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Bleaching of Kraft Pulp with Commercial Xylanases

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Abstract

The performance of commercial xylanases in totally chlorine-free bleaching of kraft pulp from conifer was tested with Pulpzyme HC (Novo Nordisk) and Cartazyme NS-10 (Sandoz/Clariant), at 500 U/kg of dry pulp, respectively. The treatment with Pulpzyme (X_P) or Cartazyme (X_C) has been combined with stages of bleaching using: oxygen (O), sulfuric acid (A), and extraction with hydrogen peroxide (E_{OP}). The following sequences have been tested: $OXpAE_{OP}$, $OXcAE_{OP}$, $XpOAE_{OP}$, $XcOAE_{OP}$, and OAE_{OP}. Kraft pulp bleached at the Klabin industrial plant using the sequence, CEH (chlorine, alkaline extraction, and hypochlorination) was used for comparison. The following average values were obtained: 1. Kappa number: OX_PAE_{OP}, 4.8; OX_CAE_{OP}, 4.9; X_POAE_{OP}, 5.0; X_COAE_{OP}, 4.9; OAE_{OP}, 5.6, and CEH, 1.9; 2. Brightness (% ISO values): OX_PAE_{OP}, 68.4; OX_CAE_{OP}, 70.1; X_POAE_{OP}, 67.9; X_COAE_{OP}, 68.8; OAE_{OP}, 63.8, and CEH, 63.6; and 3. Viscosity (cP): OX_PAE_{OP}, 27.6; OX_CAE_{OP}, 26.9; X_POAE_{OP}, 23.4; X_COAE_{OP}, 23.1; OAE_{OP}, 25.4, and CEH, 25.2. Pulps that were treated with xylanases, before or after the delignification with oxygen, have shown reduced kappa number and higher brightness than the pulp OAE_{OP}. Enzyme treatment before delignification with oxygen reduces pulp viscosity. Brightness obtained for pulp produced with bleaching sequences containing the enzymatic treatment, when compared with the control, CEH, shows that the xylanases enhance the action of the bleaching agents.

Index Entries: Chlorine free bleaching; kraft pulp bleaching; oxidative peroxide extraction; xylanase.

Introduction

Biotechnology research has been developed to find new alternatives to minimize environmental effects of the effluents from pulp and paper

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industries. The use of hemicellulases enzymes as the xylanases in the bleaching sequences of pulps has been proposed to reduce the amount of chemicals used in ECF (Elemental Chlorine Free) and TCF (Totally Chlorine Free) bleaching while retaining acceptable pulp properties. These pulps show reduced kappa number, increased brightness, and minimal fiber degradation *(1–8)*. Many paper industries from Canada, United States, Sweden, and Finland are using xylanases in bleaching sequences *(9–11)*.

Bleaching with Xylanases

In enzyme-aided bleaching, the proposed mechanism for the action of the xylanases includes:

1. The selective removal of xylan that repreciptates into pores and surface of the cellulose fibers during cooking of the kraft pulp, and
2. The partial extraction of chromophore groups linked to residual xylan, owing to degradation of lignin-carbohydrates complexes.

The xylanase action facilitates subsequent bleaching so that the quantity of bleaching reagents required to reach the same level of brightness is reduced. Therefore, xylanases are not considered direct pulp-bleaching agents, but a bleaching aid that helps to increase brightness *(11,12)*.

The allowed reduction in the use of chemical bleaching agents that is provided by the treatment of pulps with xylanase may reach 10–30%, while it is also possible to increase pulp brightness. This effect can be obtained with all the main bleaching sequences that include the chemical bleaching steps such as treatment with chlorine, chlorine dioxide, ozone, and hydrogen peroxide. An extra benefit that comes from the use of xylanases is the reduction in the level of emitted pollutants *(12)*. The first reported applications of xylanases were made with the introduction of an enzyme-treatment stage in bleaching sequences that used chlorine or chlorine dioxide.

In this article, we report the application of commercial xylanases in TCF bleaching sequences of kraft pulp produced from conifer wood. The commercial xylanases used were Pulpzyme HC, and Cartazyme NS-10, obtained from NOVO Nordisk and Sandoz/Clariant, respectively. The following bleaching sequences, among others, were tested:

1. $OXAE_{OP}$: Delignification with oxygen, xylanase, acid treatment, and oxidative extraction with hydrogen peroxide.
2. $XOAE_{OP}$: Xylanase, delignification with oxygen, acid treatment, and oxidative extraction with hydrogen peroxide.

All tests reported here were performed at the Technical Research Laboratory at Klabin Fabricadora de Papel e Celulose S.A. (Paraná, Brazil). Total annual paper production from Klabin mill is over 570,000 tons, and up until July 1997, the bleaching sequence used was the CEH sequence (Chlorination, alkaline extraction, and hypochlorination). In July 1997, TCF bleaching was installed. This bleaching process consists of the sequence $OQE_{OP}ZP$: (O) delignification with oxygen, (Q) pretreatment with quellant,

(E_{OP}) oxidative extraction with hydrogen peroxide, (Z_Z) ozone treatment, and (P_P) a stage of pressurized peroxide treatment. The pulp now produced has a significantly increased pulp brightness (up to 90% ISO) and also an increased daily production.

Materials and Methods

All the bleaching sequences used for comparison in this work were:

1. O: Delignification with oxygen.
2. OX_P: Delignification with oxygen, and treatment with Pulpzyme HC xylanase.
3. OX_C: Delignification with oxygen, and treatment with Cartazyme NS-10 xylanase.
4. OAE_{OP}: Delignification with oxygen, acid treatment, and oxidative extraction with hydrogen peroxide.
5. OX_PAE_{OP}: Delignification with oxygen, treatment with Pulpzyme HC xylanase, acid treatment, and oxidative extraction with hydrogen peroxide.
6. OX_CAE_{OP}: Delignification with oxygen, treatment with Cartazyme NS-10 xylanase, acid treatment, and oxidative extraction with hydrogen peroxide.
7. X_POAE_{OP}: Treatment with Pulpzyme HC xylanase, delignification with oxygen, acid treatment, and oxidative extraction with hydrogen peroxide.
8. X_COAE_{OP}: Treatment with Cartazyme NS-10 xylanase, delignification with oxygen, acid treatment, and oxidative extraction with hydrogen peroxide.

Pulp Sample

Mill-produced unbleached softwood kraft pulp was obtained from Klabin do Paraná, Brazil. The characteristics of that pulp was: kappa number 23.4, brightness 26.4 % ISO, and viscosity 69.7 cP.

Before being submitted to enzymatic treatment, the pulp was stabilized with a solution of 27 g of NaOH and 10 g of $MgSO_4 \cdot 7H_2O$/kg of dry pulp, while the pulp consistency was adjusted to 10% (w/v) with tap water, previously heated to 40 ± 5°C.

Pulp-Bleaching Procedures

The operating conditions for the bleaching stages are shown in Table 1.

Delignification with Oxygen

The unbleached pulp prepared as described in the Pulp Sample Section was introduced in a rotative autoclave where oxygen was injected until a manometric pressure of 7 kgf/cm^2 was reached. Then, the oxygen inlet valve was closed and the reaction proceeded for a period of 20 min at 102–108°C. At the end of this period, the pulp was washed with running tap

Table 1
Experimental Conditions for Bleaching Stages

Bleaching stage	Consistency (%)	Temperature (°C)	Time (min)	pH	Chemical addition
X_P or X_C	10	60–65	180	8.0	0.3 L/ton H_2SO_4
O	10	102–108	90	>11.0	2.7% NaOH, 1.0% $MgSO_4 \cdot 7H_2O$, @ 7 kgf/cm^2
A	10	90	60	2.0	1.3% H_2SO_4
E_{OP}	10	101–105	180	>11.0	1.5% NaOH, 0.5% $MgSO_4 \cdot 7H_2O$, 0.05% DTPA, 2.5% H_2O_2, @ 5 kgf/cm^2

water, centrifuged, separated manually into fibers, and stocked in polyethylene bags. This was later the input material for most cases with the enzymatic treatment.

Treatment with Xylanase

The enzymatic treatment of the kraft pulp was made with the commercial xylanases: Pulpzyme HC (Novo Nordisk, Denmark) or Cartazyme NS-10 (Sandoz/Clariant, UK). Pulp pH was adjusted to 8.0 with 1.0 *N* sulfuric acid, and then a solution of the xylanase was added together with tap water warmed to 40 ± 5°C, so that a consistency of 10% (w/v) was obtained. The enzyme dosage used was 500 U/kg of dry pulp, as recommended by the enzyme makers, which corresponds to 1.0 g/kg of dry pulp in the case of Pulpzyme, and 0.5 g/kg of dry pulp in the case of Cartazyme. These dosages correspond to the following protein concentrations: 46.0 mg protein/kg oven dry pulp (Pulpzyme HC), and 10.7 mg protein/kg oven dry pulp (Cartazyme NS-10). After homogenization of the pulp suspension, it was introduced in polyethylene bags and kept at 60–65°C for 180 min. At the end of the enzymatic treatment, the pulps were washed with running tap water.

Acid Treatment

Before the extractive oxidation with hydrogen peroxide, the pulp was treated with diluted sulfuric acid. The pH of the pulp suspension was corrected to 2.0 and the quantity of acid was 1.3% in relation to the dry pulp. This pulp suspension with a consistency of 10% (w/v) was kept in polyethylene bags and maintained in thermocontrolled water bath at 90 ± 5°C for 60 min.

Oxidative Extraction with Hydrogen Peroxide

The oxidative peroxide stage, was carried out at 101–105°C in a rotative autoclave kept at the pressure of 5 kgf/cm^2. The pulp suspension was

Table 2
Effect of Xylanase Treatment on the Softwood Kraft Pulps

Pulp	Kappa number	Viscosity (cP)	Brightness (%ISO)
Unbleached	23.4	69.7	26.4
X_P	23.3	67.9	26.4
X_C	23.3	66.5	26.4
O	10.5	40.4	37.3
OX_P	9.3	41.5	41.1
OX_C	9.4	39.7	41.1

conditioned with 1.5% NaOH, 0.5% $MgSO_4 \cdot 7H_2O$, 0.05% diethylenetriamine-pentaacetic acid (DTPA), and 2.5% H_2O_2. Treatment of the pulp in the control sequence OAE_{OP} was carried out under identical conditions but it was not included an enzymatic treatment stage.

Analysis of Pulp Chemical and Physical Properties

Pulp lignin content given by the Kappa number was determined by reacting pulp samples with acidified potassium permanganate (TAPPI method T 236 om-85). Viscosity, which indicates cellulose chain length, was determined by dissolving pulp in cupriethylenediamine (CED) and analyzed according to TAPPI method T 230 om-89. Pulp brightness was determined by TAPPI method T 452 om-92. Analyses were made after each treatment stage for the various sequences.

A correlation between the viscosity CED (μ_{CED}) and the viscosity given in centipoise (μ_{cP}), was established giving Eq. 1 *(1)*.

$$\mu_{cP} = 2.6249 \, [\exp \, (0.0034644 \, \mu_{CED})] \qquad (1)$$

Results and Discussion

The characteristics of the various pulps produced accordingly to the various bleaching sequences will now be discussed, highlighting the influence and advantages of the inclusion of the enzymatic treatment with xylanases in the bleaching process of conifer kraft pulps.

Effects of Xylanase Treatment on Softwood Kraft Pulps

A mill-produced unbleached softwood kraft pulp and an oxygen-bleached softwood kraft pulp were treated with the two xylanases (*see* results in Table 2). Pulpzyme HC treatment of pulp almost did not change kappa number that varied from 23.4–23.3, also maintained the same brightness, but decreased viscosity from 69.7 to 67.9 cp. Cartazyme NS-10 treatment of pulp had the same effect on kappa number, maintained practically the same brightness, but decreased viscosity from 69.7 to 66.5 cP. The effect of xylanase treatment on the oxygen-bleached softwood kraft pulp was better than the xylanase treatment on the unbleached softwood pulp. Pulpzyme

Table 3
Comparison of Some Properties of Softwood Pulps Obtained with Different Bleaching Sequences

Bleaching sequence	Kappa number	Viscosity (cP)	Brightness (%ISO)
OAE_{OP}	5.6	23.4	63.8
OX_PAE_{OP}	4.8	27.6	68.4
OX_CAE_{OP}	4.9	26.9	70.1
X_POAE_{OP}	5.0	23.4	67.9
X_COAE_{OP}	4.9	23.1	68.8
OQE_{OP}	7.0	29.7	57.9
CEH	1.9	25.2	63.6

HC treatment decreased kappa number from 10.5 to 9.3, increased viscosity from 40.4 to 41.5 cP, and increased brightness from 37.3 to 41.1% ISO. Cartazyme NS-10 treatment decreased kappa number from 10.5 to 9.4, increased brightness from 37.3 to 41.1% ISO, but decreased viscosity from 40.4 to 39.7 cP.

Comparison of Some Properties of Pulps Bleached in Different Sequences

A comparison of some properties of softwood kraft pulps bleached at the laboratory with different sequences is presented in Table 3. As a reference, the softwood pulp bleached at the Klabin mill using the sequences CEH and OQE_{OP} were also presented in Table 3.

Pulps that were treated with xylanases have shown kappa numbers practically identical, in the range of 4.8–5.0. These values correspond to a reduction of 10.7–14.1% of the kappa number in relation to the control pulp OAE_{OP}, and 28.6–31.4% in relation to the pulp bleached at Klabin mill using the sequence OQE_{OP} (Fig. 1).

All pulps treated by the enzymatic stage have shown reduction in the kappa number in relation to the control pulps. This reduction can be attributed to the better delignification accomplished with the inclusion of a xylanase treatment stage. Better delignification in this case does not mean necessarily a greater reduction in the lignin content, but a greater selectivity regarding color removal. It was observed that although the sequence CEH produces a lower kappa number, it is not the pulp produced by this sequence that shows the highest brightness, but the pulps treated with xylanases and extracted with peroxide.

It is known that the kappa number is proportional to the concentration of the Klason lignin *(13)*, according to the relation given by Eq. 2:

$$\% \text{ Klason lignin} = \text{kappa number} \times 0.15 \quad (2)$$

Therefore, it can be concluded that the chromophore characteristics of the residual lignin, after xylanase treatment followed by oxidative extrac-

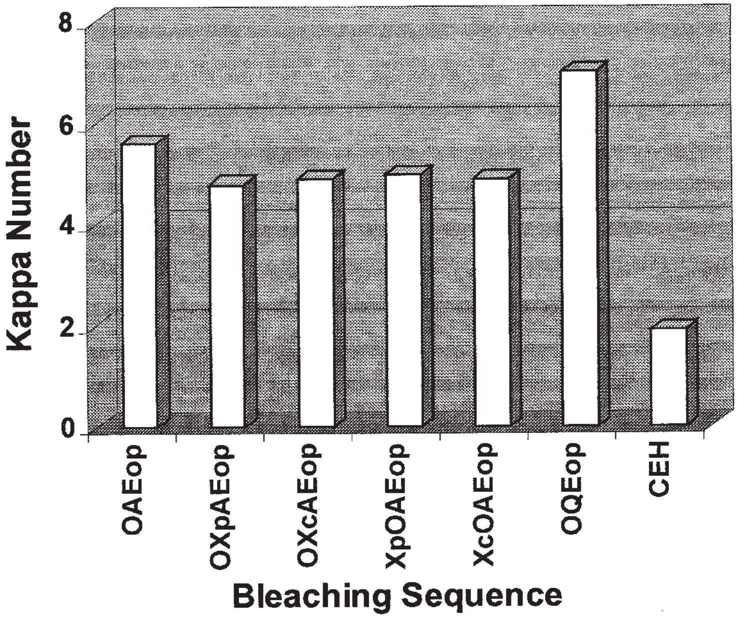

Fig. 1. Comparison of the kappa number of softwood kraft pulp bleached in different sequences.

tion with peroxide, are of reduced light absorption, because the pulps bleached with the xylanase sequence have kappa number about 5 and brightness around 70% ISO, whereas pulp produced by chlorination (CEH) have lower kappa number about 1.9 and lower brightness around 63.6% ISO.

The commercial xylanases Pulpzyme HC and Cartazyme NS-10 used as indicated in the TCF bleaching sequences discussed in this work have led to approximately equivalent results.

The viscosity of the pulp treated with Pulpzyme, before delignification with oxygen, remained practically constant, whereas the viscosity of the pulp treated with Cartazyme suffered a small reduction, which was not sufficient to undermine the value of this enzyme.

Pulps that were obtained with bleaching sequences where the enzymatic treatment followed delignification with oxygen have shown higher viscosity and brightness than treatments in the reverse order. The difference in viscosity between both cases was 3.8 with Cartazyme and 4.2 with Pulpzyme (Fig. 2). The brightness values obtained were: 70.1% ISO for OX_CAE_{OP} and 68.4% ISO for OX_PAE_{OP}, whereas X_COAE_{OP} gave 68.8% ISO and X_POAE_{OP} gave 67.9% ISO. As shown in Fig. 3, all these values are higher than those obtained for the control pulp OAE_{OP} (63.8% ISO) and the reference pulps, CEH (63.6% ISO) and OQE_{OP} (57.9% ISO). It is important, however, to stress that the bleaching conditions at the mill are different from those used in this work. The better results shown with pulps obtained with bleaching sequences where the enzymatic treatment followed delignification with oxygen is thought to occur because of the incorporation of $MgSO_4$ at the delignification stage.

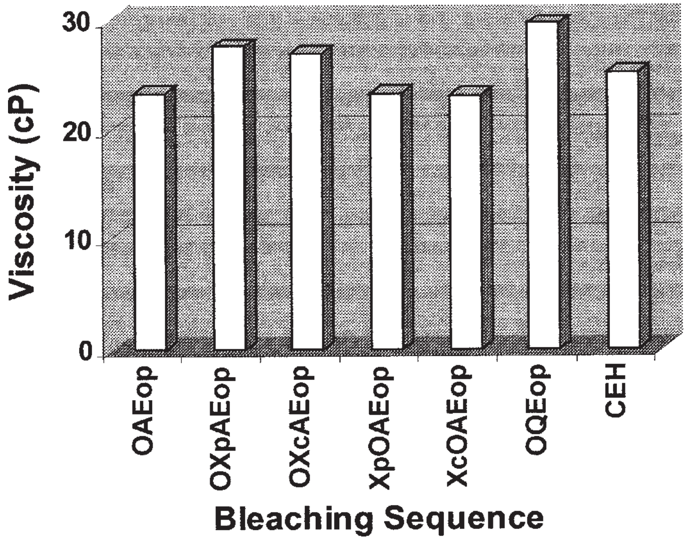

Fig. 2. Comparison of the viscosity of softwood kraft pulp bleached in different sequences.

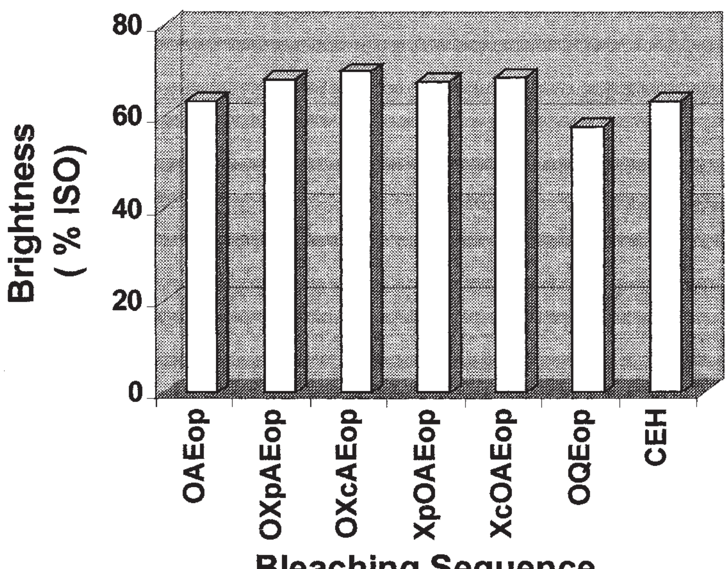

Fig. 3. Comparison of the brightness of softwood kraft pulp bleached in different sequences.

Because both xylanases used in the TCF bleaching sequences of this study have shown similar results, and Cartazyme NS-10 charge (10.7 mg protein/kg o.d. pulp) was lower than Pulpzyme HC (46 mg protein/kg o.d. pulp), this may favor Cartazyme NS-10 application.

The results from the four different enzyme-bleaching sequences show that the xylanase treatment produces significant results. These are increased brightness and reduced kappa number, with some loss in viscosity.

Additional data *(2)* demonstrate that the two xylanases used in this study permit reduction of chemical requirements for bleaching and allow higher brightness to be reached. Xylanase treatment as one bleaching stage of softwood kraft pulps facilitates bleaching of the treated pulps in subsequent stages and it may allow the hydrogen peroxide stage to become more effective.

Despite xylanase treatment being generally more effective on a hardwood than on softwood kraft pulps, partly because of their chemical composition *(8)*, we obtained a softwood kraft pulp with characteristics interesting to industrial application.

The application of xylanase in a mill is very simple—usually only a small laboratory pump is needed to deliver the enzyme solution to the pulp system. It is also necessary to adjust the pH levels to a range compatible with the enzyme activity. The delivery can be done before the brownstock storage tower, or xylanase charge could be divided half to the brownstock storage tower and half to the oxygen-bleaching pulp tower *(9)*.

For future studies, the conditions for xylanase treatment can be optimized. For example, it would be desirable a reduction in xylanase treatment time and charge, and a xylanase stage compatible with temperatures above 65°C and pH levels above 8.0.

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