CELLULOSE CHEMISTRY AND TECHNOLOGY

APPLICATION OF HYDROLITIC ENZYMES AND REFINING ON RECYCLED FIBERS

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The present study analyses the effects of the enzymatic treatment with Pergalase A40 (a blend of cellulases and hemicellulases) on an industrially recycled pulp made up of old corrugated container (OCC) fibers, kraft liners and a low percentage of white office paper.

The enzymatic treatment was carried out through a 2^3 experimental design, by varying pulp concentration, enzyme dosage and treatment time. Furthermore, a combined treatment (enzyme plus PFI mechanical refining) was also evaluated, to obtain a greater improvement in drainability, while maintaining or improving the properties of secondary fibers.

Enzymatic pre-treatment of recycled fibers without refining increases the initial freeness degree of pulp, practically without any loss in tensile strength, for most of the conditions analyzed.

Generally, combined treatments (enzyme + refining) show that a higher tensile index level may be attained, with significant drainability improvement and minor specific energy consumption – comparatively with the reference pulp.

Keywords: recycled pulp, cellulases, hemicellulases, experimental design, drainability, physical properties

INTRODUCTION

During the last decades, the use of recycled paper as a fiber resource for paper and paperboard manufacture has become increasingly popular worldwide. The annual consumption of recycled fibers has grown at a rate of 3-4% per year, reaching[1] a recovered paper production of about 195 million tons in 2008.

The original properties of pulps, especially of chemical pulps, change according to the number of utilization cycles applied in the commercial recycling of paper and paperboard. Pulp drainability and paper strength diminish as a result of repeated refining mechanical actions, thus increasing cuts and generating more fines in the recycled pulps.

After several drying and rewetting cycles, the cellulosic fiber loses its water retention value (WRV) and becomes thinner and stiffer (fiber hornification). Fiber conformability, given by the relative bonding area (RBA), is substantially reduced during the process, which results in a decrease of strength properties.[2]

Pommier *et al.*[3] showed clear improvements in the strength of secondary fibers after an enzymatic treatment. By applying low concentrations of cellulases and mixtures of cellulases and hemicellulases, they obtained improvements in pulp drainability without losing properties. When mechanical refining was used before the enzymatic treatment, better properties were obtained at the same drainability value, as compared to those of untreated pulp.

Later on, Bhat *et al.*[4] confirmed Pommier's findings, but none of them proposed a mechanism of action for the observed phenomena.

Some basic effects of the enzymatic treatment were studied by Jackson *et al.*,[5] with a preparation made of xylanases and two different mixtures of cellulases and xylanases on a softwood kraft pulp. With cellulases, pulp drainability improved and it was verified that fiber hydrolysis occurs as a consequence of the treatment. Low enzyme dosages produced fines content reductions, which were related to a possible effect of flocculation produced by the enzyme, similar to the one of polymeric drainage aids. The highest enzyme dosages led to increased fines contents, which were attributed to the fiber disintegration produced by cellulases.

Stork *et al.*,[6] who evaluated the treatment effects on recovered paper using different enzymes of the cellulase and hemicellulase systems, concluded that endoglucanase (CMC_{ase}) activity is a prerequisite for improving drainage of recycled fibers.

Eriksson *et al.*[7] studied the freeness improvement for recycled fibers using enzymes (mixtures of cellulases and xylanases) with refining. Their results confirmed drainage improvements for recycled fibers with minimal strength losses, particularly for board grades.

Pala *et al.*[8] studied the effect of different enzymatic preparations on the secondary fiber upgrading of OCC and found out that all enzymes improved pulp drainability, even if, in most cases, this enhancement was obtained at the expense of paper strength.

In the present work, the effects of the variables of the enzymatic treatment with Pergalase A40 on the drainability and physical properties of an industrial pulp made of 100% recycled fibers were studied. By using a combined treatment, enzyme + mechanical refining, the possibility of obtaining a greater drainability was evaluated, while maintaining or improving the strength properties of the secondary fibers.

MATERIALS AND METHOD

Pulp

Recycled industrial pulp, made of 56.5% old corrugated containers (OCC), 37.5% kraft liners and a low percentage (6%) of printing and writing papers (white office), was provided by Papelera Entre Ríos (Argentina).

Enzyme

The enzyme used in the study – Pergalase A40, a commercial product provided by Genencor International, Inc. – is a blend of enzymes, mainly cellulases and hemicellulases, obtained from *Trichoderma longibrachiatum* (manufacturer's information).

The enzymatic activity was tested by the dinitrosalicylic acid method (DNS), by measuring the generated reducing sugars, following the standards of the Commission of Biotechnology, IUPAC. Cellulase activities were tested using carboxymethyl cellulose (CMC) and Whatman Nº 1 filter paper (FP) as substrates, for 30 and 60 min, respectively, at 45 ºC and pH 6. Xylanase activity was determined using birchwood xylan (XYL) as substrate, for 30 min, at 45 ºC, adjusted to pH 6 with 0.1 M phosphate buffer.

One unit of activity, IU, was defined as 1 μmol of reducing sugar produced per min under the tested conditions. The results of enzymatic activities, in UI mL^{-1} of solution, were the following:

- CMC_{ase} = 2624 IU mL^{-1}
- FP_{ase} = 27.4 IU mL^{-1}
- XYL_{ase} = 267.5 IU mL^{-1}

These results indicate that the enzyme solution has an important cellulase activity.

Experimental design

In this study, a 2^3 factorial design, two levels and three factors were used. The values of the three independent factors were as folows: 5 and 10% of C (pulp concentration), 30 and 90 min of T (treatment time), and 2.6 and 5.2 IU/g of E (enzyme dosage/o.d. pulp).

The experimental results obtained from the factorial design were analyzed to estimate the effects of each factor and their interactions, with statistical software at a 95% confidence level.

Enzymatic treatments

Enzymatic treatments were performed at pH 6 and 45 ºC, in a stainless steel batch reactor with indirect heating and mixing.

After the enzymatic treatment, the pulp was filtered on a Büchner funnel, using a laboratory vacuum pump. The reaction was stopped by pouring the slurry into a sodium hydroxide solution (pH = 12) and by mixing it for 15 min at room temperature. The pulp was then washed to guarantee complete alkali removal. The reducing sugars released during the enzyme treatment were analyzed in the residual liquor, using the DNS method, to determine the extent of enzymatic hydrolysis.

Refining treatments

Both the initial and the enzymatically treated pulps were refined in a laboratory PFI mill at 1000 and 2000 revolutions. Energy consumption was measured on a wattmeter inserted in the original control panel of the PFI mill. The no-load energy of refining was obtained by running the mill without any load removed before and after each pulp refining. Although these results do not match – in absolute value – with the industrial ones, they could be considered valid at a relative level.

Evaluation of pulp properties

Fines analysis was performed with Britt's dynamic drainage jar, according to Tappi test method T 261 cm-00, the Canadian standard freeness (CSF) value being measured by SCAN-C 21:65.

Laboratory handsheets, produced according to the SCAN-C26:76 method, were tested for their physical properties using TAPPI standards, except for the tear index and light scattering coefficient, which were determined with SCAN methods.

Table A lists the physical properties of the reference pulps.

RESULTS AND DISCUSSION

Effects of enzymatic treatments according to a factorial design

The analysis of the independent contributions of each factor and of their interactions concerning the examined properties has shown significant effects in reducing sugar production, drainability, fines analysis and tear index.

Figure 1 presents the results of statistical analysis: Graphs 1a to 1d show the effects of the independent factors on pulp properties and Graphs 1e to 1f illustrate the interactions.

In the case of reducing sugars, drainability and fines, increases can be observed when the independent factors shifted from the lowest to the highest values while, for the tear index, an opposite effect was observed. The interactions inducing significant effects in reducing sugars and pulp concentration and enzyme dosage (C*E) for drainability were treatment time and enzyme dosage (T*E).

The main effects of the three factors increased the reducing sugars production (kg/t) with the rise of enzyme addition, pulp concentration and treatment time (Fig. 1a). In the longest treatment (90 min), the reducing sugar production was more marked and higher at a 5.2 IU/g enzyme dosage (Fig. 1e).

Significant changes in fines content (%) were produced by enzyme dosage and treatment time. One can observe (Fig. 1b) that fines variation with the enzyme dosage is slightly higher.

The change in pulp drainability with enzyme dosage is more obvious than with pulp concentration (Fig. 1c). Figure 1f shows that the highest drainability was obtained at the highest levels of enzyme dosage and pulp concentration. Low enzyme dosages lead to higher drainability at 5% pulp concentration.

Figure 1d shows that all analyzed factors have a negative impact on the tear index. The most significant impact is due to the enzyme treatment time, while pulp concentration and enzyme dosage produce similar reductions of the tear index.

Effects of enzymatic and mechanical treatments

The treated pulps were refined in a PFI mill, to evaluate the enzymatic pretreatment effects on the development of the properties.

Figure 2 shows the evolution of drainability *vs.* tensile index. For the initial state, treatments with 10% pulp concentration and 5.2 IU/g enzyme dosage showed the greatest improvements in drainability, although only a slight decrease in bonding, as shown by the tensile index values. While, at the lowest enzyme dosage (2.6 IU/g), no noticeable differences were seen in drainability, small bonding increments were found, comparatively with the reference pulp.

In all cases, 5% pulp concentration increases in drainability and, sometimes, little improvements in bonding were verified.

Refining at 1000 PFI revolutions for all combined treatments (enzyme + refining) showed important improvements in the TI/CSF relation, comparatively with the reference pulp, especially for a drainability range between 300-350 mL CSF.

Table A
Physical properties of reference pulps

PFI Revol.	Energy consumption (kWh/t)	Drainability (mL CSF)	Apparent density (g/cm^3)	Tensile index (Nm/g)	Tear index (mNm^2/g)	Scatt. Coeff. (m^2/kg)	RCT (kN/m)
0	0	430	0.524	38.0	10.2	32.0	1.11
1000	214	290	0.562	47.2	8.5	26.9	1.31
2000	423	220	0.589	56.9	8.6	26.9	1.45

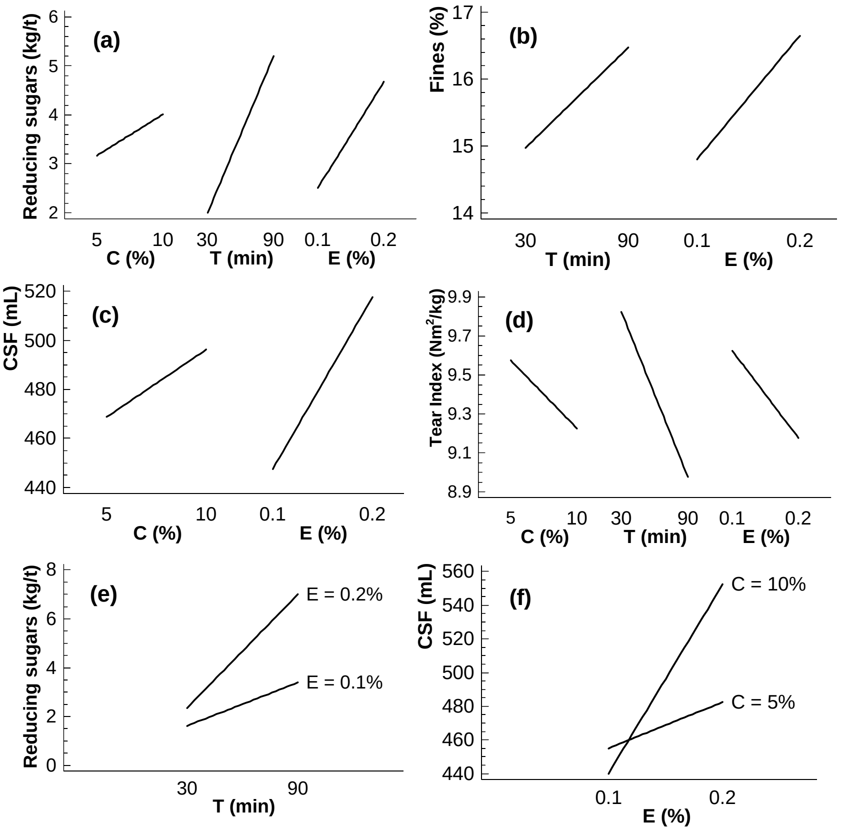

Figure 1: Significant effects on properties. Main effects: (a) Reducing sugars, (b) Fines, (c) Drainability and (d) Tear index. Interactions: (e) Reducing sugars and (f) Drainability

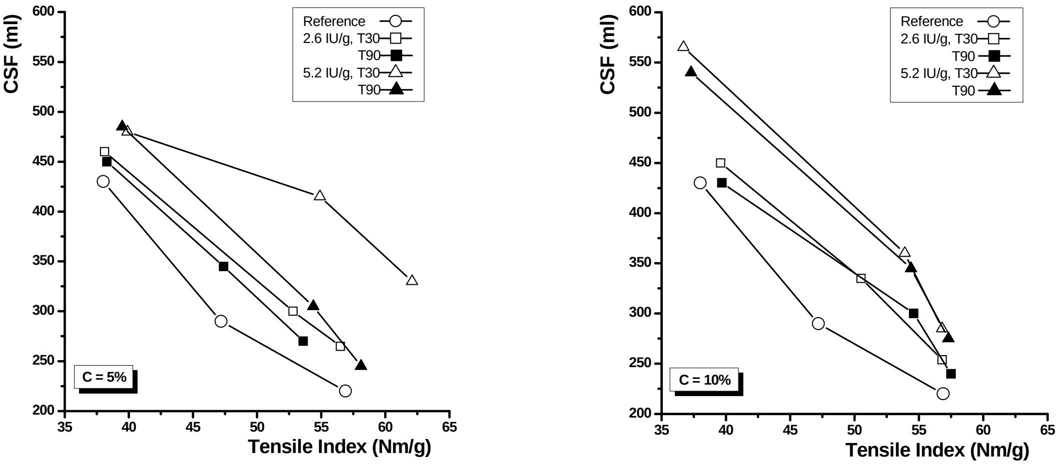

Figure 2: Drainability *vs*. Tensile Index. C: Pulp concentration

The best value in drainability and bonding was obtained under the following conditions: 5.2 IU/g of enzyme dosage, 30 min treatment time, 5% pulp concentration and refining at 2000 revolutions of the PFI mill. Only this pulp reached a tensile index of 62 Nm/g at the highest final drainability (330 mL CSF).

As shown in Figure 3, almost no differences in energy consumption were observed between the combined treatments at both levels of consistency.

In enzymatically treated pulps, without refining, slight increases in density were obtained under all applied conditions. At the same time, as shown in Figure 2, improvements in tensile index were obtained for both 5% pulp concentration, at the highest enzyme dosage (5.2 IU/g), and 10% pulp concentration, respectively, at the lowest enzyme dosage.

As refining advances (as energy consumption increases), density increases directly and proportionally, reaching higher values than in the reference pulp, except for the 5% pulp concentration treatment with 2.6 IU/g of enzyme dosage, 90 min and 1000 rev. of PFI refining, when density is slightly lower than that of the reference pulp subjected to the same mechanical treatment.

At 90 min and 10% pulp concentration, enzymatic treatment and similar refining energy consumption, a higher density value is achieved at the highest enzyme dosage (5.2 IU/g), followed by the lowest one (2.6 IU/g). Small differences in pulp density values were obtained for 30 min treatments.

Figure 4 shows the ring crush test values (RCT) *vs.* tensile index values. These variables have been compared for detecting the possible differences in the response to enzymatic treatments and subsequent refining in PFI mill, considering technical variables of industrial use, such as drainability and specific energy consumption.

In all cases involving no refining, the enzymatically treated pulps showed higher RCT values than the reference pulp, except for the enzymatic treatment at the lowest enzyme dosage and for the lowest treatment time for both consistency values (Fig 4). The higher values could be due to the increases in fiber flexibility and to the presence of fines with different surface characteristics, as reflected in the increments of the properties directly related to bonding, such as density and tensile index values.

As the mechanical treatment in PFI mill advances, increments in fiber bonding degree and RCT can be observed. Although these values are higher than those for the reference treatment, they do not show a clearly established order as to pulp concentration, dosage and treatment time.

Although an important influence of interfiber bonding on RCT is acknowledged,[9] the mentioned differences could be explained by a differential enzyme action on fibers under the applied conditions, and their subsequent response to the refining process. This could cause different mechanical failures in the interface between the S1/S2 fiber walls, when treated using compression load.[10]

Table B shows the percent variations in the initial state (without refining and enzymatic treatment) of drainability, tensile index and density, resulting from combined treatments *vs.* refining, only for the mechanical treatment levels applied.

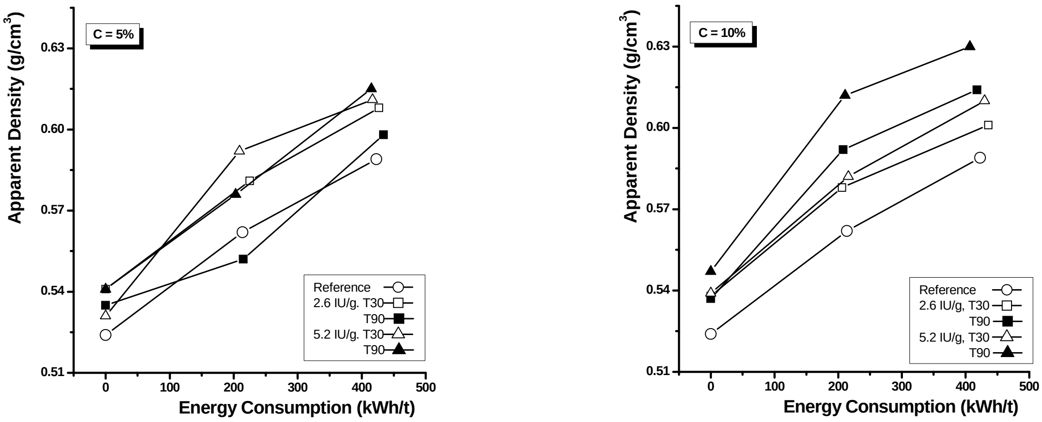

Figure 3: Apparent Density *vs.* Energy Consumption. C: Pulp concentration

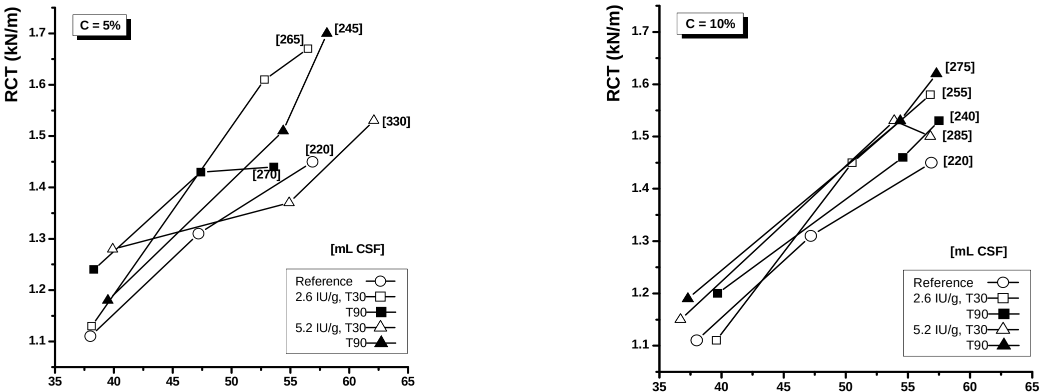

Figure 4: Ring Crush Test (RCT) *vs.* Tensile Index. C: Pulp concentration

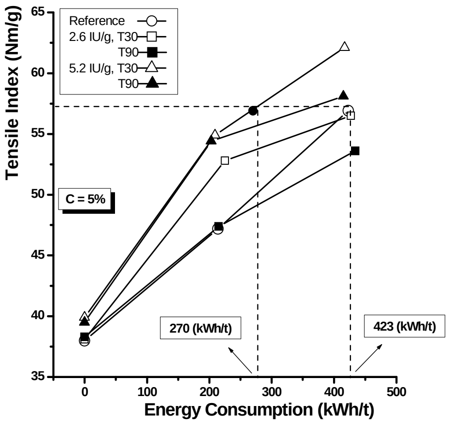

Figure 5: Tensile Index *vs*. Energy Consumption. C: Pulp concentration

Table B
Percentage variations *vs*. initial state of recycled pulp

	Variations (%)					
	Drainability (mL CSF)		Apparent density (g/cm^3)		Tensile index (Nm/g)	
PFI revolutions	1000	2000	1000	2000	1000	2000
Refining only	- 32.6	- 48.8	7.3	12.4	24.2	49.7
C_5, T_{30}, $E_{0.1}$	- 30.2	- 38.4	10.9	16.1	39.0	48.6
C_5, T_{30}, $E_{0.2}$	**- 3.5**	**- 23.3**	13.0	16.6	**44.5**	**63.4**
C_{10}, T_{90}, $E_{0.1}$	- 30.2	- 44.2	13.0	17.2	43.7	51.3
C_{10}, T_{90}, $E_{0.2}$	- 19.8	- 36.0	**16.8**	**20.3**	43.2	50.8

C: Pulp concentration; T: Time; E: Enzyme dose

As a conclusion, energy consumption was similar for the combined treatments, even if important variations were observed. A possible explanation might refer to the positive synergistic combination of content and quality of fines, fiber flexibilization and improvements of the surface condition for “bonding”, as mentioned by Mansfield *et al.*[11] for the enzymatic action on fibers.

At 2000 PFI mill revolutions, the density increases in the pulps treated with enzymes were higher than those subjected only to refining. The similarity in tensile index values would be only understood by the counterbalanced effects of the factors that affect the mentioned fiber bonding degree.

In the relationship between density and tensile index *versus* reference pulp, the positive synergistic effects, occurring at 5.2 IU/g, and the null or negative ones – appearing at 2.6 IU/g Pergalase enzyme dosage (Fig. 2), show that this enzyme has produced an important action on fibers, affecting paper properties, which could be only explained by a proper combination of variables which affect bonding.

As a general rule, combined treatments (enzyme + refining) show that it is possible to reach a higher tensile index level with significant drainability improvements and minor specific energy consumption, compared to the reference pulp. At the highest tensile index value (about 57 Nm/g) reached for the reference pulp, with the combined treatment of 5.2 IU/g enzyme dosage, 5% pulp concentration and 30 min time, a saving of around 36% in energy consumption could be obtained (Fig. 5), as well as important improvements (77%) in drainability (Fig. 2) at the same tensile index value.

The pulps treated with the Pergalase enzyme at 5% pulp concentration reached the highest RCT values (1.70 kN/m), under extreme conditions of enzyme dosage and time.

For the treatments performed at 10% pulp concentration, the differences in RCT are of about 12% for a TI value of 57 Nm/g, with very similar specific energy consumption, but with important drainability improvements, up to 25% for the pulp treated with a 5.2 IU/g enzyme dosage, for 90 min.

The results here presented show that, under certain conditions, TI improvements at higher drainability values were reached.

Previous studies gave similar results. Kim *et al.*[12] achieved freeness improvements and better dewatering ability of unbleached pulp fibers of hardwood, without any loss in the mechanical strength of the paper treated with cellulases and xylanases. Gil *et al.* [13] obtained drainability improvements of up to 80%, without affecting the strength properties, by applying commercial preparations of enzymes on bleached kraft pulp fibers, with the same mechanical treatment.

CONCLUSIONS

The enzymatic treatment with Pergalase A40 of a commercial pulp from recycled paper can be used as a drainage improvement agent, under all conditions applied in the present study, which is very important for papermaking mills using recycled fibers.

In most of the enzymatic treatment conditions studied, increases in apparent density and tensile strength with a reduction in tear strength were verified.

At equal tensile index, refining energy consumption was lower, as a consequence of the bonding increase obtained at a higher pulp density. The verified density increases seem to be one of the primary effects of the enzymatic treatment,[14] possibly attributable to an increased flexibility of the treated fiber. Wong and Mansfield[15] concluded that the enzymatic treatment increases fiber flexibility *via* mechanisms different from those associated with mechanical refining.

A 19% increase in the RCT values was obtained by improving the drainability of linerboard pulp from recycled fibers. Depending on the RCT and TI levels required, the most convenient enzymatic treatment condition could be selected.

Pulp concentration and its influence on implementation costs should be carefully considered, since the enzymatic treatments have been performed at a temperature of 45° C, which means that, at 5% pulp concentration, a higher amount of caloric energy is necessary (approximately 110% higher than at 10% pulp concentration).

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