Enzymatic hydrolysis of *Pinus pinaster* kraft pulp

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Kraft pulp from *Pinus pinaster* was treated with two enzyme preparations – Cartazyme MCX-A (which presents both cellulase and xylanase activity) and Cartazyme PS-10 (a xylanase preparation) to enhance papermaking properties of the fibres. Both preparations reduced Kappa number and improved brightness, while the effect on papermaking properties was different.

Keywords

Kraft pulp, *Pinus pinaster*, enzymatic treatment, papermaking properties

The application of biotechnological processes to improve manufacturing processes and products is gaining global attention. In fact, the use of enzymes in the pulp and paper industry to selectively modify and improve pulp properties offers alternative means to enhance processes and products. Enzymes are being produced on a commercial scale and are available at a relatively low price. Hemicellulolytic enzymes have been found to be commercially feasible for pulp bleaching (*1-2*). Thus, xylanase treatments facilitate chemical extraction of lignin from pulp, reducing bleaching chemical consumption and environmental impacts.

Research to establish the effect of enzymatic treatment continues in an effort to improve the effect of enzymes on bleaching (*3-6*). Xylanase systems have been developed to ensure selective hydrolysis of the xylan hemicellulose without loss of fibre strength (*7*). In Portugal, kraft pulps from *P. pinaster* are generally darker than those obtained from other common softwoods (e.g. *P. sylvestris*). Moreover, they also show inferior bleachability. This paper deals with the study of some hydrolytic enzymes to improve the fibre characteristics of kraft pulp from *P. pinaster*.

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EXPERIMENTAL

Material

The *P. pinaster* kraft pulp was prepared with a liquor-to-wood ratio of 4:1 and under a heating program of 90 minutes to cooking temperature and 60 minutes at the cooking temperature of 170°C, 21% alkalinity (active alkali on o.d. wood) and 30% sulfidity. At the completion of the cook, the chips were mechanically disintegrated and the pulp washed with cold water. The Kappa number was 52.9.

Enzymatic treatment

Enzymatic treatments were realised at a temperature of 60°C, using Cartazyme MCX–A, (a mixture of cellulase, activity 1.76 IU/g and xylanase, activity 0.001 IU/g) and a xylanase preparation, Cartazyme PS-10 (10.01 IU/g), at the doses presented in Table 1. The pulp stock concentration was 10%, pH 7 and treatment time 120 minutes.

Control pulps were similarly treated, without the addition of enzymes.

Pulp analysis

Kappa number and viscosity were determined according to Tappi methods T 236 cm-85 and T 230-om 89, respectively. Laboratory handsheets were made according to Tappi Standard T 205 om-889 and the strength properties were evaluated according to Tappi methods as follows: T 403 om-91 – burst index, T 404 cm-92 – tensile strength and T 496 cm-85 – tear index. The beating degree was determined according to SCAN C19-65; fibre classification was by Bauer MacNett fractionation according to Tappi Standard T 233 cm-82. Brightness was measured with a Technidyne ISO 2 colourimeter. Fibre morphology was determined using the MorFi LB01 instrument.

RESULTS AND DISCUSSION

Effect of enzymatic treatment on viscosity and pulp properties

From Table 2 it is evident that all enzymes used improved the delignification level, but the decrease of Kappa number after treatment with Cartazyme PS-10 was higher than with Cartazyme MCX-A.

The xylanase preparation Cartazyme PS-10 was able to maintain viscosity, as seen from Table 2, while treatment with Cartazyme MCX-A shows a small viscosity reduction. Also, with increasing enzyme addition, the reduction in viscosity was accentuated, a result of cellulase action on the fibre morphology. This behaviour could be correlated with the reduction in fibre length resulting from the enzymatic treatment. The average untreated pulp fibre length was found to be 1.177 mm.

Table 1
Enzymatic treatment conditions.

Enzyme preparation	Cellulase, IU/g o.d.	Xylanase, IU/g o.d.
1 – Cartazyme MCX-A	0.12	0.06×10^{-3}
2 – Cartazyme MCX-A	0.24	0.12×10^{-3}
3 – Cartazyme MCX-A	0.36	0.24×10^{-3}
1 – Cartazyme PS-10	–	0.45
2 – Cartazyme PS-10	–	0.9

Table 2
Influence of enzymatic treatments on pulp properties.

Sample	Kappa number	Viscosity, mPa.s
Reference	52.09	21.05
1 – MCX-A	48.04	20.23
2 – MCX-A	46.79	18.89
3 – MCX-A	44.04	17.69
1 – SP-10	45.21	20.88
2 – SP-10	43.64	19.81

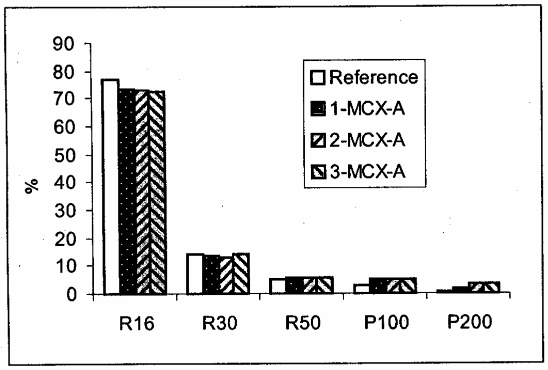

Fig. 1 **Influence of enzymatic treatment with Cartazyme MCX – A on fibre length distribution.**

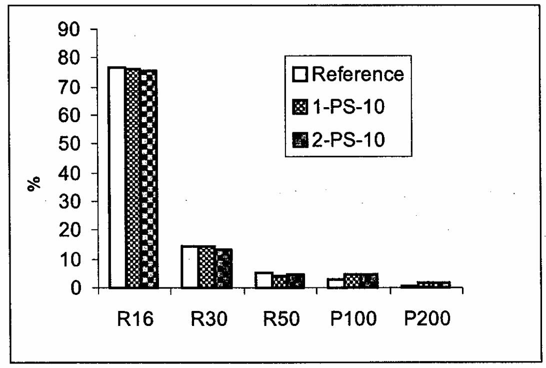

Fig. 2 **Influence of enzymatic treatment with Cartazyme PS – 10 on fibre length distribution.**

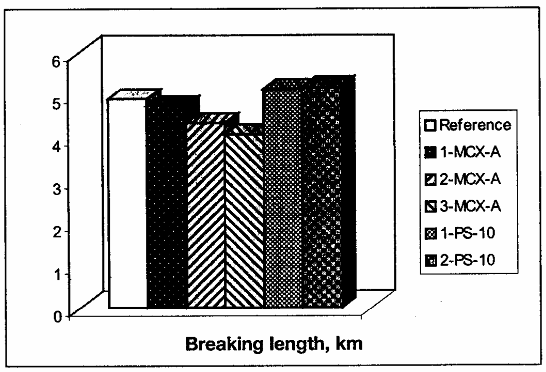

Fig. 3 **Influence of enzymatic treatment on breaking length.**

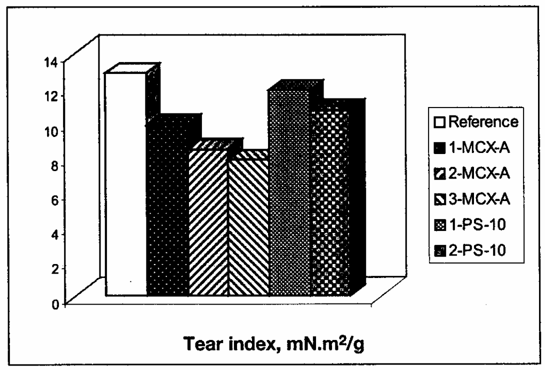

Fig. 4 **Influence of enzymatic treatment on tear index.**

As seen in Table 3, fibre length was more affected by enzymatic treatment with Cartazyme MCX-A than with Cartazyme PS-10 treatments.

Fibre classification was also carried out and the results obtained are presented in Figures 1-2. There are significant changes in the fibre fractions as a function of the enzymatic preparation. Thus, the results show that R16 and R30 fractions are slightly affected by Cartazyme MCX, while Cartazyme PS influences mainly the R50 fraction.

Generally, the fines modification reflects changes such as wall peeling and fibre shortening. The formation of fines was more significant with Cartazyme MCX-A compared with that determined for Cartazyme PS-10. Fine fibres are more flexible and collapsible, forming denser sheets upon papermaking (*8*).

The pulp physical properties were tested before and after enzymatic treatment.

Table 3
Influence of enzymatic treatments on fibre morphology.

Sample	Average fibre length, mm	Coarseness, mg/m
Reference	1.177	0.144
1 – MCX-A	0.824	0.092
2 – MCX-A	0.631	0.074
3 – MCX-A	0.928	0.069
1 – PS-10	0.975	0.104
2 – PS-10	0.871	0.108
3 – MCX-A	44.04	17.69
1 – SP-10	45.21	20.88
2 – SP-10	43.64	19.81

In Figure 3 it can be seen that the tensile strength (as breaking length) for Cartazyme SP-10 treated pulps showed a small increase; this could be due to increased fibre flexibility, allowing them to conform to the shape of neighbouring fibres. This enhances interfibre bonding (with a reduction in light scattering). Figure 4 shows that the tear strength of enzyme-treated pulps was strongly affected by the enzyme preparation used. The lower tear index of pulp treated with CartazymeMCX may be due to cellulose degradation during enzymatic treatment and reduction of fibre length.

As seen in Figure 5, burst index decreases for all enzyme-treated pulps, probably due to fibre fibrillation and reduction of fibre length.

The wet zero-span tensile test has been suggested as a method for removing the influence of fibre bonding on zero-span tensile strength (*9*). This is based on the assumption that in wet sheets, all inter-

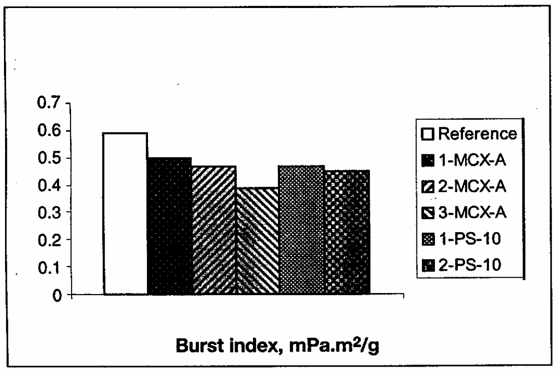

Fig. 5 Influence of enzymatic treatment on burst index.

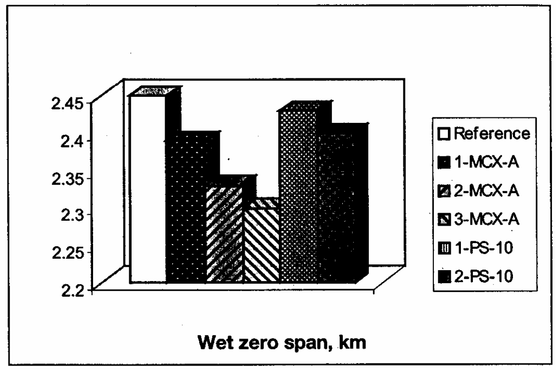

Fig. 6 Influence of enzymatic treatment on wet zero-span tensile strength.

Table 4
Influence of enzymatic treatment on optical properties.

Sample	Light scattering coefficient, m^2/kg	Brightness, %
Reference	26.02	22.2
1 – MCX-A	25.37	23.8
2 – MCX-A	25.02	23.2
3 – MCX-A	24.98	22.9
1 – PS-10	22.8	25.6
2 – PS-10	21.62	24.4

fibre bonds are effectively broken. The wet-zero span tensile strength is lower for a wide range of pulps due to the weakening of the individual fibres that make up the paper sheets. This loss in strength depends on the extent of chemical and mechanical damage of the interfibrillar matrix of the fibres during processing (*10*).

The weakening of the lignin-hemicellulose matrix holding the cellulose microfibrils together determines the reduction of zero-span tensile strength upon wetting. The treatments with enzymes could degrade this interfibrillar matrix.

Indeed, for all enzyme-treated pulps, a reduction of wet zero-span tensile strength was registered (Fig. 6), probably as a result of interfibrillar matrix degradation and a reduction in fibre length. The greatest reduction was registered for pulps treated with Cartazyme MCX-A due to weakening of the individual fibres that make up the sheets. Also, increasing enzyme addition produced increasing loss of zero-span tensile strength.

Effect of enzyme treatment on optical properties

The trial results indicate that enzyme treatments improve pulp brightness (Table 4), but the xylanase preparation was more effective.

This fact, combined with a decrease in Kappa number could indicate action on the lignin-hemicellulose complex and the removal of some residual lignin from the pulp.

The decrease in light scattering coefficient indicates an increase in fibre-fibre bonding (*11*). For all enzyme-treated pulps, the light scattering coefficient was lower, probably due to enhanced fibre flexibility; xylanase treatments seem to be more effective in decreasing light scattering coefficient. Further investigation is required to confirm this supposition.

CONCLUSIONS

It is clear that all enzymatic treatments resulted in increased delignification and brightness compared to the control pulp. These preliminary results show that, for the enzymes tested, Cartazyme PS-10 performed best on *P. pinaster* kraft pulp and could improve the bleaching capacity and some papermaking properties. Optimising the enzymatic treatment conditions could lead to pulps with better papermaking characteristics.

ACKNOWLEDGEMENT

Support for this work was received from the PRAXIS XXI and it is gratefully appreciated.

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Revised manuscript received for publication 11.1.01.