INFLUENCE OF XYLANASE TREATMENT ON *PINUS PINASTER* KRAFT PULP

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Received July 27, 2001

In Portugal, pulp and paper industry uses especially two wood species, *Eucalyptus globulus* and *Pinus pinaster*. The second species gives pulps with low bleachability (compared with other common softwood species, like *Pinus silvester*), utilised for packaging papers. It is known that treatments with different hydrolytic enzymes could improve the bleaching capacity of softwood pulp. That is why, xylanases were used to improve *Pinus pinaster* kraft pulp characteristics. The enzymatic hydrolysis improved brightness and some papermaking properties.

Key words: kraft pulp, *Pinus pinaster*, xylanases, fiber properties.

INTRODUCTION

Enzymes are enabling new technologies for the processing of pulps and fibers. Xylanases reduce the amount of chemicals required for bleaching, cellulases smooth fibers, enhace drainage and promote ink removal, while lipases reduce pitch deposits.

The concept of hemicellulase used for improving kraft pulp's bleachability was introduced by L.Viikari *et al.*[1] The use of hemicellulases in combination with other bleaching agents led to a substantial decrease of bleaching agent consumption and discharge of toxic compounds in the environment.

Although xylanases-aided bleaching treatments have been developed and several studies were published,[2–5] there are many unanswered questions concerning the mechanism of reaction during the enzymatic process. Several theories have been developed to explain the consequences of the enzymatic treatment, one of them based on structural studies indicating the presence of lignin-hemicelluloses bonds.[6–7] According to this theory, by the enzyme treatment, xylan is hydrolysed into small fragments, allowing the lignin associated to these small fragments to be more easily removed by extraction.

A second theory proposes that, by xylanase treatments, the reprecipitated xylan from the fiber surface should be removed. This reprecipitation phenomenon occurs late in the kraft cooking, when the liquor cooking has a pH of about 13. Xylan reprecipitation onto the fibers is further enhanced by the hydrolysis of acetyl and glucuronic acid groups, which determines straight chains of xylan. Thus, by removing the reprecipitated xylan, fiber permeability and lignin accessibility could increase and, finally, lignin extractability should be improved.[8–9] As xylan's removal was accompanied by lignin release (evidenced by measurements of UV absorbance at 280 nm), it appears that xylanases contribute to increasing ligninic substances' solubilization.[10]

Good results were obtained for oxygen delignified pulp,[11] while other papers reported that xylanase's pre- and post-treatments have the same effect on final brightness in a peroxide bleaching sequence;[12–13] thus, a difference between the response of kraft and kraft-oxygen resulted.[14] The smaller increases in brightness with post-xylanase treatment, followed by chlorine dioxide bleaching, was associated with smaller decreases in the absorption coefficient and smaller increases in whiteness.

This work was designed to study the influence of xylanase treatments on *Pinus pinaster* kraft pulp.

EXPERIMENTAL

In this study, a conventional *Pinus pinaster* kraft pulp, treated with a xylanase preparation, Cartazyme PS, was employed.

Treatments were carried out at 80^0, time 90 minutes, pH = 7,10 % consistency pulp, at different doses of enzymes, such as: sample A- 0.45 IU/g; sample B- 0.9 IU/g; sample C- 1.2 IU/g; sample D- 2.4 IU/g.

The reference pulp was treated in the same conditions, without addition of enzyme.

Pulp and fiber analysis

Kappa number and viscosity were determined according to Tappi methods: T 236 cm-85 and T 230-om 89, respectively. The sheets were obtained using a Rapid Kothen apparatus (T 205 om-88) and the papermaking properties were evaluated by Tappi methods, as follows: T 403 om-91 - burst, T 404 cm-92 - tensile and T 496 cm-85 - tear resistance. Brightness was measured with a Technidyne ISO 2 colorimeter.

Fiber length, width and coarseness were determined on MorFi LB01, while RBA and IF on a CyberflexMetrics.

The carbohydrates content was quantified by high-performance anion-exchange chromatography of TFA hydrolysate pulp (Perkin Elmer 250 chromatograph equipped with Polysphere OH-PB column by Merck Co.).

RESULTS AND DISCUSSION

In agreement with our previous observations,[15-16] the xylanase treatment improved bleachability and some papermaking properties.

It is known that hemicelluloses increase the area of interfiber contact, participating in interfiber bonds and filling out the void space at the contact areas. This improves interfiber bonding and the strength properties that mainly depend on it (tensile and burst).

During treatment with hemicellulolytic enzymes, some hemicelluloses are dissolved and degraded, resulting in weaker fibers. As seen from Table 1, pulp carbohydrates were solubilized to different extents by enzymatic hydrolysis. With increasing the enzyme dose, more xylan was solubilised.

Other carbohydrates, glucan and glucomannan, were less affected, as compared with the xylan fraction.

TABLE 1

Influence of enzymatic treatment on carbohydrates composition

Sample	Solubilised sugars, mg/g pulp				
	Glucose	Xylose	Mannose	Arabinose	Galactose
A	0.17	8.78	0	0.62	0.09
B	0.21	9.23	0	0.79	0.12
C	0.43	10.29	0	0.84	0.17
D	0.64	12.83	0	1.01	0.19

The evolution of carbohydrates' content is sustained by other modifications induced by the xylanase treatment.

Effect of enzymes on fiber morphology

The enzyme treatment caused a minimum degradation of fibers, and fiber length was less affected. Also, coarseness and width were modified (Table 2). Coarseness decrease suggests that the enzymes hydrolysed the fines and defibrillated or cleaned the outer surface of the fiber. With increasing enzyme addition, the effect on fiber was more pronounced, as confirmed by the evolution of viscosity.

TABLE 2

Influence of the enzymatic treatment on fiber properties

Sample	Fiber length, mm	Coarseness, mg/m	Width, μm
Reference	2.095	0.383	36.4
A	1.986	0.369	35.1
B	1.943	0.358	34.2
C	1.902	0.349	33.8
D	1.879	0.337	33.2

TABLE 3

Influence of the enzymatic treatment on kappa number and pulp viscosity

Sample	Viscosity, cm^3/g	Kappa number
Reference	968.9	49.87
A	959.7	47.62
B	945.2	46.28
C	941.9	45.18
D	932.9	45.1

of the enzymatic treatment on strength properties

nase enzymes attack selectively xylan, leaving the cellulose relatively intact, the strength of fiber.[17] It seems that it solubilizes the xylan from the surface ers, as confirmed by the low levels of the fiber degradation observed.
effect on fiber strength, as measured by the wet zero span tensile, is in Figure 1. It seems that alterations of the fiber strength with larger adings resulted. Thus, with increasing the enzyme dosage, the wet-zero ing length slowly decreased.
ution of the relatively bonded area (Table 4) confirms the decrease of the pan tensile index with the addition of enzyme.

TABLE 4

Influence of the enzymatic treatment on fiber flexibility and the relatively bonded area

Sample	Index flexibility, %	Relatively bonded area
Reference	1.20×10^{-11}	19.3
A	1.49×10^{-11}	18.2
B	1.81×10^{-11}	17.7
C	2.06×10^{-11}	15
D	2.12×10^{-11}	14

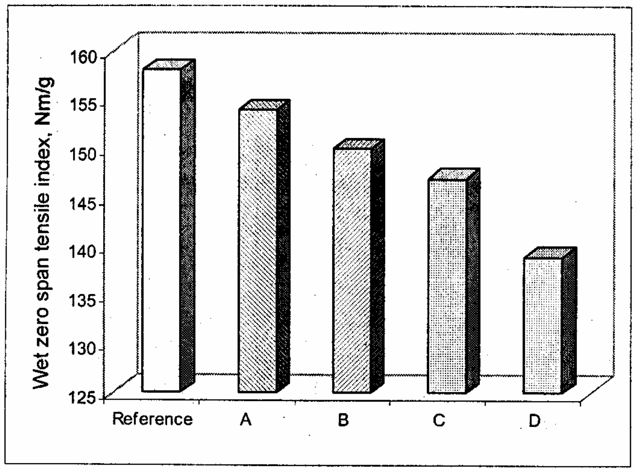

Fig. 1 – Influence of enzymatic treatment on wet zero span tensile index.

In spite of the fact that the enzyme caused a reduction in individual fiber strength, it did not decrease bonding strength, as indicated by the burst index (Fig. 2).

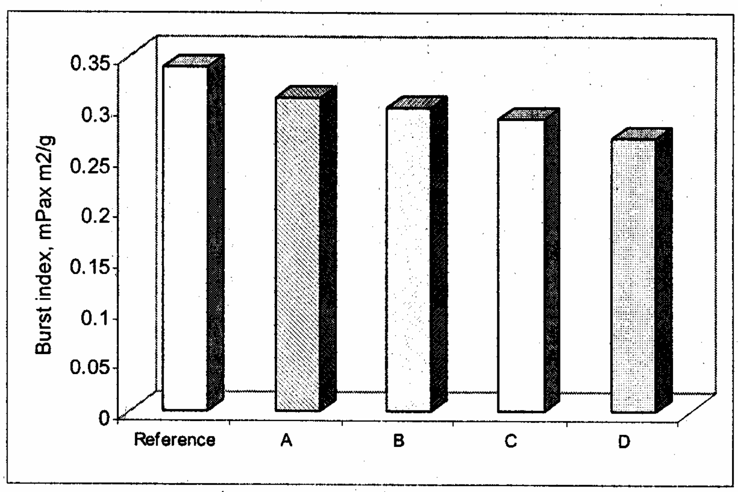

Fig. 2 – Influence of enzymatic treatment on burst index.

Tensile index (as breaking length - Fig. 3) evidences a slow enhancement, probably as a result of fines content' increase, which improves fiber-fiber strength, while the tear index is reduced, as a result of enzymatic treatments on fiber length (Fig. 4).

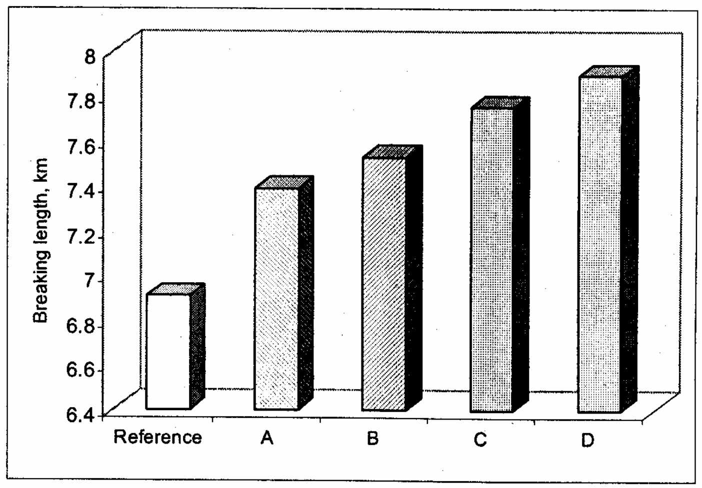

Fig. 3 – Influence of xylanase treatment on breaking length.

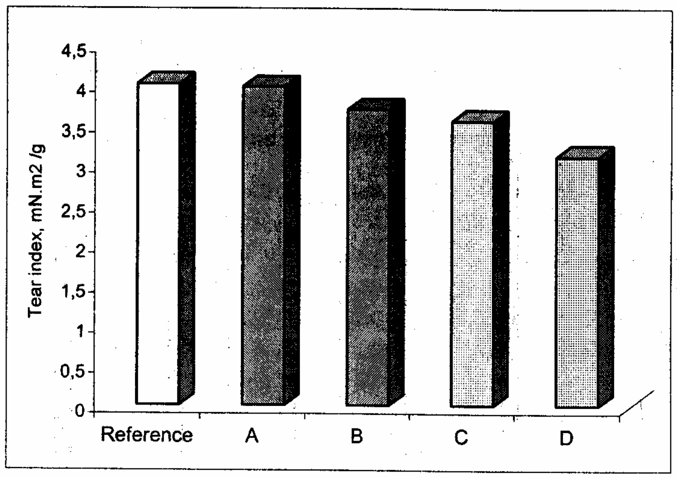

Fig. 4 – Influence of enzymatic treatment on tear index.

Effect of the enzymatic treatment on the optical properties

In agreement with brightness measurements, changes in the specific light absorption and scattering coefficients of the kraft pulp could be discerned after xylanase treatment.

As seen in Table 5, brightness registered a slow increase, that could be associated with similar decreases in the specific absorption coefficient and kappa number. Decrease in the scattering coefficient after xylanase treatment was also observed, which can be due both to the solubilization of arabinoxylan and to the changes in fiber network.

TABLE 5

Influence of the xylanase treatment on pulp's optical properties

Sample	Brightness, %	Scattering coefficient, m^2/kg
Reference	36.7	89.76
A	37.9	79.24
B	39.1	77.35
C	40.4	68.92
D	41.2	65.38

CONCLUSIONS

The xylanase treatment of *Pinus pinaster* kraft pulp determines a selective removal of xylan and modification of fibers' bonding potential. Thus, RBA slowly decreases, while fiber's flexibility records a positive evolution. Fibers became more flexible and improve their interfiber bonding capacity, alongwith the tensile index. At the same time, brightness is improved.

ACKNOWLEDGEMENT. The financial support for this work, received from PRAXIS XXI, is gratefully appreciated.

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