Research article

E. Globulus Vessel and Fibre Chemical Analysis

Álvaro Vaz[1]*, João Coelho[1], Vera Costa[1], Ana Marques[2], Thaddeus Maloney[3], Phiri Josphat[3], Paula Pinto[4], Ricardo Oliveira[4], Rogério Simões[1], and António M. Sousa[2]

[1]FibEnTech, Chemistry Department, University of Beira Interior, R. Marquês de Ávila e Bolama, 6201-001 Covilhã, Portugal.
[2]Department of Chemical Engineering, IST, University of Lisbon, Av. Rovisco Pais, 1, 1049-001 Lisboa, Portugal.
[3]Department of Bioproducts and Biosystems, Aalto University, P.O. Box 11000 (Otakaari 1B), FI-00076 Aalto, Finland.
[4]RAIZ – Forest and Paper Research Institute, Quinta de S. Francisco, 3800-783 Eixo, Aveiro, Portugal.

Abstract.
Hardwood species have a complex cellular structure consisting of fibres, vessel elements and parenchyma cells with different chemical compositions. However, the presence of vessels with significant dimensions in their structure is a recurrent problem in the operation of industrial UWF paper printing. Since the 1980s, vessel picking and ink refusal are problems that paper professionals have tried to solve, but solutions for these have not yet been fully found. If vessels are concentrated in a stream, they can be pre-treated (e.g., by mechanical refining) and reincorporated into the pulp. Other strategies aim at vessel enzymatic and/or chemical passivation and sheet surface chemical treatment, altering the vessel adhesion to the fibre network. This requires vessel concentration at laboratorial level for proper chemical studies, such as FE-SEM, μ-XPS, TOF-SIMS and μFTIR. The main objective of our experimental study was to examine bleached kraft pulp *E. globulus* vessel and fibre composition. For this we performed EDX and μ-FTIR analysis on both fibre and vessel elements, and obtained the carbohydrate composition, the total acids content, the hexenuronic acids content and the zeta potential.

Keywords: *E. globulus*, vessel, EDX, μ-FTIR, sugar content, zeta potential

Corresponding Author: Álvaro Vaz; email: avaz@ubi.pt

Published 10 August 2022

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the FibEnTech21 Conference Committee.

1. Introduction

Vessels represent an important percentage of the volume of eucalyptus wood, 10 to 30%, corresponding to 3 to 5% weight [1]. Vessel elements are weakly bonded to fibres and fines in the paper structure, particularly on its surface. Morphologically, their length can vary between 200 and 600 μm, their width can be greater than 500 μm and the width/length ratio can be between 1:1 and 1:3 [2, 3]. Vessels specific characteristics and their behaviour in the uncoated wood free (UWF) paper production process remains poorly understood [4]. Some of the main problems associated with vessel elements

arise when UWF papers are subjected to offset printing, such as vessel picking and ink refusal. The vessel picking phenomenon manifests itself as some of the of hardwoods vessel elements detachment from the paper surface due to their weak bonding and to the printing ink high viscosity [5]. The ink refusal phenomenon is characterized by white spots in the printing areas; in this case, the vessel is present on the paper surface, but the ink did not adhere to it due to its low surface energy [6]. Preventing problems related to vessel picking and ink refusal during papermaking can be achieved through various operations, namely with pulp suspension refining, paper surface sizing, vessel elements fractionation and vessel surface passivation [7]. Any of the proposed options entails production costs and must be weighed against the obtained benefits. Pulp stock refining has been investigated with the intention of minimizing vessel related problems, but with the negative effect of over refining the pulp for printing papers [8]. In addition to the costs inherent to this operation, the reduction in drainage and the loss of porosity, specific volume, opacity, and dimensional stability are also documented. Pulp refining promotes vessel fragmentation and increases the fibre-vessel cohesion resulting in a greater adhesion to the paper surface and a reduction of vessel picking. Starch sizing is another operation that has been investigated to reduce problems associated with vessels. It is proven that a greater amount of starch on the paper surface promotes vessels adhesion, however with a loss in opacity, in addition to obtaining a paper with greater rigidity. The use of modified starches in the paper surface sizing as well as treatment with carboxymethyl cellulose showed positive results in the vessel picking problems [9]. However, it should be noted that vessels detachment from the paper surface in the sizing operation is also a frequent problem in terms of contamination of the sizing bath. The use of strength agents can have a positive effect in preventing vessel picking, nonetheless, high dosages are required to have a significant impact. The fractionation of the vessels can be carried out using hydrocyclones, flotation followed by sieving, sieving with different sized meshes or flocculation of fibres with subsequent separation of the vessels. Any of these solutions allows fractions rich in vessels to be obtained, nevertheless they are not 100% effective [10,8,11,12]. However, Orblin *et al*. [4] propose a new method using a Britt Jar with greater efficiency in separating vessels. Fractions rich in vessels can be previously subjected to physical (refining) or chemical (passivation) treatments and be later added to the furnish. Adequate refining of the vessels and their reincorporation into the stock seems to be an interesting alternative to approach the problem while avoiding losing a substantial amount of material. Likewise, the chemical modification of the vessels surface, namely their ionic charge and hydrophobicity, is

one of the most attractive and promising alternatives that has not been yet extensively investigated.

2. Material and methods

2.1. Fibres and vessels quantification and morphological characterization

The methodology for the primary fibre and vessel content quantification was based on the use of the Morfi Analyzer - version LB-01 (2002), a prototype implemented by Techpap. The system consists of a measuring cell (connected to a PC), a hydraulic system (pump, tank, solenoid valves) and an electrical system. The measuring cell analyses the suspension at two consistencies: 30 mg / L and 300 mg / L. The optical resolution is 10 µm, but the working resolution reaches 4 µm thanks to specific grey image analysis treatments.

Optical microscopy was also used to estimate vessels length, width, and aspect-ratio, to compare with the values provided by Morfi. A Micros microscope was used, coupled with a MicroVisible 4.0 image capture and data treatment software.

2.2. Separation methodology and optimization

Primary dimension separation was carried out using a Bauer-McNett equipment, fitted with U.S. mesh # 30, # 50 and # 200 screens. The #30 screen retained long vessels, while #200 screen let fines pass.

Laboratory prototypes were developed to apply the Jacquelin method, in which the effect of continuous rotation promotes the consolidation of flakes and the maintenance of suspended vessels. According to Soszynski [13] and the 1972 Jacquelin's patent [14], the estimated value for the peripheral rotation speed would be 30 m/min for hardwoods. Two systems were used to cause this rotational acceleration: a rotary evaporator and a stirring rotor. The rotary evaporator allowed a closer approximation to the scheme idealized by Jacquelin, but only with about one tenth of the required peripheral speed, compensated with a prolonged period of rotating action (about 24 hours). The stirring rotor allowed speed values closer to those suggested in the literature but moving away from the proposed system.

A Britt Dynamic Drainage Jar was also set up according to the method generically described by Orblin *et al.* [15], adapted with a recirculation system. A two-step system

was developed, initially for vessels accumulation within the jar and afterwards for vessels extraction.

2.3. Analytical methods

Microscopy observations were performed UBI Optics Center using a Hitachi S-2700 scanning electron microscope (SEM) operated at 20 kV. Images were formed through secondary electrons. All of the samples were previously gold sputtered by cathodic spraying (Quorum Q150R ES). Elemental analysis of the samples was performed using Energy-dispersive X-ray spectroscopy (EDX) using the same SEM equipmentto estimate silica, carbon and oxygen contents. The most relevant result is the O/C ratio, which may indicate the presence of different functional groups.

Fibre and vessel analysis of *E. globulus* were performed using a Perkin-Elmer μ-FTIR from the Chemical Engineering Department of Instituto Superior Técnico.

The samples neutral carbohydrate composition was determined by ionic chromatography after quantitative saccharification upon acid hydrolysis according to an adaptation of the Tappi T222 om-88 proceeding guidelines for the determination acid-insoluble lignin in wood and pulp. The samples total acidic groups content was determined through a conductimetric titration method, adapted from the standard SCAN-CM 65:02. Hexenuronic acid groups content was determined using a colorimetric method proposed by Chai *et al*. [16]. The Zeta potential of fibre rich and vessel rich aqueous suspensions was measured using a Mütek SZP-06 System Zeta Potential at a 0.2 % consistency. KCl was added to the suspensions to increase the conductivity of the samples.

3. Results and discussion

Fibre and vessel quantification results for *E. globulus* bleached kraft pulp using Morfi Analyser are compiled in Table 1, namely fibres number per gram, vessels number per gram and fibre/vessel ratio, and in Table 2 vessels and fines area percentage. Fibre and vessel microscopic study is shown in Table 3, specifically length (L), width (D), and aspect ratio (L/D). These data are fundamental for any separation process design.

Table 1: *E. globulus* fibre and vessel quantification (Morfi Analyser).

Fibre number (10^6fibers/g)	30.3 ± 0.2
Vessel number (10^6vessels/g)	0.147 ± 0.06
Fibre-Vessel ratio	206.1 ± 9.6

Table 2: *E. globulus* vessel and fines area (Morfi Analyser).

Vessels (%)	0.32 ± 0.01
Fines (%)	6.6 ± 0.8

Table 3: Fibre and vessel morphology by optical microscopy.

	L (µm)	D (µm)	L/D
Fibres	1072 ± 137	15,9 ± 2,6	67 ± 20
Vessels	300 ± 32	154 ± 18	1,95 ± 0,44

Attending to the global purpose of our work a proper vessels and fibres chemical composition analysis is fundamental. So, a proportion of 206 fibres per vessel requires a vessel concentration process. The use of a three stage Bauer-McNett was fundamental for fines and parenchyma removal but was not enough to attain the required vessel concentration. Just a 3% increase in vessel content was attained at this stage. The Jacquelin method was essayed, but it was not the most viable process for a scale-up of vessels removal. As described earlier, a Britt Jar was used to achieve a size exclusion separation in two steps; the first phase retained the vessels and allowed fibres to pass through; the second phase with wider screen holes let vessels pass through and retained long fibres. The results of the first phase may be observed in Fig. 1-a), while in the second phase it was possible to accumulate a practically pure vessel fraction.

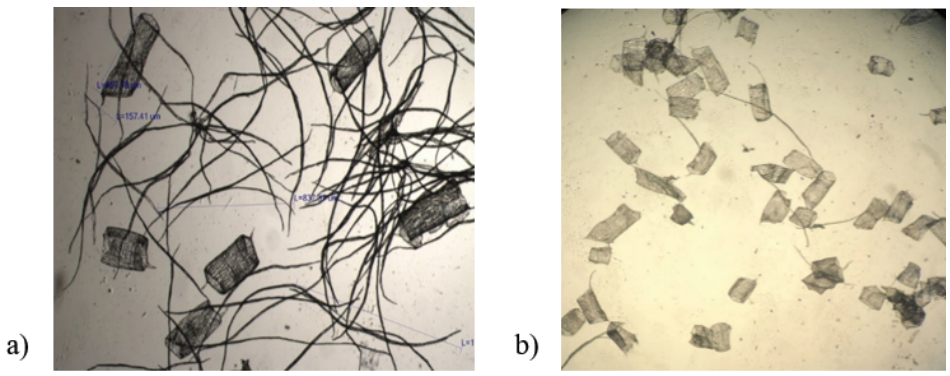

Figure 1: Vessel separation: a) 1st phase enrichment; b) 2nd phase enrichment.

SEM imaging was performed on the surface of a sheet produced from the vessel rich fraction. Fig. 2 depicts two noticeable vessels amongst the fibres The EDX results are presented in Table 4, where the most relevant result is the higher O/C ratio for *E. globulus* fibres (0.9) comparatively to vessels (0.7), suggesting higher lignin and extractives content for the latter.

Fig. 3 shows the µ-FTIR spectra obtained for E. globulus fibres and vessels. The spectra obtained from vessels and fibres are quite similar, but there is mainly a noticeable

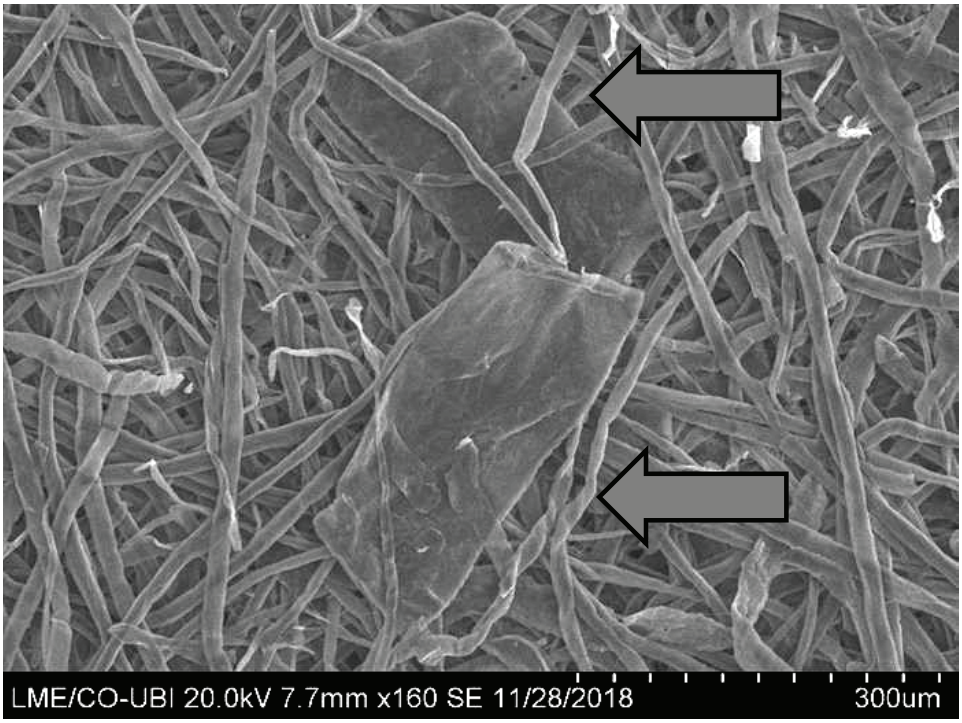

Figure 2: SEM image of a vessel rich sheet surface (the arrows indicate vessels).

Table 4: EDX *E. globulus* elemental composition.

Elemental Composition (%)	Fibre	Vessel
C	48.2	54.6
O	43.4	37.9
O/C Ratio	0.90	0.70

Table 5: Chemical Analysis and Zeta Potential

	XMG (%) *	Hexenuronic Acid (µmol/g)	Total Acids (µmol/g)	Zeta Potential (mV)
Fibres	18.8	7	133	-20.8
Vessels	25.4	12	149	-9.8

* XMG: Xylose, Mannose and Galactose content.

difference in the peaks relative to the CH bonds and to the COC ether group. Vessel spectra have a slightly higher peak at ca. 900 cm^{-1} (CH stretch and COC stretch), 1105 cm^{-1} (COC strain) and 1160 cm^{-1} (aromatic C-H strain in plane, asymmetric C-C stretch). The presence of higher hydrocarbon concentration may be related to the higher vessel hydrophobicity [4]. These results seem to be coherent with the data obtained with EDX.

Table 5 compiles the values for the hemicellulose content (percentage of Xylose, Mannose and Galactose, referred as XMG), hexenuronic and total acids contents (µmol/g) and the pulp suspension Zeta potential (mV). Zeta potential values suggest that fibres are more anionic than vessels. XMG content in vessels is 35% higher than in fibres, thus having a higher hemicellulose percentage. Concerning the total acids content, this

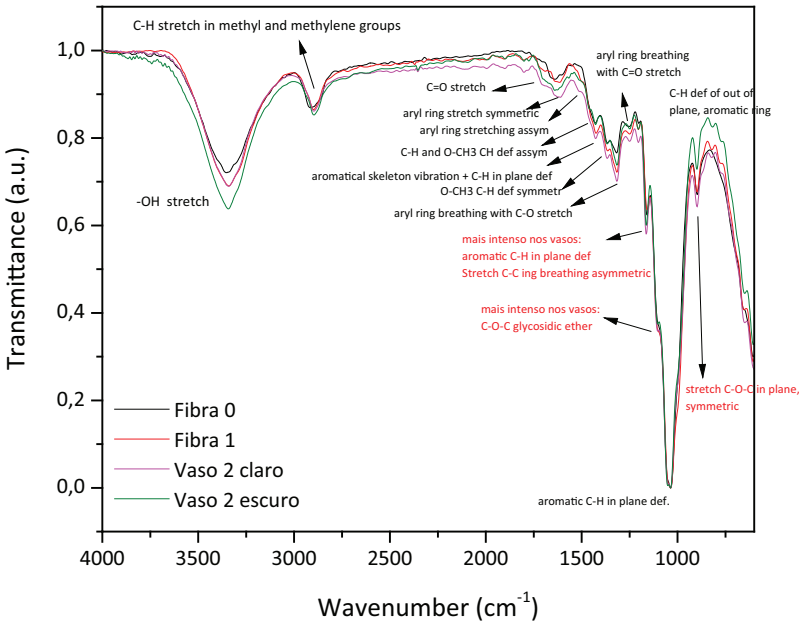

Figure 3: *E. globulus* vessel and fibre spectra obtained by μ-FTIR.

value is also higher in vessels (12%), difference even more evident for the hexenuronic acid content (71%). Considering the higher hexenuronic and total acids content in the vessels it would be expected a higher zeta potential for the vessel, however, this is not the case, and the issue is currently under investigation.

4. Conclusions

The main results compiled in this paper are:

1. **Separation methods:** Size exclusion methodology in two steps, preceded by fines removal with Bauer-McNett has proven to be an effective method for obtaining a vessel rich fraction.

2. **EDX:** Lower O/C ratio observed in vessels suggests a higher lignin and extractives content.

3. **μ-FTIR:** The spectra obtained from the vessels and fibres are in general similar, but there is a noticeable difference in the peaks relative to the CH bonds and to the COC ether group. The possible presence of higher hydrocarbon concentration may be related to the higher hydrophobicity shown by vessels.

4. **Chemical Analysis:** Vessels have a higher hemicellulose content and a higher total and hexenuronic acids content, nevertheless being less anionic than fibres in the zeta potential measurement, which requires further investigation.

This work was carried out under the Project inpactus – innovative products and technologies from eucalyptus, Project N.º 21874 funded by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of COMPETE 2020 nº246/AXIS II/2017.

References

[1] Dadswell H, Wardrop A. Some aspects of wood anatomy in relation to pulping quality and to tree breeding. Appita. 1960;13(5):161-173.

[2] Alén R. Papermaking science and technology. Stenius P, Pakarinen H, editors. Helsinki: FapetOy; 2000.

[3] Chen F, Evans R. A robust approach for vessel identification and quantification in eucalypt pulps woods. Appita. 2005;58(6):442-447.

[4] Orblin E, Lindström N, Fardim P. Probing the chemical and surface chemical modification of vessel cell walls during bleaching of eucalyptus pulp. Holzforschung. 2012;66(8):945-950.

[5] Ohsawa J. Vessel picking in printing papers. Paper presented at: Tropical Wood Pulp Symposium; 1988 Jun 21-23; Singapore.

[6] Jopson N. Coping with hardwood vessels. Pulp & Paper International. 2005;47(11):36-37.

[7] Chen C, Liu H-B. The causes and solutions of the vessel picking. China Pulp and Paper. 2013;32(12):66-69.

[8] Heintze H, Shallhorn P. Hardwood vessel picking and manufacturing process. Pulp and Paper Canada. 1995;96(11):28-30.

[9] Rakkolainen M, Kontturi E, Isogai A, Enomae T, Blomstedt M, Vuorinen T. Carboxymethyl cellulose treatment as a method to inhibit vessel picking tendency in printing of eucalyptus pulp sheets. Industrial & Engineering Chemistry Research. 2009;48(4):1887–1892.

[10] Hardell H, Leary G, Stoll M, Westermark U. Variations in lignin structure in defined morphological parts of spruce. Svensk Papperstidning. 1980;83(2):44-49.

[11] Panula-Ontto S, Fuhrmann A, Kariniemi M, Särkilahti A. Evaluation of vessel picking tendency in printing. Paper presented at ICEP International Colloquium on Eucalyptus Pulp; 2007 Mar 4-7; Belo Horizonte, Brazil.

[12] Backfolk K, Henricson K, Kajanto I, Karjalainen M, Niinimäki J, Rousu P. Wheat straw pulp fractionation part 1. The effect of cells, vessels, and fines on paper properties. Cellulose Chemistry and Technology. 2013;47(5):443-453.

[13] Soszynski R. The formation and properties of coherent flocs in fibre suspension [Ph.D. thesis]. University of British Columbia, Vancouver, Canada; 1987.

[14] Jacquelin G. Methods of treating suspensions of fibres to form fibrous aggregates. United States patent. US 3, 679, 542. 1972 July 25.

[15] Orblin E, Eta V, Fardim P. Surface chemistry of vessel elements by FE-SEM, μ-XPS and ToF-SIMS. Holzforschung. 2011;65:681-688.

[16] Chai XS, Zhu JY, Li J. Simple and rapid method to determine hexeneuronic acid groups in chemical pulps. Paper presented at: 10^{th} International Symposium on Wood and Pulping Chemistry; 1999 June 7-10; Yokohama, Japan.