence, for the same chlorine dioxide load in the final D stage, higher brightness and lower reversion were achieved, when compared with the DEDD sequence. Interference of xylanase with structures responsible for the pulp color and brightness reversion may be inferred.<sup>13,21</sup> The extraction of stabilised quinones chromophoric structures has been mentioned as a result of the xylanase treatment.<sup>21</sup> Moreover, previous studies have revealed the negative effect of carboxylic group containing moieties in xylan on brightness stability, such as the hexenuronic acid residues.<sup>17,18,22</sup>

In the final P stage, an increase in hydrogen peroxide charge always led to an increase in brightness values of bleached pulps either with or without a previous enzymatic treatment (Fig. 6(a)). However, for the same peroxide charge, a gain of 1.3–1.6% ISO brightness is achieved when the pulp was previously treated with enzyme. Indeed, with an enzymatic treatment only (DEDX),



**Figure 6.** Effect of chlorine dioxide (as active  $\text{Cl}_2$ ) or hydrogen peroxide loads in the final bleaching stage on (a) brightness and (b) PC number of DEDD, DEDXD, DEDP and DEDXP pulps (X stage:  $T = 57.5^\circ\text{C}$ ,  $\text{pH} = 7.5$ ,  $1 \text{ AXU g}^{-1} \text{ odp}$ , 2 h).

it is possible to achieve approximately the same brightness as obtained after the final peroxide stage (DEDP) with the lowest peroxide charge of 0.3%. Moreover, in order to reach a brightness of 91%, a peroxide charge in the DEDXP sequence of 0.5% is needed. The same brightness was unattainable even with 0.9% peroxide load in conventional DEDP bleaching.

In conclusion, the application of an enzymatic treatment at the final stages of an ECF sequence allowed pulps to reach higher brightness and brightness stability than in conventional DEDD and DEDP bleaching with the same consumption of bleaching reagents. Hence, chemical savings can be achieved if the same final brightness is the target. However, the gains in brightness and brightness stability of pulp achieved in the X stage are dependent on its placement in the bleaching sequence (e.g. previous and posterior bleaching stages). The beneficial bleaching effect observed for the X stage at the end of the bleaching sequence is consistent with results of previous works, which document well the bleaching improvement when an X stage is applied at the beginning of the bleaching sequence.<sup>26,30</sup> The advantage of using the xylanase stage at the end of the bleaching sequence is the removal of new unsaturated structures in xylan formed in the previous D stages which contribute to the brightness reversion.<sup>12</sup>

### Economical evaluation

Looking for eventual economic benefits of X stage implementation, the bleaching trials with similar brightness, as high as 90% ISO, with and without an enzymatic treatment were compared (DEDD vs DEDXD; DEDP vs DEDXP). Application of the enzymatic stage to DED pulp leads not only to savings of chemical reagents, but also to an increase in brightness stability and/or to costs reduction (Table 4). The enzyme associated cost is offset by the

**Table 4.** Economic analysis for the implementation of an X stage\*

Stages after DED	D	XD	P	XP
Charge/dosage, % odp	0.5	$X_4 = 0.05$ ; $D = 0.15$	$P = 0.9$	$X_1 = 0.05$ ; $P = 0.5$
ISO brightness %	91.0	91.0	90.3	90.6
PC number	0.45	0.39	0.28	0.22
$ClO_2$ , €/ton odp§	2.47	0.74	–	–
$H_2O_2$ , €/ton odp	–	–	5.94	3.30
X, €/ton odp	–	1.75	–	1.75
Total, €/ton odp	2.47	2.49	5.94	5.05

\*Assumed reagents prices, € ton<sup>-1</sup>:  $ClO_2 = 1300$ ;  $H_2O_2 = 660$ ; Xylanase = 3500; see Fig. 5 and Table 2 for X notation.

§the charge in active  $Cl_2$  base was divided by 2.63 to convert to  $ClO_2$  base.

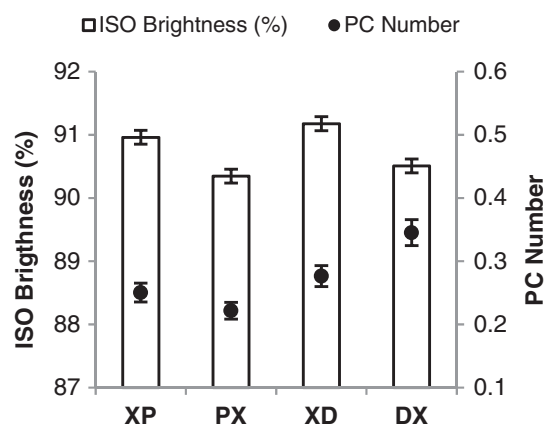
reagent savings in DEDXD bleaching compared with DEDD for pulp with the same brightness, c. 91% ISO. On the other hand, reagents costs in DEDXP bleaching are inferior to those in DEDP for pulps of c. 90.5% ISO revealing economic benefits of 0.9 € ton<sup>-1</sup> odp. Nevertheless, a complete economics evaluation would require knowledge of the equipments amortization costs for the X-stage implementation, as well as the environmental costs and the changes in the papermaking properties of pulp. The latter are essential for paper grade pulps and a follow-up study has recently been accomplished.<sup>39</sup> In general, xylanase does not affect the tensile strength, but improves the tear resistance of bleached pulp, which is in agreement with the results obtained in other studies.<sup>40</sup>

### Location of X stage: DEDXP, DEDPX, DEDXD, and DEDDX bleaching sequences

The location of enzymatic treatment (before or after the final D or P stages) is another factor to consider. Based on the results of Fig. 5, the operating conditions of the 8th experiment ( $X_8$ ) were selected as the best (Table 2). Figure 7 shows that the enzymatic treatment is advantageous when placed before a chemical stage. In the case of DEDXD bleached pulp, the brightness achieved is significantly higher and the reversion lower than those of the DEDDX pulp. Using the DEDXP sequence, higher pulp brightness was reached when compared with DEDPX bleaching although without the advantage in brightness reversion.

A series of experiments (Table 5) were chosen to prove the removal of hexenuronic acids (HexA) employing the xylanase stage in the studied bleaching sequences. It is commonly accepted that HexA residues in pulp may positively correlate with pulp brightness and brightness reversion, even though no correlation was found in other works.<sup>16–18,21,22,41</sup> As could be expected, pulps bleached with hydrogen peroxide had higher HexA content when compared with pulps bleached with chlorine dioxide, since hydrogen peroxide does not react with HexA. However, despite the higher HexA content in pulps bleached by hydrogen peroxide than in pulps bleached by chlorine dioxide, the former revealed lower brightness reversion. This fact is in tune with the previous suggestion that HexA are not the only structures responsible for brightness reversion.<sup>8,12,21</sup>

Although much more HexA residues were removed in the D stage than in the X stage (e.g. DEDD vs  $DEDX_8$  pulps), brightness reversion values of DEDD bleached pulps are higher than those of



**Figure 7.** Effect of X stage position on pulp brightness and PC number for the bleaching sequences: DEDXP, DEDPX, DEDXD and DEDDX.

**Table 5.** Content of HexA and xylose determined in different bleached pulps

Pulp*	HexA (mmol kg <sup>-1</sup> )	Xylose (% pulp)	Pulp*	HexA (mmol kg <sup>-1</sup> )	Xylose (% pulp)
Original DED	2.2	17.1			
DEDD	1.2	16.7	DEDP	1.6	16.8
$DEDX_8$	1.6	15.3			
$DEDX_8D$	1.2	14.2	$DEDX_8P$	1.5	14.2
$DEDDX_8$	1.1	–	$DEDPX_8$	1.2	–

\*See Fig. 5 and Table 2 for notation;  $X_8$  stage: 60 °C, pH = 8; 1.5 AXU g<sup>-1</sup> odp; final D stage: 70 °C, 150 min, 0.15% odp; final P stage: 70 °C, 1 h, 0.5% odp.

DEDX pulps (Fig. 5). Substantially higher removal of xylooligosaccharides (XOS) in X than in D stage was also confirmed in a complementary study on final X stage application (Table 5).<sup>38</sup> It was also suggested that the xylan remaining in pulp possessed a higher degree of substitution with uronosyl substitutes in the backbone than xylan before the enzymatic treatment due to the preferential removal of linear XOS.<sup>38</sup>

The DEDXD bleaching sequence removes more HexA residues than the DEDX sequence, but similar amounts to the DEDD sequence for the same chlorine dioxide load. Hence, the removal of HexA by chlorine dioxide was more efficient than by enzymatic treatment. The removal of HexA was slightly better when the X stage was applied after D or P stages rather than before these stages (DX vs. XD and PX vs. XP).

## CONCLUSIONS

An enzymatic treatment of DED pre-bleached eucalypt kraft pulp by xylanase Pulpzyme® HC allowed a brightness gain of about 1.5% (from 87.8 to 89.3% at 60 °C, pH = 7, 1.5 AXU g<sup>-1</sup> odp, 2 h) and a decrease in brightness reversion by 0.11 PC units. However, an additional chlorine dioxide (D) or hydrogen peroxide (P) stage was needed after the enzymatic treatment to reach a pulp brightness of 90–91% ISO.

DEDD pulps attained higher brightness and lower brightness reversion than DEDD pulps at the same  $ClO_2$  charge, indicating that xylanase treatment promoted the reduction of structures responsible for brightness reversion. To obtain the same final

brightness of c. 91%, DEDXD pulps required c. 70% less  $\text{ClO}_2$  in the last D stage than DEDD pulps. This saving more or less offset the enzyme cost and has environmental benefits.

Regarding DEDP bleaching, the implementation of an enzymatic stage to DED pulp led to a significant increase of pulp brightness at the same loads of hydrogen peroxide (DEDXP vs DEDP). Thus, to reach an ISO brightness close to 91% in DEDXP pulp bleaching (X dosage of 0.05% odp and P charge of 0.5% odp) the saving of hydrogen peroxide was higher than 45% when compared with the DEDP sequence (P charge of 0.9% odp). In this case, the economics analysis showed a positive balance, corresponding to a cost saving of 0.9 €  $\text{ton}^{-1}$  odp.

Because of the higher brightness gain, the enzymatic stage must be applied before the final P or D stage (DEDXP or DEDXD sequences), rather than after the chemical stage (DEDPX or DEDDX sequences), although in the case of DEDPX sequence a lower brightness reversion is achieved when compared with the DEDXP sequence.

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