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Vessel picking in *Eucalyptus globulus* bleached kraft pulp sheets: Effect of mechanical and enzymatic treatment

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ABSTRACT

Vessel picking is a phenomenon that hampers printing quality, consisting of white spots due to plucked vessel elements in the paper surface. This study aims to understand the mechanism behind vessel to fibre bonding and its relation to picking. *Eucalyptus globulus* bleached kraft pulp beating aided by enzymatic treatment was used to achieve that purpose. Beating by itself reduced vessel picking over 90 %. Concentrated vessels prepared at lab scale were mixed with refined fibres. When these vessels were subject to enzymatic treatments (xylanase and a cellulase plus laccase cocktail), a reduction up to 94 % was obtained. Bulk enzymatic treatments followed by beating on the original pulp decreased its vessel picking up to 96 %. Water contact angle and surface energy showed vessels to be more hydrophobic than fibres. Enzymatic treatments improved vessels hydrophilic character aiding its adhesion to fibres, leveraged by its higher flexibility and better retention with beating.

1. Introduction

Vessels are hardwoods main sap conducting mechanism (Foelkel, 2007). They are composed of hundreds of unitary aligned single cells, known as vessel elements, that have varying size and distribution between species. Eucalyptus vessels represent a significant part of the wood volume, its fraction representing between 10 and 30 %, equivalent to 3 to 5 % by weight (Dadswell and Wardrop, 1960; Ilvessalo-pfäffli, 1995). Morphologically vessel elements are shorter than fibres, its width varying from 60 μm up to 250 μm and its length from 150 μm up to 600 μm; its length/width ratio varies between 1:1 and 3:1 (Alén, 2000; Chen and Evans, 2005; Foelkel, 2007).

Vessel elements related problems, such as vessel picking and ink refusal, remain poorly understood. These phenomena cause difficulties in uncoated wood-free (UWF) papermaking and printing industries and are likely to continue causing problems. Paper properties like tensile, bond, and surface strength are influenced by the different pulp elements, with vessel elements having inferior bonding properties and thus a smaller contribution to paper strength (Marton and Agarwal, 1965; Fardim and Durán, 2002; Orblin et al., 2011).

The vessel picking problem is common in hardwood pulp-based papers and it manifests with surface white rectangular specks in the printed areas smaller than 1 mm in length (Sari et al., 2010). This phenomenon results from vessel elements detachment from the paper surface due to the ink tackiness in the printing machine (Ohsawa, 1988). The number of picked vessel elements is related to its content in the pulp, mainly the larger ones, and it gets worse when the bonding strength between vessel elements and fibres is weaker (Ohsawa, 1987). Some factors can directly influence the number of vessel elements picked in the printing process, such as their number, size, bonding strength in the paper surface and the number and bonding strength of the fibres covering vessel elements in the paper surface (Colley, 1975; Ohsawa, 1987). This problem will maintain for hundreds of impressions in offset printing, unless the process is stopped and the machine cleaned, or until the defect eventually fades away (Shallhorn and Heintze, 1997).

To reduce vessel picking problem in hardwood papers some steps can be done, namely reducing vessel elements content, and improving their bonding to the paper structure. In general, this reduction can be achieved by reducing its content in the stock, reducing its size, and increasing vessel to fibre bonding strength (Ohsawa, 1987). The primary step consists of selecting the proper hardwood raw material to control vessel picking (Ohsawa et al., 1982). The second step can be achieved by using industrial hydrocyclones or separation methods to remove the larger squared vessel elements (Mukoyoshi et al., 1986b; Ponpued,

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1987). Although the use of hydrocyclones is not 100 % effective, vessel fractionation can be achieved through a few extra steps or operations, e.g., flotation, sieving, screening with different screen meshes and fibre flocculation with subsequent vessel elements separation. Any of these solutions obtains a vessel rich fraction, none of which being 100 % effective methods (Ponpued, 1987; Ohtake et al., 1987and Ohtake and Okagawa, 1988; Heintze and Shallhorn, 1995; Panula-Ontto et al., 2007). The increase of bonding between vessel elements and fibres can eventually be achieved by pulp refining (Ohsawa et al., 1984 and 1986; Nanko et al., 1988), increasing the conformability of fibres (Mukoyoshi et al., 1986a), treating the pulp with carboxymethyl cellulose (Arndt, 2008; Blomstedt et al., 2008; Rakkolainen et al., 2009), using enzymes (Cooper III, 1998; Uchimoto et al., 1988; Bajpai, 1999; Köhnke, 2010) or adding a final fibre coat to cover the vessel elements in the paper surface (Nanko et al., 1987). Although fibre beating mitigates vessel picking problems by increasing vessel elements fibrillation and flexibility, it can have a negative effect by causing poor drainage. Besides these parameters, the papermaking machines properties and the type of ink used in the printing process also influences the vessel picking phenomenon.

There are already decades of information about the use of enzymes in the treatment of paper pulp, as for example, the patent filed by Uchimoto and associates, in 1988, where it is described the use of commercial cellulases to improve the flexibility of hardwood vessel elements, and the patent filed by Elwood W. Cooper III, in 1998, where chemical changes were found in hardwood vessel elements when they were treated with a mixture of cellulases and xylanases, making them more likely to break when subjected to normal beating conditions. Other works report the positive effect of enzymes in the pulp treatment, especially with the use of cellulases and xylanases (Jeffries, 1992; Bajpai, 1999), and pulp quality improvement (Žnidaršič-Plazl et al., 2009). In addition, studies have been made on vessel and fibre chemistry (Fardim and Durán, 2002; Vaz et al., 2023), but its relation with vessel picking is not fully evaluated. So, we focused on the study of different enzymatic treatments complemented by adequate pulp beating with the goal of vessel picking reduction. The purpose of these treatments was the increase of vessel to fibre adhesion. A new improved separation technique was implemented in order to obtain pulps with higher vessel elements content, to study its effect on vessel picking and to develop strategies for its reduction and control. To characterise the vessel picking phenomena, pulp samples enriched with vessels were prepared. The effect of beating and of enzymatic treatments were explored, separately and jointly. Pulp sheets were produced using standard procedure and the vessel picking and other pulp sheets properties were evaluated and analysed. IGT printability test was used to evaluate vessel picking count.

2. Materials and methods

2.1. Materials

Commercial *Eucalyptus globulus* bleached kraft pulp was used as raw material. Deionized water, diiodomethane (99 %, Sigma-Aldrich) and ethylene glycol (99.5 %, Merck) were used in the contact angle measurements. *IGT picktest ink 2*, with medium tack, was used to perform IGT tests.

2.2. Separation method

E. globulus commercial bleached kraft pulp (hereinafter referred as “raw pulp”) was treated to obtain vessel rich pulp. The pulp was initially disintegrated as described in Tappi T 205, prior to being submitted to a Bauer-McNett fractionation (Tappi T 233). This method consists of a series of tanks with screening devices to separate fibres in different fractions. Screens of #30 mesh (595 μm width), #50 mesh (297 μm width) and #200 mesh (74 μm width) were used. The objective of this first step was to discard the longer fibres fraction (retained in the #30 mesh screen) and remove the fines fraction passing the #200 mesh screen.

The remaining portions, retained in the #50 and #200 mesh screens, were collected and air-dried. Fibres collapse in this stage, facilitating the ensuing separation process. This pulp fraction is referred as “McNett pulp”.

After one day the air-dried fibres were resuspended in water and then disintegrated. That pulp suspension proceeded to the Laboratory Strainer. Some modifications were made on the Strainer to fit the separation requirements. A recirculation system containing a centrifugal pump and a water reservoir was added, and an additional screen of #140 mesh for effective separation (105 μm width/150 μm diagonal) was inserted in the Strainer. Vessel elements and medium fibres were retained in the Strainer, and smaller fibres passed through the screen and were collected in a #400 mesh screen.

The optimal working pulp consistency was between 0.5 %–1 %, and about 6 h were required to process 30 g of pulp.

A vessel rich pulp fraction was obtained at this stage, with approximately 10 % (*w*/w) of vessels content, referred as “vessel rich pulp”.

This vessel rich pulp could be further purified in a dynamic Britt Jar tester in case of need. Based on the vessel elements average size, evaluated by optical microscopy and also with Morfi Neo© analyser version 1.0.55, an appropriate screen was selected to be used in the Britt Jar to separate vessel elements. A #70 mesh equivalent screen (approximately 210 μm hole diameter; 60 M - Paper Research Materials Inc. measure) with conical holes and a constant flow rate of 0.41 L/min and stirring of 350 rpm was used, operating at a consistency of approximately 0.5 %. This low consistency allowed vessel elements to pass when its concentration in the bulk suspension was still considerable. Another important factor was the fibre concentration to be low enough to avoid flocculation and vessel elements dragging in sedimentation. This procedure provided a sample with a vessel content of about 50–70 % (*w*/w), referred from now on as “concentrated vessels”.

2.3. Enzymatic treatment

Two enzymatic preparations were used for the samples enzymatic treatment, Novozymes endo-1,4-xylanase NS51121 (xylanase activity of 8850 IU/mL) and the commercial enzymatic cocktail Celodase-083S containing cellulase and laccase activities (with sorbitol, cellulase, laccase and 1,2-benzisothiazol-3-one; cellulase activity of 100–1000 IU/mL, and laccase activity of 5–50 IU/mL). The treatment with xylanase was performed in a thermostatic bath at 45 °C with constant reciprocating agitation for 1 h. This treatment was performed at a consistency of 1 % with pH about 7 in a vial of 45 mL with glass beads to provide agitation. Regarding the treatment with the enzymatic cocktail the same bath was used but at 40 °C with constant reciprocating agitation for 1 h. For this enzymatic cocktail a higher pulp consistency was used, 4.5 %, and the treatment was also carried out with pH about 7, also in a vial of 45 mL with glass beads to provide agitation. The enzymatic loads used were 100 g of enzyme suspension per ton of pulp for the xylanase and 1 kg of enzyme cocktail per ton of pulp for the commercial cocktail. After the enzymatic treatment, the samples were washed thoroughly with distilled water.

2.4. Experimental plan

Fig. 1 summarizes the experimental procedure for the case where 2–3 % of “concentrated vessels”, with or without enzymatic treatment, were added to the McNett pulp previously beaten in the PFI (2000 revolutions).

Fig. 2 shows the corresponding experimental procedure for the “vessel rich pulp” (about 10 % *w*/w vessel elements content). In this case, the enzymatic treatment was applied on both fibres and vessels, i.e., the pulp resulting from the strainer separation. In this set of samples, we tried to simulate industrial conditions, performing tests with/without beating and with/without enzymatic treatment. The use of

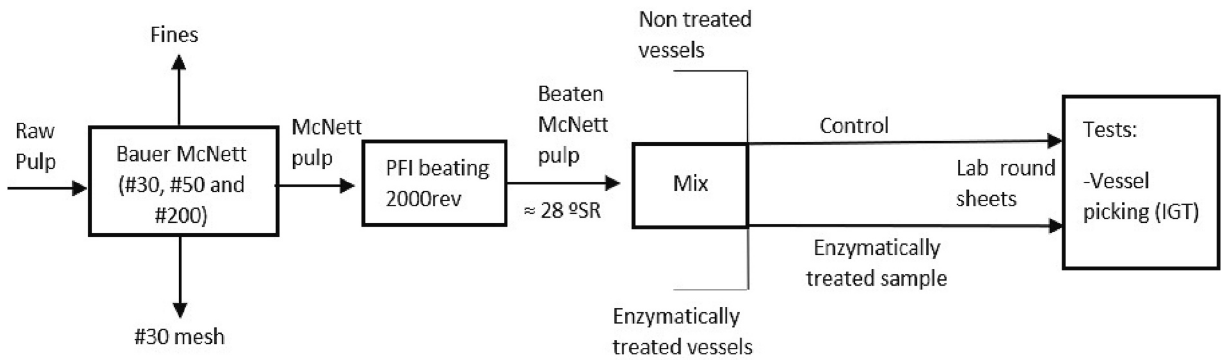

Fig. 1. Experimental design for McNett pulp with vessel addition.

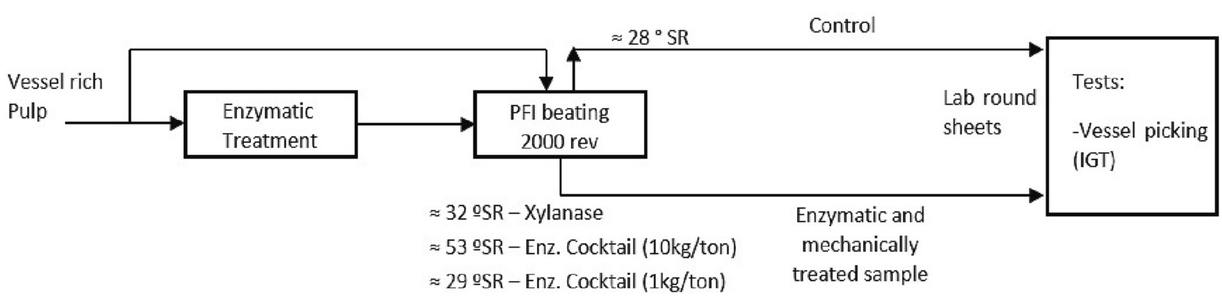

Fig. 2. Experimental design for “vessel rich pulp”

vessel rich pulp in this design allowed a lot of more pulp to be processed in the strainer, producing the necessary quantity to perform the tests.

2.5. *Pulp sheets preparation*

The pulp sheets were produced according to Tappi T 205 om-88, with a basis weight of 60 g/m^2, from the raw pulp, from “McNett pulp” with or without vessel addition and from the “vessel rich pulps”, with or without enzymatic treatment and with or without beating.

2.6. *Pulp beating*

After disintegration according the Tappi standard T 248, the pulps were beaten in a PFI mill, at 10 % consistency, under a specific edge load of 3.33 N/mm.

2.7. *Vessel picking characterisation (IGT testing systems)*

In modern multicolour offset printing processes, high printing speeds and high tackiness inks result in high stress on the paper surface. When the printing form is lifted from the paper surface, the ink exerts a force on the paper which increases with ink viscosity and tack and with increasing speed. In other words, vessels are pulled out from the paper structure when the ink tackiness force is higher than the vessel cohesion to the paper. When this force surpasses a critical value, which depends on the paper, the vessel is picked, and the paper surface is damaged.

In the present study, the IGT testing system was used to characterise the vessel picking; the system consists of an ink distribution system (IGT Reprotest B.V. Inking unit AE) and a printing apparatus (IGT Reprotest B.V. AIC2–5 printability tester). The printing tests were carried out with inks of medium viscosity, increasing printing speed and different final printing speed (0, 0.5, 2, 4 and 6 m/s). For each final printing speed, the printing apparatus start at zero and increases gradually. All assays were carried out accordingly and based on the standards (ISO3783:2006, IGT Site, Tappi 459 (Wax pick test) and Tappi UM 591).

To perform the analysis on the printed samples, an optical/digital method was implemented, although in some cases it was possible to distinguish the missing points/vessels with the naked eye. Fig. 3 shows an exemplification photo, taken with a magnifying glass, in which white spots are identifiable as defects in the inking. Under magnification (20×), it can be confirmed that some of these defects have a rectangular shape, suggesting they correspond to pulled out vessels and not to pulled out fibres. This is a typical example of what is observed in a case of vessel picking.

To quantify pulled out vessels in the IGT assays and thus quantify vessel picking, the samples were initially digitized (HP ENVY 4520), converted into high-definition images, treated and then analysed with ImageJ© software (Heintze, 2007). Afterwards they were digitized and converted into high-definition images, the obtained images were edited and binarized. “FOTOR” software was used to achieve that, a grey filter being applied for each image, the brilliance was reduced, and the contrast raised (Fig. 4). This process converts images to black and white, where each of the white spots corresponds to the picking (Fig. 4).

The resulting black and white images were then analysed with ImageJ© software to count the picking. After the file opening, the first step was to invert the colours of the sample image and minimize the noise without interference in the picks of vessel picking. This image treatment was made in the menu “Image”, then “Adjust” and “Threshold”. The resulting image was a white image with small black dots (Fig. 4). In the “Analyse Particles” menu the particle size (in pixels) and the shape factor could be defined. The program was set to exclude areas below 30 px^2 (corresponding to an area of 20,270 μm^2); the objects circularity was set to be between 0.4 and 0.9, eliminating fibre-like shapes with similar areas. After all parameters being defined and accepted, two windows were displayed: one with “Results” consisting of all the detected points and their respective information; and a second one named “Summary” with the results compilation. The picking degree was defined as the picking count per unit area (picks/dm^2).

2.8. *Zero span strength*

To investigate the possible effect of the enzymatic treatment on the

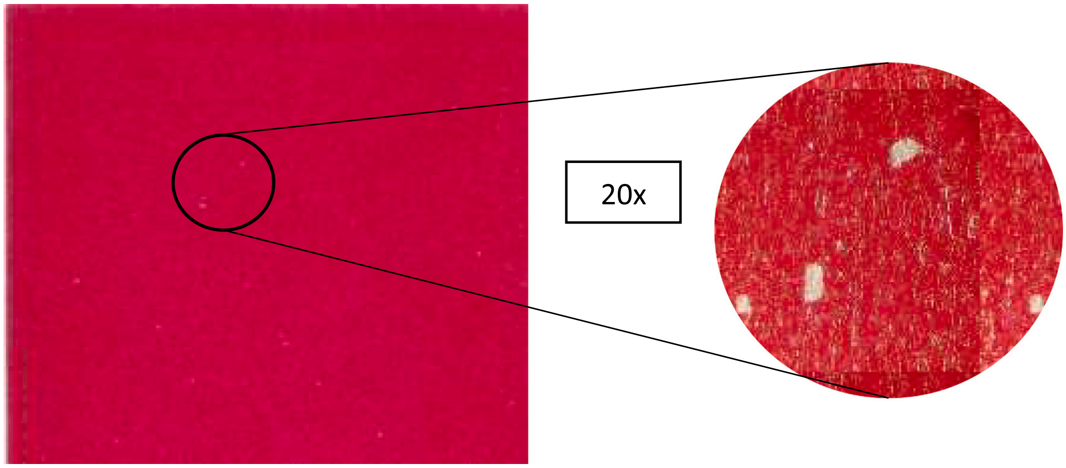

Fig. 3. Magnifying glass photo, with the aim of showing picks in one of the samples.

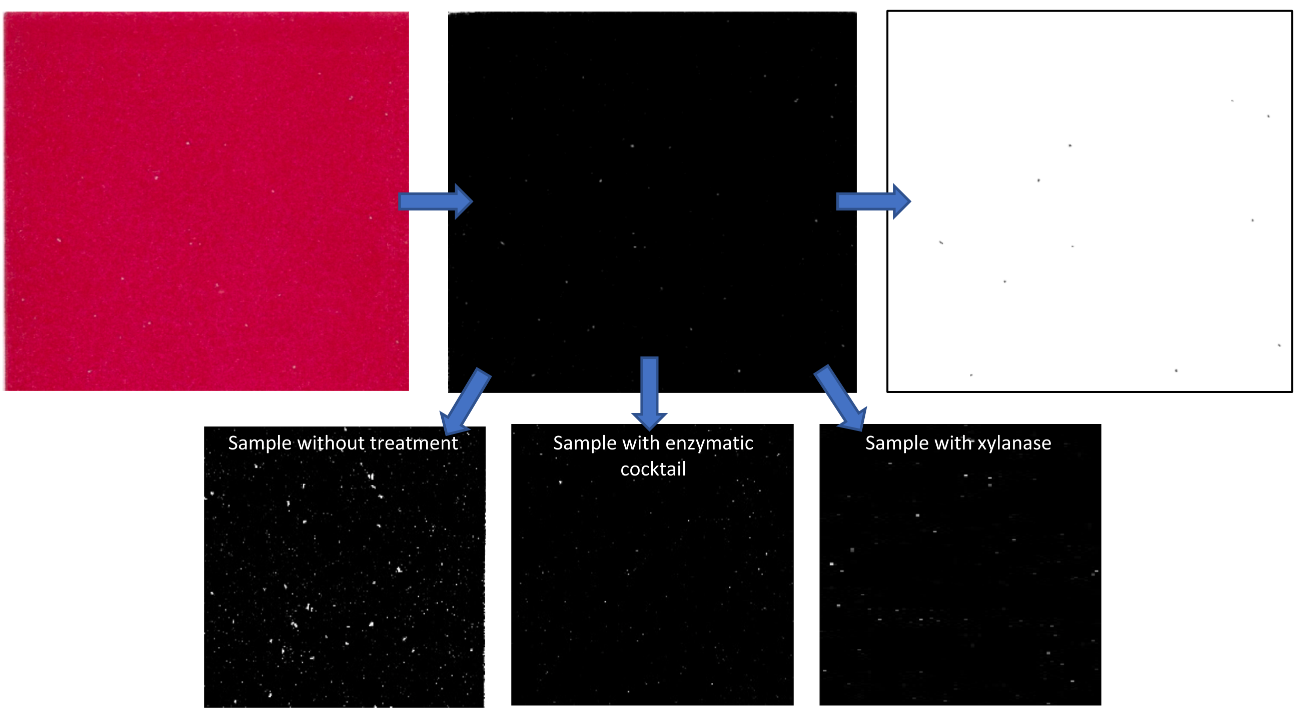

Fig. 4. Illustration of the imaging process of a sample and comparison of three real examples.

fibre intrinsic resistance, the tensile strength of the pulp sheets at "zero-span" in dry and wet state was evaluated, following the Tappi standard T231 cm-07 (Zero Span – breaking strength of pulp (dry zero-span tensile)) and Tappi standard T273 (Wet Zero-span tensile strength of pulp).

2.9. Tensile strength

Tensile tests were carried out using a standard testing machine Thwing-Albert Co (EJA series), according to ISO 1924-2:2008. The essays were performed with a constant rate of elongation of 20 mm/ min and a span length of 100 mm. Tensile indexes (Nm/g) and tensile energy absorptions (J/m^2) were obtained. A minimum of three essays were performed for each sample and arithmetic averages were calculated, as well as the standard deviations.

2.10. Internal cohesion

Scott-Bond tests were carried out to evaluate internal cohesion (J/m^2) evolution due to beating and enzymatic treatments, using a Scott internal bond tester Model-B (Precision Scientific, Petroleum Instruments) according to Tappi standard T-569 om-22.

2.11. Optical microscopy

Optical microscopy was performed using a NIKON Labophot-2 optical microscope, coupled with a computer with Leica Application Suite software to carry out measurements. This software assesses parameters such as areas, perimeters and distances.

2.12. Contact angle and surface free energy

Contact angle measurement is probably one of the most common methods for evaluating wettability and surface energy of a material. Contact angles measurements were performed in an OCAH 200 (DataPhysics Instruments, Filderstadt, Germany) apparatus. Samples surface energies can be evaluated by measuring the contact angles of three pure liquids (deionized water, diiodomethane and ethylene glycol). Contact angle is defined as the angle formed between the baseline, the liquid drop and the sample, measuring the tangent at the solid-liquid-vapor triple point. The surface tension reference values of the selected liquids were withdrawn from the equipment software library [Ström – H_2O ($V_{droplet}$ = 4 μL) and diiodomethane ($V_{droplet}$ = 2 μL); Erbil–Ethylene glycol ($V_{droplet}$ = 4 μL)] and the surface free energy values were calculated using the Owens-Wendt-Rabel-Kaelble (OWRK) method. Between six to eight measures were made for each liquid in each sample and the average was calculated.

This method follows Folkes model which assumes the free energy of a solid (γ_{sv}) and the surface tension of a liquid (γ_{lv}) to be the sum of independent components, associated with specific interactions, namely, γ_{sv}^{d}, γ_{sv}^{p}, γ_{sv}^{h}, γ_{sv}^{i}, γ_{sv}^{ab} and γ_{sv}^{o} where the exponents d, p, h, i, ab and o correspond, respectively, to the components of dispersion, polar, hydrogen bonds, induction, acid-base and other interactions. The Owens and Wendt model synthesizes the components into just two, the dispersive one that includes the dispersive forces and the polar one that includes all the rest.

According to the Owens-Wendt method, the relation between the liquid surface tension, the surface free energy of the solid and the contact angle between the liquid and the solid can be described in the following Eq. (1):

$$\gamma_{LV}\,(1+cos\theta) = 2\left[\left(\gamma^{D}{}_{SV}\gamma^{D}{}_{LV}\right)^{\frac{1}{2}} + \left(\gamma^{P}{}_{SV}\gamma^{P}{}_{LV}\right)^{\frac{1}{2}}\right] \tag{1}$$

The contact angle between the liquid and the solid is defined by θ. It is important to highlight that in this model certain principles are assumed, such as: liquids are pure, the material is smooth and its composition is homogeneous, and there are no reactions between the liquids and the material (Good and Van Oss, 1991; Luis et al., 2014; Owens and Wendt, 1969; Silva et al., 2016).

To minimize the material porosity and roughness, small pellets of known basis weight (≈150 g/m^2) were prepared from the different samples in a mechanical press, exerting a pressure of 527,5 N/mm^2 for 3 min.

3. Results and discussion

3.1. Preliminary results

To evaluate the potential of the IGT printing system to characterise the vessel picking phenomenon, pulp sheets were prepared from the raw pulp and from the corresponding pulp beaten at 2000 PFI revolutions. The results in Table 1 demonstrate the sensitivity of the implemented analytical system to characterise the vessel picking phenomenon. The unbeaten raw pulp, with Schopper-Riegler degree of 16, exhibited a very high picking count of 128 picks/dm^2, even at a very slow printing speed (final speed of 0.5 m/s). At 2 m/s the picking count was above perceivable values. After submitting the pulp to 2000 PFI revolutions, the picking count decreased to 22 picks/dm^2 with a final printing speed of 2 m/s (with a final printing speed of 0.5 m/s, no significant picking could be measured), while the picking count increased from 22 picks/dm^2 to 48 picks/dm^2 when the final printing speed was further increased from 2 m/s to 4 m/s, which also highlighted the key importance of the printing speed on the vessel picking phenomenon, as expected.

Table 1
Picking count values for raw pulp, beaten raw pulp, McNett pulp and beaten McNett pulp with different final printing speeds.

Sample	°SR	Final printing speed (m/s)	Pressure (N/m)	Picking count (picks/dm^2)	Picking reduction (%)
Raw pulp	16	0.5	125	128 ± 4	–
Raw pulp	16	2	125	>>>128	–
Raw pulp → PFI beating	30	2	125	22 ± 1	–
Raw pulp → PFI beating	30	4	125	48 ± 1	–
McNett pulp	14	2	125	109 ± 5	Control
McNett pulp → PFI beating	28	2	125	9 ± 1	91

3.2. Effect of beating on vessel picking

The effect of beating was investigated for two pulps, as seen in Table 1 for the raw pulp and the McNett pulp obtained after fines (<#200) and long fibres (>#30) removal in the Bauer McNett (one of the required steps in the vessel rich pulp production). Comparing both pulps (Table 2), the sheets apparent densities (Table 2) were respectively 0.47 g/cm^3 for the raw pulp and 0.40 g/cm^3 for the McNett pulp, respectively. The decrease in apparent density of the McNett pulps can be explained mainly by the loss of fines in the Bauer McNett (<#200) and some long fibres (>#30), which is also supported by the reduction of tensile index and tensile energy absorption (Table 2). While a huge amount of material was picked up for the raw pulp with a final printing speed of 2 m/s (not possible to quantify), for the McNett pulp, which is less dense than the raw one, the number of removed vessels were perfectly measurable (109 picks/dm^2), suggesting a better retention of vessels in the structure.

Due to the lower apparent density of the McNett pulp and the corresponding lower tensile strength and internal cohesion (Table 2), it would be expected higher vessel picking, but this is not the case. The removal of long fibres in the McNett pulp may hypothetically produce a fibre structure with more numerous but smaller pores, providing higher fibre/vessel contact area entrapping the vessels. This topic deserves further investigation.

Beating has an important effect on vessel picking as the results from Table 1 show for the two pulps. Although the values from the raw pulp and the beaten raw pulp can't be directly compared due to the different final printing speed, the decrease in picking count is drastic. As it was previously referred, the picking count roughly doubled with the duplication of the final printing speed (2 m/s up to 4 m/s), from 22 picks/dm^2 to 48 picks/dm^2; therefore, the picking number for the unbeaten raw pulp would be certainly higher than 200 picking count (to use a conservative estimative, for the same printing speeds). For the McNett pulp, the reduction of picking count was over 90 % for a PFI beating of 2000 revolutions (Table 1). The pulp sheets apparent density (Table 2) increased 57 % and 53 % with PFI beating, respectively, for the raw and the McNett pulp, indicating a significative increase in inter-fibre

Table 2
Raw pulp, beaten raw pulp, McNett pulp and beaten McNett pulp sheet density, internal cohesion and tensile strength.

Sample	Sheet density (g/cm^3)	Internal cohesion (J/m^2)	Tensile energy absorption (J/m^2) at maximum	Tensile index (Nm/g)
Raw pulp	0.47 ± 0.01	32 ± 11	2.4 ± 1.3	13.9 ± 2.2
Raw pulp + PFI (2000 rev)	0.74 ± 0.02	>1051	105.3 ± 29.9	85.9 ± 8
McNett pulp	0.40 ± 0.01	<21	0.8 ± 0.3	7.3 ± 1.1
McNett pulp + PFI (2000 rev)	0.61 ± 0.01	652 ± 49	65.1 ± 5.8	48.4 ± 1.7

bonding due to internal and external fibrillation, which was confirmed by the internal cohesion and tensile measurements. Comparing the raw and McNett pulps, the tensile tests also highlighted the contribution of fines and larger fibres to the paper structure consolidation. This increase may contribute to vessel elements retention inside the sheet structure (Hirn and Bauer, 2008), but the contribution of this effect on the surface is uncertain. Vessel elements were also exposed to the beating process and some additional flexibility and external fibrillation certainly occurred, which potentiated their adhesion to the structure. Vessel elements were also subject to breakage and dimensions reduction, as observed by microscopy, minimizing the effect of vessel picking in the printing process. The vessel elements smaller dimensions and aspect ratios promotes its retention in the structure, at the same time reducing the printing flaw area. The relative role of these two mechanisms, paper structure (including surface structure), and vessel morphological characteristics, requires further investigation.

In summary, from these first assays it can be stated that the major factor in vessel picking reduction is PFI beating. Either raw or McNett pulps had high pick counts that dropped drastically when the pulp was beaten. The same beating effect was also reported by other researchers, such as Sari et al. (2010), that managed to reduce the vessel picking tendency in a vessel rich pulp with beating, managing to decrease its value in the vessel rich pulp to the same or even lower level than the raw unbeaten pulp.

3.3. Effect of enzymatic treatment on vessel picking

To study the isolated effect of enzymatic treatments, “concentrated vessel” obtained from the vessel rich pulp was added to the “McNett pulp” previously beaten to 28°SR, according to the experimental plan expressed in Fig. 1. The same amount of “concentrated vessel” without and with enzymatic treatment was added to the pulp. The final vessel content of the pulp was about 3–5 %. The results of vessel picking assays of the different samples are expressed in Table 3.

Comparing the results from Tables 1 and 3, it is evident the effect of vessel addition on the McNett pulp; the picking count increase from 9 picks/dm^2 to 161 picks/dm^2. Although the samples have different vessel contents, these results clearly indicate that vessels without any kind of treatment (mechanical or enzymatic) are extremely susceptible to picking. However, when the same amount of vessel pre-treated with xylanase or the enzymatic cocktail was added to the same beaten pulp, the vessel picking was substantially reduced. The picking count decreased from 161 picks/dm^2 to 39 picks/dm^2 and 10 picks/dm^2, respectively with the xylanase (100 g/ton) and the enzymatic cocktail (10 kg/ton) treatments. As the apparent density of the pulp sheets remained practically unchanged (Table 4), all the effect can be attributed to the action of the enzymes on vessels, highlighting the positive role of the enzymatic treatment on the vessel adhesion/cohesion to the other stock elements (mainly fibres). Interestingly, the internal cohesion of the pulp structure decreases significantly (from 652 J/m^2, Table 2, to around 520 J/m^2, Table 4) with vessels addition, either enzymatically treated or not, despite the apparent density remaining practically unchanged, suggesting that the insertion of the vessels, with low potential of adhesion with the fibres, as the main responsible for this loss of internal cohesion. The other mechanical properties also decrease accordingly (Table 4 vs Table 2). Despite the internal cohesion and the other mechanical properties remaining low, vessel picking decreased between 76.1 % and 94 % with the enzymatic treatments (Table 3), suggesting that the conditions of the vessels are more important that the conditions of the fibrous structure.

Table 3
Picking count values for beaten McNett pulps with vessels addition, with and without enzymatic treatment.

Sample	°SR	Final printing speed (m/s)	Pressure (N/m)	Picking count (picks/dm^2)	Picking reduction (%)
(McNett pulp → PFI beating) + Vessels	28	2	125	161 ± 8	Control
(McNett pulp → PFI beating) + Xylanase treated vessels (100 g/ton)	28	2	125	39 ± 2	76
(McNett pulp → PFI beating) + Enzymatic cocktail treated vessels (10 kg/ton)	28	2	125	10 ± 1	94

Table 4
Beaten McNett pulps with vessels addition, with and without enzymatic treatment, sheet density, internal cohesion and tensile strength.

Sample	Sheet density (g/cm^3)	Internal cohesion (J/m^2)	Tensile energy absorption (J/m^2) at maximum	Tensile index (Nm/g)
(McNett pulp + PFI) + Vessels	0.63 ± 0.01	520 ± 24	46.5 ± 9.2	41.5 ± 1.1
(McNett pulp + PFI) + Vessels treat. w/ Xylanase (100 g/ton)	0.64 ± 0.02	500 ± 51	50.4 ± 9.6	42.1 ± 2.1
(McNett pulp + PFI) + Vessels treat. w/ Enzymatic cocktail (10 kg/ton)	0.62 ± 0.03	563 ± 47	50.6 ± 11.6	44.6 ± 2.3

Therefore, the positive effect of the enzymes can be attributed to chemical passivation, i.e., chemical surface modification enables better adhesion of vessels to the fibrous structure (Vaz et al., 2023), even though vessel elements morphological modifications may also play a role (Kibblewhite and Brookes, 1977). In the present case, however, Fig. 5 suggests that the enzymatic treatment by itself had little impact on vessels morphology. On the other hand, the water contact angles measurements (Table 5) on fibres and vessels pellets, with and without enzymatic treatment, provide the following data: fibres: 54.1°; vessels without enzyme: 63.7°; vessels with xylanase: 62.1°; vessels with enzymatic cocktail (1 kg/ton): 58.4°; vessels with enzymatic cocktail (10 kg/ton): 60.5°. The results clearly indicate that vessels are more hydrophobic than fibres, that agree with the surface chemical analysis realized by Vaz et al. (2023). The surface O/C ratio measured by XPS on fibres and vessels, gave 0.633 and 0.616, respectively, and this difference can be explained by the deposition of lignin and/or extractives on the vessel surface, and/or its higher initial extractives content. The XPS results also reveals that vessels also present a higher content of C1s % on the surface (Vaz et al., 2023; Gellerstedt, 2009). Regarding the effect of enzymes on the water contact angle, no significant change was observed, although a trend for lower contact angles was observed, approaching fibres behaviour.

The presence of residual enzyme in the vessel surface cannot be excluded (Vaz et al., 2023), which may affect the water contact angle. To test this hypothesis, an enzyme pellet was prepared for both enzymes to measure the water contact angles. The measured values were approximately 50° for xylanase and 75° for the enzymatic cocktail; therefore, we can speculate the real water contact angle with vessel treated with the enzymatic cocktail may be lower than measured.

These trends are supported by the results obtained in the measurements of the fibres and vessels surface free energies. Vessels dispersive/polar ratio show a tendency to approach the values of fibres with enzymatic treatment (Table 5).

The total surface free energy trend is similar, the enzymatically treated vessels values approaching those of fibres. In summary, it can be

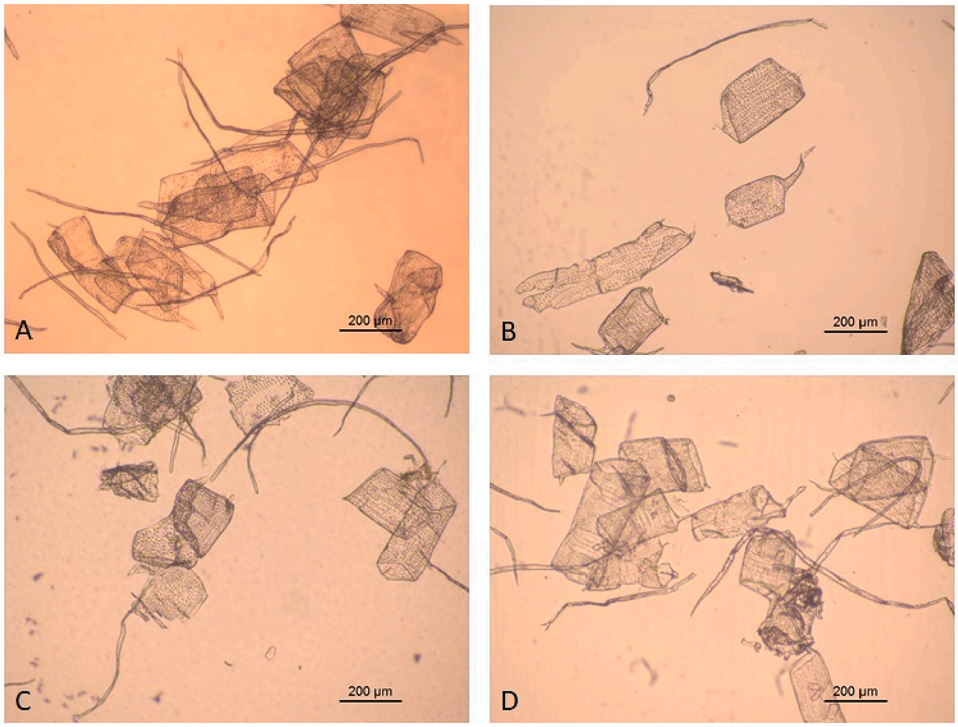

Fig. 5. Vessels with and without enzymatic treatment: A – Without enzyme; B – Enzymatic cocktail treated (1 kg/ton); C – Enzyme cocktail treated (10 kg/ton); D – Xylanase treated (100 g/ton).

Table 5
Water contact angle, total energy and dispersive/polar components ratio comparison for the fibres and for the treated and non-treated vessels.

Sample	Water contact angle (°)	Total energy	Dispersive/polar components ratio
Fibres	54,1	45,8 ± 1,6	7,2
Vessels	63,7	41,7 ± 0,8	18,3
Enzymatic cocktail treated vessels (1 kg/ton)	58,4	45,9 ± 1,5	6,0
Xylanase treated vessels (100 g/ton)	62,1	48,4 ± 0,8	11,3

said that some chemical or structural change has occurred in vessels due to the enzymatic treatment, although vessel picking reduction could be leveraged with beating.

At industrial scale it is not viable to separate vessels from the mainstream to submit them to the enzymatic treatment. For this reason, we applied the enzymes directly on the pulp to study its effect. In this phase of the investigation, a vessel rich pulp (Laboratory Strainer) was prepared, and the enzymes were applied directly on this pulp. This procedure enables the preparation of a significant amount of pulp with acceptable man-power effort and with a vessels content about 10 %, whereas the corresponding value for pulp after fines removal in the Bauer McNett is about 1–2 % The picking count values for this vessel rich pulp are expressed in Table 6, with and without enzymatic treatments, with no beating.

The picking count for this modified pulp was much higher (257 picks/dm^2, at final printing speed of 0.5 m/s) than the corresponding pulp from Bauer McNett (109 picks/dm^2, at final printing speed of 2 m/s). The pulp sheets densities were 0.39 and 0.40 g/cm^3, respectively (Tables 7 and 2).

As we can see in Table 6, the vessel rich pulp without beating exhibited a very high level of vessel picking even after enzymatic treatment. The first line contains the results for vessel rich pulp without beating as such, while the second line contains the results for the same pulp after xylanase treatment of 100 g/ton and the third after the

Table 6
Picking count values for vessel rich pulp with and without enzymatic treatments (without beating).

Sample	°SR	Final printing speed (m/s)	Pressure (N/m)	Picking count (picks/dm^2)	Picking reduction (%)
Vessel rich pulp	11	0.5	125	257 ± 6	Control
Vessel rich pulp → Xylanase treatment (100 g/ton)	11	0.5	125	160 ± 11	37
Vessel rich pulp → Enzymatic cocktail treatment (1 kg/ton)	11	0.5	125	120 ± 13	53

Table 7
Vessel rich pulp and vessel rich pulp with enzymatic treatments, sheet density and internal cohesion.

Sample	Sheet density (g/cm^3)	Internal cohesion (J/m^2)	Tensile energy absorption (J/m^2) at maximum	Tensile index (Nm/g)
Vessel rich pulp	0.39 ± 0.01	41 ± 25	0.84 ± 0.10	7.6 ± 0.4
Vessel rich pulp + Xylanase (100 g/ton)	0.38 ± 0.01	<21	1.01 ± 0.03	7.7 ± 0.2
Vessel rich pulp + Enzymatic cocktail (1 kg/ton)	0.39 ± 0.01	33 ± 11	1.28 ± 0.60	8.7 ± 1.9

enzymatic cocktail treatment of 1 kg/ton.

The vessel picking was reduced about 37 % and 53 % after xylanase and enzymatic cocktail treatment, but the vessel picking remained very high, even at a final printing speed of 0.5 m/s. Although the pulp sheet density of these fibrous structures (Table 7, unbeaten pulp) were not comparable with those of Table 4 (beaten pulp), the effects of the enzymes seem to be more effective when applied directly on vessels (Tables 3 and 4) regarding its application on the pulp as a whole (Tables 6 and 7), which is an expected result considering the specific enzymes charges in both cases.

Regarding the effect of the enzymatic treatments on the mechanical properties, the observed changes are not significant.

In summary, from the last two groups of assays (enzymes applied only on vessel and enzymes applied on the vessel rich pulp), it can be concluded that both pulps had a high number of vessels, so the incorporation of vessels in the McNett pulp and the vessel rich pulp was successful. Regarding picking count, just altering enzymatic treatments, it can be said that the enzymatic treatment was effective. In the first case, where the vessels and the treated vessels were added to the beaten McNett pulp, vessel picking reduction was around 76 % for xylanase and 94 % for the enzymatic cocktail. In second case, where enzymes were applied on the vessel rich pulp without beating, a reduction of picking count was observed of around 37 % for xylanase and 53 % for the enzymatic cocktail. For the vessel rich pulp, the assays had to be done with low final printing speed due to lack of beating and so a paper with low cohesiveness (Table 7) was obtained.

3.4. *Effect of enzymatic and mechanical treatment on vessel picking*

To approach a more realistic situation, using the vessel rich pulp (laboratory strainer) with around 10 % of vessels, simulating an increase in the vessel content of a paper mill pulp stream, assays with mechanical and enzymatic treatments were carried out, with both enzymes, according to the experimental plan delineated in Fig. 2. The very positive effect of beating was once again confirmed, and the IGT tests carried out with the final speed of 2 m/s did not show any picking. Tests were then carried out with higher final speeds of 4 m/s and 6 m/s.

3.4.1. *Printing speed 4 m/s*

The assays with mechanical and enzymatic treatment all revealed the same tendencies. As expected, the major part of vessel picking reduction occurs due to pulp beating, nonetheless the enzymatic treatment effect is also noticed. However, with the final printing speed of 4 m/s (Table 8), the additional effect of enzymes was not properly revealed and assays with higher final printing speed were also made to enhance the observed effects (next section).

The effect of beating and enzymes treatment on sheet density, internal cohesion and tensile strength were also evaluated (Table 9). There is a drastic increase in mechanical properties with beating, as expected, but a significant decrease regarding only beating, when the beating was carried after enzymatic treatment, particularly for assays with much higher enzymatic charge (10 kg of cocktail/ton). Comparing enzymatically treated vessel rich pulp (Table 7) with enzymatically treated vessel rich pulp followed by beating (Table 9), the huge effect of beating is revealed.

3.4.2. *Printing speed 6 m/s*

For the assays made with the final printing speed of 6 m/s (Table 10), the positive effect of enzymes was notoriously revealed. With xylanase treatment the picking degree reduced around 42 % and for the enzymatic cocktail it reduced around 62 %, despite the decrease of tensile resistance of the paper structure (Table 9).

Comparing these results with those from the same pulp solely subjected to enzymatic treatment (Table 6), we can conclude that beating enhances the effectiveness of the enzymatic treatment, going from, in the case of xylanase, 160 picks/dm^2 at a final speed of 0.5 m/s to 15 picks/dm^2 at a final speed of 6 m/s, and for the enzymatic cocktail, 120 picks/dm^2 at a final speed of 0.5 m/s to 10 picks/dm^2 at a final speed of 6 m/s. Previous studies on the effect of enzymes were made by Uchimoto and associates (1988), where enzymatic treatment with commercial cellulases and beating provided a decrease in vessel picking around 85 %, and also by Elwood *W. cooper* III (1998) in a filed patent, in which a mixture of cellulase and xylanase was used in order to make the vessels susceptible to breakage under normal mill refining. The small increase of

Table 8
Picking count values, with final printing speed of 4 m/s, for beaten vessel rich pulp and beaten vessel rich pulp with and without enzymatic pre-treatments.

Sample	°SR	Final printing speed (m/s)	Pressure (N/m)	Picking count (picks/dm^2)	Picking reduction (%)
Vessel rich pulp → PFI beating (1000 rev)	15	4	125	81 ± 4	Control
Vessel rich pulp → PFI beating (2000 rev)	28	4	125	4 ± 1	95 / Control
(Vessel rich pulp + Xylanase treatment (100 g/ton)) → PFI beating (2000 rev)	32	4	125	3 ± 1	25
(Vessel rich pulp + Enzymatic cocktail treatment (1 kg/ton)) → PFI beating (2000 rev)	29	4	125	3 ± 1	25
(Vessel rich pulp + Enzymatic cocktail treatment (10 kg/ton)) → PFI beating (2000 rev)	53	4	125	1 ± 1	75

Table 9
Sheet density, internal cohesion and tensile strength of vessel rich pulp, vessel rich pulp with beating and vessel rich pulp with beating and with enzymatic treatment.

Sample	Sheet density (g/cm^3)	Internal cohesion (J/m^2)	Tensile Energy Absorption (J/m^2) at maximum	Tensile Index (Nm/g)
Vessel rich pulp	0.39 ± 0.01	41 ± 25	0.84 ± 0.10	7.6 ± 0.4
Vessel rich pulp → PFI beating (1000 rev)	0.56 ± 0.01	252 ± 34	34.89 ± 2.10	53.9 ± 1.3
Vessel rich pulp → PFI beating (2000 rev)	0.69 ± 0.04	>1050	131.88 ± 3.80	86.7 ± 1.7
(Vessel rich pulp + Xylanase treatment (100 g/ton)) → PFI beating (2000 rev)	0.72 ± 0.01	>1050	118.70 ± 5.29	85.5 ± 0.3
(Vessel rich pulp + Enzymatic cocktail treatment (1 kg/ton)) → PFI beating (2000 rev)	0.66 ± 0.05	>1050	78.00 ± 25.05	66.2 ± 5.9
(Vessel rich pulp + Enzymatic cocktail treatment (10 kg/ton)) → PFI beating (2000 rev)	0.81 ± 0.01	>1050	7.04 ± 4.62	40.6 ± 12.1

Table 10
Picking count values, with final printing speed of 6 m/s, for beaten vessel rich pulp and beaten vessel rich pulp with and without enzymatic treatments.

Sample	°SR	Final printing speed (m/s)	Pressure (N/m)	Picking count (picks/ dm^2)	Picking reduction (%)
Vessel rich pulp → PFI beating (1000 rev)	15	6	125	99 ± 5	Control
Vessel rich pulp → PFI beating (2000 rev)	28	6	125	26 ± 3	74 / Control
(Vessel rich pulp + Xylanase treatment (100 g/ton)) → PFI beating (2000 rev)	32	6	125	15 ± 2	42
(Vessel rich pulp + Enzymatic cocktail treatment (1 kg/ton)) → PFI beating (2000 rev)	29	6	125	10 ± 1	62

the sheet density of the beaten vessel rich pulp after xylanase pre-treatment, regarding the corresponding beaten pulp, also suggests some level of vessel degradation.

4. Conclusions

Different pulps were prepared to study the issue of vessel picking in bleached Kraft *Eucalyptus globulus* printing papers: raw pulp; McNett pulp without and with addition of vessels obtained with the Britt Jar separation method; vessel rich pulp obtained with the strainer separation method. These pulps were submitted to beating and part of them, namely those with vessels addition and the vessel rich pulp, were also submitted to enzymatic treatments (xylanase and an enzymatic cocktail containing cellulase and laccase activities).

The major portion of the vessel picking reduction is due to pulp beating, with a reduction of at least 90 % in the studied pulp samples with different levels of vessel content.

Pulp samples reinforced with “concentrated vessels”, previously subjected to enzymatic treatment, show picking reduction of 76 % for the xylanase and 94 % for the enzymatic cocktail, regarding the corresponding assay with the “concentrated vessels” without enzymatic treatment. When the enzymes were applied on the whole pulp (“vessel rich pulp”), the picking reduction decreased to 37 % and 53 %, respectively for xylanase and the enzymatic cocktail.

Vessels morphological characteristics seem have no relevant changes with the enzymatic treatment in the absence of beating, while picking tests, water contact angle and surface free energy assays show significative changes. These results confirm the importance of vessel bulk and surface chemistry alterations due to the enzymatic treatments (Vaz et al., 2023).

The effect of beating after enzymatic treatment of the “vessel rich pulp” was also investigated. A reduction of 42 % and 65 % in vessel picking was observed, respectively for the xylanase and the enzymatic cocktail, regarding the same sample submitted solely to beating. The combined effect of beating after enzymatic treatment revealed a picking count reduction of 94 % for the xylanase and 96 % for the enzymatic cocktail.

In summary, a major part of the vessel picking problem can be controlled by pulp beating, although it is not a fully efficient solution. Enzymatic pre-treatments enhances the beating effect and therefore revealed to be efficient in terms of vessel picking reduction. Anyhow, attention must be given to some concomitant decrease of tensile properties. From the industry's point of view, when occasionally subject to vessel picking problems, the enzyme treatments should be considered prior to beating and is a good solution to mitigate the problem.

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CRediT authorship contribution statement

João Coelho: Conceptualization, Methodology, Software, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Vera Costa:** Methodology, Software, Formal analysis, Investigation, Data curation. **António Mendes de Sousa:** Resources, Project administration. **Paula Pinto:** Resources, Funding acquisition. **Ana Ramos:** Methodology, Validation. **Rogério Simões:** Conceptualization, Methodology, Validation, Formal analysis, Writing – review & editing, Supervision. **Álvaro Vaz:** Conceptualization, Methodology, Validation, Formal analysis, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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