Pulp and Paper from Sugarcane: Properties of Rind and Core Fractions

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ABSTRACT Two distinct lignocellulosic fractions (rind and core) can be obtained through a physical separation of sugarcane stalks. Although presenting differences in morphology, both fractions can be employed to produce pulps and papers. The pulps and paper sheets produced from the core and rind fractions were characterized by their chemical composition, physical properties and mechanical properties. The pulps obtained from the core presented a higher amount of fines, lower drainage ability and rendered denser and stiffer sheets. The pulps from the rind, which have a higher content of fibers and higher degree of polymerization, produced sheets with higher air permeability and water absorption. Both paper sheets presented mechanical and physical properties comparable to commercial papers and papers from different cellulosic sources. The different properties exhibited by the papers produced from each fraction allow their use for distinct purposes, and expands the opportunities in the context of sugarcane biorefinery.

KEYWORDS Sugarcane, core and rind fractions, papermaking, pulp and paper

1 INTRODUCTION

Recently, a new concept of using renewable resources in industry has emerged: the biorefinery. In this concept, the renewable resources are fractionated into their different macro components that are then used for making a large range of products [1]. The large availability of lignocellulosic materials makes them a key renewable resource when considering the biorefinery concept [2]. In this context, the main commodity derived from lignocellulosic resources is cellulosic pulp [1], which is used mainly for paper production [3]. In Brazil, about 85% of the cellulosic pulp produced comes from hardwood sources, mainly *Eucalyptus* [4].

The largest agricultural lignocellulosic by-product in Brazil is sugarcane bagasse. The 2015/2016 sugarcane harvest processed over 650 million tons [5], generating about 165 million tons of bagasse with 50% moisture [6]. Many studies have already been developed on the production of paper from annual cellulosic sources [7, 8], including sugarcane bagasse [9–11]. Although Brazil has only a few industrial bagasse paper factories, around 30 countries produce paper from depithed sugarcane bagasse, corresponding to a market of over $10 billion. Currently, 2 to 5% of the global production of pulp and paper products uses sugarcane bagasse as a lignocellulosic source [12].

Morphologically, sugarcane is composed of four different kinds of cells: fiber cells (~50%), parenchymal cells (~30%), vessel cells (~15%) and epidermal cells (~5%) [13]. When compared, these cells have very different characteristics. While fiber and vessel elements are ~1.1 mm long, parenchymal cells are ~0.3 mm long [14]. Fiber cells have a much lower diameter (~20 μm) when compared to vessel cells (~80 μm) and parenchymal cells (~60 μm) [14]. Therefore, sugarcane papers with different contents of these kinds of cells may produce papers with specific mechanical characteristics.

Studies of sugarcane paper production and its industrial production use depithed sugarcane bagasse, since the pith fraction (small particles, smaller than 0.4 mm, mainly parenchymal cells and damaged cells) [9, 12]

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promotes lower water drainage in the paper machine [12, 15, 16]. In this sense, there are not many studies documenting the physical and mechanical characterization of paper sheets produced from fractions with higher contents of pith cells. The original vegetal, fiber, parenchymal and vessel cells are arranged in a very specific way; the parenchymal cells are less abundant and closer to the epidermis compared to fiber cells that are more abundant and closer to the epidermis [17, 18]. Thus, the current milling process of sugarcane disrupts the natural cell array, and the resulting bagasse corresponds to a mix of pith and fiber cells. In this context, the separation of the fiber-rich fraction preceding the milling of the sugarcane would allow the obtainment of two fractions: the integral rind, mostly constituted of fiber cells, and the crushed core bagasse, enriched in parenchymal cells. One example of such a process is the "Tilby Cane Separation System" [19]. In this system, sugarcane billets are split lengthwise, followed by their scraping, resulting in two separate materials, the rind (19%) and the crushed core (79%) [19–21].

In the context of a biorefinery of sugarcane, the separation into core and rind allows their separate use without losing the sugarcane juice, the main product of the current sugarcane mill. The present study reports the production and characterization of pulps and papers from the rind and core of sugarcane.

2 EXPERIMENTAL

2.1 Materials

Sugarcane stems were harvested manually from the sugarcane plantation of the Iacanga ethanol and sugar mill, located in the city of Iacanga in the state of São Paulo, from the 2013 harvest.

The reagents n-hexane, sodium hydroxide, anthraquinone, sodium chlorite, glacial acetic acid, methanol and copper(II) ethylenediamine solution were purchased from Sigma-Aldrich.

2.2 Preparation of the Sugarcane Fractions

Initially, the leaves and tips of the plants were removed. The stems were then cut into disks of approximately 1 cm thick. From the disks, the rind was separated from the core using cylindrical stainless steel punches of varied diameters. The average diameter of the stems was 30 mm, from which 1 mm thick rinds were separated, resulting in core disks with an average diameter of 28 mm.

Sugarcane juice was extracted from the core fraction using a hydraulic press equipped with a stainless steel piston and perforated cup. To remove any residual free sugars, the core bagasse was extracted with water in a Soxhlet apparatus. Finally, this bagasse was oven dried at 50 °C with air circulation, until moisture of approximately 10% by mass.

The rind fraction underwent a Soxhlet extraction with n-hexane to remove waxes present in the cuticle of sugarcane stalks. Then, the rind fraction was extracted in Soxhlet apparatus with water in order to remove residual sugars. Finally, the extracted rind fraction was oven dried with air circulation at 50 °C to moisture of 10% by mass.

2.3 Pulping and Bleaching Processes

From the rind and crushed core fractions, bleached pulps were produced. The lignocellulosic materials underwent an anthraquinone-catalyzed soda alkaline pulping process, followed by a sodium chlorite bleaching process.

For the pulping process, a solution of 20.6 $g.L^{-1}$ of NaOH and 0.15 $g.L^{-1}$ of anthraquinone were used for a solid liquid ratio of 10% by mass of lignocellulosic biomass. The pulping reactions were carried out in a 7L Parr reactor at 160 °C for 120 min with a heating ramp of approximately 2.5 $°C.min^{-1}$. After the reaction time, the reactor was quenched in cold water to cease the reactions. The pulps were disintegrated for 3 min with the black liquor, then filtered and washed with water until neutrality.

After the pulping process, the materials were still light brown, indicating the presence of some residual lignin. In this manner, a bleaching process was applied. The bleaching processes were carried out in a glass reactor heated by a water bath at 70 °C and under constant stirring. The bleaching was performed in three 60 minute steps: the first with 7.2 g of sodium chlorite, 2 mL of acetic acid and 640 ml of distilled water for 20 g of unbleached cellulose; in the second and third steps, 0.75 g of sodium chlorite and 0.25 mL of acetic acid were added to the previous suspension. After the bleaching process, the pulps were filtered and washed thoroughly with cold water and at the end with a small amount of methanol to remove residual bleaching reagents and thereby recover the bleached pulps.

2.4 Paper Production

The paper handsheets were produced using an automatic sheet-making machine by the standard method. Each sheet was prepared using about 2 g of bleached pulp (dry basis), resulting in a circular sheet of approximately 20 cm in diameter. The cellulosic pulp samples were suspended in distilled water using a stirrer in order to go through the sheet forming process. The sheets of paper were made in triplicate for each pulp.

2.5 Pulp and Paper Characterization

The characterization of the bleached pulps consisted of determining their chemical composition, degree of polymerization, cell morphology, drainability and crystallinity. For the paper sheets, some physical properties were determined: their basis weight, thickness and specific volume. Additionally, some mechanical properties were determined: burst, tensile and fiber tensile strengths (zero-span tensile strength). Finally, water absorption, air permeability and microscopy images of the handsheets were obtained. All measurements were made with the felt side of the paper sheets facing up. All assays were performed at least 5 times; however, in some cases the assay was repeated up to 10 times.

The chemical composition of the pulps was determined through a process of cold solubilization of the fraction of hemicelluloses in alkaline medium, based on the ASTM Standard D1103 method. In this process, a sample of 2 g dry lignin-free pulp was mixed with 10 mL of a 17.5% in mass NaOH solution in a glass reactor under constant stirring. Every 5 minutes, another 5 mL of the same NaOH solution was added until a total solution of 35 mL. After 30 min the solution was diluted to 7.5% and allowed to stir for 1 h. The resulting solid was recovered by vacuum filtration on a sintered plate funnel. After washing with an 8.3% NaOH solution and distilled water, the solid was washed using a 10% acetic acid solution in order to neutralize any residual hydroxide. Finally, the solid was washed with water to neutrality and dried in an oven at 105 °C for 24 h.

The degree of polymerization was determined using a viscometric method based on the standard test TAPPI T230 om-04. In this method, an aliquot of the cellulosic pulp is solubilized in a copper(II) ethylenediamine solution and its viscosity measured in a capillary viscometer at 25.0 °C [22]. The measurements were performed with 25 mL of a 1 $g.L^{-1}$ solution of cellulosic pulp. The analyses were made at least in triplicate.

Cell dimensions were determined using an automated fiber analyzer (MorFI – Fiber & Shive Analyzer). The drainage ability was determined by obtaining the Schopper-Riegler degree (°SR) using the standard method SCAN-C19:65.

Crystallinity index of the pulps was evaluated through X-ray diffraction. The diffractograms were recorded using a PW 1720 (Philips) X-ray generator operated at 45 kV and 40 mA with radiation at wavelength of 0.154 nm and 2θ ranging from 6 to 56°. The analyzed samples were previously powdered using an agate mortar and pestle. Crystalline Index (C_I) was determined using the method of Segal *et al.* [23]. For that, the following equation was used, where I_{200} corresponds to the overall intensity of the peak at 22.5° I_{am} and the contribution of the baseline around 18.0° [24]:

$$C_I = \frac{I_{200} - I_{am}}{I_{200}} \times 100$$

Paper analyses were conducted with specific equipment, according to the following standard methods: TAPPI T220 sp-01 (grammage and specific volume); TAPPI T411 om-05 (thickness); TAPPI T403 om-02 (burst strength); TAPPI T494 om-01 (tensile strength); TAPPI T231 cm-96 (tensile strength of the fiber); TAPPI T441 om-04 (water absorption); and AFNOR NFQ 03-075 (air permeability).

The environmental scanning electron microscopy (ESEM) images of paper were obtained using a Quanta 200 (FEI) microscope with a magnitude of 800×, high voltage of 10.0 kV and working distance of 9.4 mm. Images of both sides and cross-sectional images of the paper samples were obtained.

3 RESULTS AND DISCUSSION

Table 1 shows the results of the characterization of the bleached pulps of sugarcane rind and crushed sugarcane core.

In other studies it was observed that both the fiber and pith fractions of sugarcane bagasse had similar contents of the main macromolecular constituents [12, 14], therefore it can be assumed that the two original lignocellulosic fractions (rind and core) have the same chemical composition. Novo *et al.* [25] determined that the chemical composition of sugarcane bagasse is about 50% cellulose, 25% hemicelluloses

Table 1 Characterization of the bleached pulps and fibers of sugarcane rind and crushed sugarcane core.

	Sugarcane rind pulp	**Crushed sugarcane core pulp**
Cellulose (% in mass)	79.0 ± 0.7	77.2 ± 3.0
Hemicelluloses (% in mass)	21.0 ± 0.7	22.8 ± 3.0
°SR	14.5 ± 1.5	43.0 ± 4.0
Average length (μm)	661	552
Average width (μm)	31.9	32.7
Fine elements (% in surface)	7.12	16.24
Polymerization degree	2524 ± 16	1372 ± 20
Crystallinity index (%)	64.06	67.49
Diffraction pattern	Cellulose Iβ	Cellulose Iβ

and 22.5% lignin. In this sense, the exclusive removal of lignin would produce a material with about 67% of cellulose and 33% of hemicelluloses. Comparing these values with those obtained and considering the conservation of the cellulose fraction, it is verified that about 40 to 50% of the hemicelluloses fraction was removed in the pulping and bleaching processes.

Although both materials underwent the same treatment, the core fraction presented a higher °SR value, similar to pulps with some refinement. It indicates that this pulp promotes a greater hindrance of water passage or higher water absorption. This can be explained by the greater amount of fine particles in this fraction in relation to the rind fraction, as observed in Table 1. These fine particles promote both the clogging of the canvas and the formation of more compact cellulose film, making the °SR higher.

Comparing the average cell dimensions of the cellulosic pulps with the original cell dimensions, a large discrepancy is observed. For both the rind and core fraction, lengths 40 to 45% smaller are observed when compared to fiber cells and double the value when compared to parenchymal cells. Likewise, it is observed that the average widths are divergent from the original cells in both cases. Three factors explain these findings: (i) the fiber analyzer calculates only a mean of values, thus for both fractions the average is shown for fiber, parenchymal and vessel cells in different ratios; (ii) the automatic fiber analyzer has a size limit on which it counts the particle in the average, therefore fines don't contribute to the average; (iii) the pressing process promotes the collapse of the cells and in some cases their rupture. Figure 1 shows the size distributions for cells counted in the average for both materials.

Although the behavior of both materials seems very similar, some differences can be observed. For both the width and the length, it is observed that the cells with smaller sizes have higher counts for the core fraction. In addition, for both dimensions, the inversion of higher cell counts from the core to the rind fraction occurs in the third range of sizes. When comparing the total cell counts of the three first size ranges ("small" cells) between the two fractions it is observed that the core fraction has 1.5% more cells with lower width and 8.5% more cells with lower length.

The higher amount of fines and smaller cells determined from these measurements corroborate with the predominance of parenchymal cells in the core fraction and of fiber cells in the rind fraction.

Figure 2 shows the diffractograms for the core and rind pulp samples. The diffraction pattern observed in Figure 2 corresponds to the cellulose I pattern, as shown in the peak assignment and its corresponding reflection planes in this figure [26–28]. With the data of the diffractograms of Figure 2, it was possible to calculate the crystallinity of the pulps shown in Table 1. The pulps have about 65% of cellulose crystallinity, similar to that obtained for other vegetal biomass cellulose sources [29]. Teixeira *et al.* [30] produced a cellulosic material from sugarcane bagasse through a $NaOH/H_2O_2$ bleaching process and calculated a crystallinity index of 76.0%. Agarwal *et al.* [31] showed that the presence of hemicelluloses can lower the crystallinity index values. Therefore, since different chemical treatments were used to produce the pulps, the difference in the crystallinity index values can be understood.

The values of degree of polymerization are shown in Table 1. Wang *et al.* [32, 33] obtained polymerization degrees in the range of 1500 to 2700 for bagasse pulps produced under several conditions. The chemical and physical processing of the materials can change cellulose's degree of polymerization [22], thus, since both pulps underwent the same treatments it is possible to compare them. It is observed that the degree of polymerization of the cellulose from the rind fraction is approximately double that

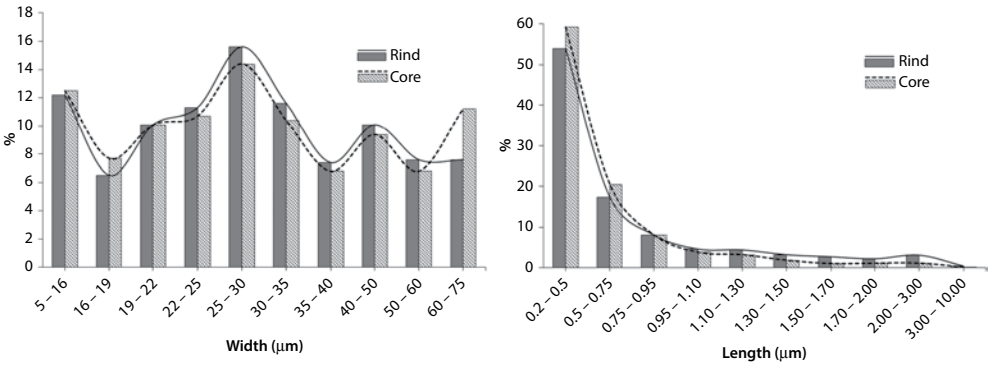

Figure 1 Width and length size distribution for rind and core pulps.

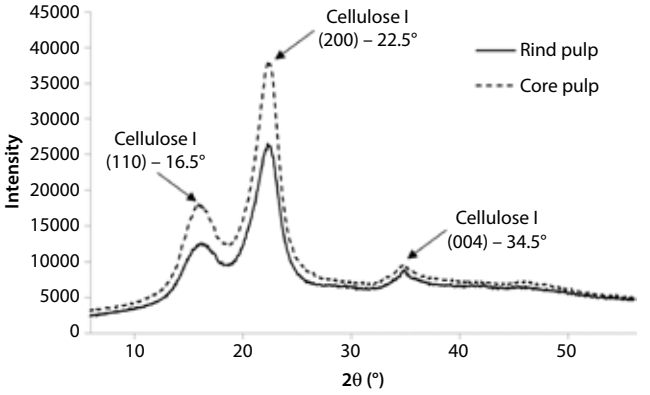

Figure 2 Diffractograms of the cellulosic pulps of rind and core sugarcane.

of the core fraction. It is important to remember that in these cases, these values do not correspond to cellulose from fiber and parenchyma, since in both materials there is a mixture of various cells. However, knowing the greater amount of parenchymal cells in the core fraction, it can be inferred that the degree of polymerization of cellulose in these cells would be lower than that in fibers. Contrary to this result, Abe and Yano [34, 35] observed that the microfibril aggregates of fiber and parenchymal cells of bamboo had the same characteristics, suggesting that the synthesis of cellulose microfibrils is identical in these two cell types. It is important to punctuate that, in contrast to sugarcane parenchymal cells, parenchymal cells of bamboo are used as an energy reservoir in the form of starch granules [36].

The ESEM images of the rind and core paper sheets are shown in Figure 3. Comparing the two substrates, the presence of the different cells can be observed. In the sheets of rind paper (Figure 3a,c) most cells have fibrillar characteristics. Still, some vessel elements can be observed to have fibrillar appearance but with larger width and smaller length. For the sheets of core paper (Figure 3b,d) fibrillar elements are still found, however, most elements have a rounded shape, which is characteristic of parenchymal cells.

In the images of the cross sections of the papers (Figure 3e,f) more voids are observed in the sheet of rind paper when compared to the core paper. The difference in the compaction between the samples is evident when observing the thickness of the cross section. Since both papers have similar basis weights (Table 2), it is possible to conclude that the core paper is denser than the rind counterpart. This can be confirmed when observing the specific volumes of the papers, as summarized in Table 2. While the cross section of the rind paper (Figure 3e) seems homogeneous in terms of cell distribution, the cross section of core paper (Figure 3f) presents a clear difference between the felt and wire sides. For the core paper sheet, the felt side has a much more compact appearance, while the wire side exhibits some small voids. This heterogeneity may contribute to the air permeability of the paper sheet. In fact, the analyses were performed only with the felt side up.

Table 2 shows the characterization data for the paper sheets obtained from sugarcane rind and crushed core. Both sheets have a slightly higher basis weight compared to the standard weight of 60 $g.m^{-2}$. The papers produced from the rind have a thickness of 0.096 mm, about 30% greater than the thickness of the core paper sheets. The specific volume of the rind paper is found to be about 15% greater than the specific volume of the crushed core paper.

By comparing the obtained values from the mechanical tests performed in Table 2, it can be verified that the results for the rind and core paper sheets are very different. The physical separation of the sugarcane stalks prior to the crushing step follows the biorefinery principle, as it permits the obtainment of different substrates from the same raw material.

When compared to the results from the literature, it is observed that both papers have higher values of burst index than that of unbleached eucalyptus papers (1.35 $KPa.m^2.g^{-1}$) and are similar to papers produced after mechanical refining process [37]. The burst index results are also comparable to results of papers obtained from annual biomasses, such as wheat straw [38], *Stipagrostis pungens* stems [39], *Achnatherum inebrians* stems [40] and sugarcane bagasse [41].

It can be seen in Table 2 that the tensile results for the core paper are much higher than for the rind paper. Both the tensile index value and Young's modulus of the core paper are about 70 to 75% greater than for the rind paper. When compared to results from eucalyptus pulp, these values are similar or even higher [37]. Yuan *et al.* [42] produced Kraft papers from bamboo with tensile index from 50 to 70 $N.m.g^{-1}$. Wimmer *et al.* [43] obtained a tensile index of 57 $N.m.g^{-1}$ for Kraft papers from eucalyptus and 110 $N.m.g^{-1}$ after refining the Kraft pulp. The Young's modulus of the core paper (8.64 GPa) is much higher than values obtained for several papers reported in the literature, in some cases being 4 times higher [37, 39], which indicates its greater stiffness. In this way, it is verified that the fractioning of the sugarcane into rind and core can produce promising materials for the papermaking industry.

Although most of the physico-mechanical properties showed different values, the tensile strength of the fiber (zero-span tensile strength) for both pulps (paper) presented very close values. This indicates that the intrinsic resistance of the fibrils in both rind

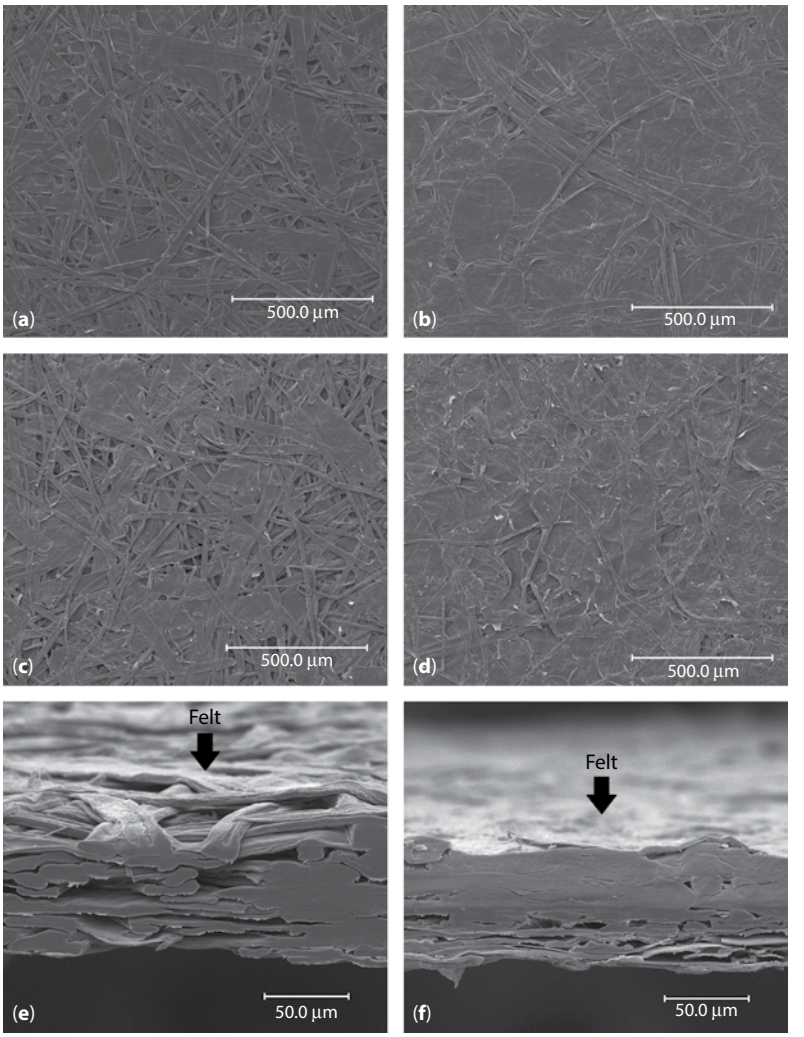

Figure 3 ESEM images of the papers: (**a**) felt face of rind paper, (**b**) felt face of core paper, (**c**) wire face of rind paper, (**d**) wire face of core paper, (**e**) cross section of rind paper, (**f**) cross section of core paper.

and core sugarcane fractions is similar, regardless of its origin.

The compaction observed in the core paper suggests that this paper should have lower air permeability, which was confirmed, as observed in Table 2. The higher amount of parenchymal cells in this fraction may explain the lower air permeability and higher compaction. Since these cells have thinner walls (1.7 µm for parenchyma vs. 4.0 µm for fibers) they should therefore be more easily compacted. While the rind paper has a high air permeability value comparable to commercial office papers [44], the core paper has an air permeability comparable to commercial high-density papers [45], recyclable papers [44] and papers from agricultural residues [38, 46].

Both paper sheets presented water absorption comparable to other non-sized paper sheets reported in the literature [47, 48]. Water absorption depends on

Table 2 Characterization of the paper sheets of sugarcane rind and sugarcane core.

	Sugarcane rind paper	**Crushed sugarcane core paper**
Basis weight ($g.m^{-2}$)	69.10 ± 0.63	64.26 ± 0.66
Thickness (µm)	96 ± 6	75 ± 7
Specific volume ($cm^3.g^{-1}$)	1.4 ± 0.1	1.2 ± 0.1
Burst index ($KPa.m^2.g^{-1}$)	3.71 ± 0.18	4.74 ± 0.10
Water absorption ($g.m^{-2}$)	156.5 ± 18.6	86.9 ± 6.5
Air permeability ($\mu m. Pa^{-1}.s^{-1}$)	12.81 ± 1.37	0.22 ± 0.03
Tensile strength of the fiber ($N.m.g^{-1}$)	13.75 ± 1.08	13.16 ± 0.76
Young's module (GPa)	4.97 ± 0.42	8.64 ± 0.58
Tensile index ($N.m.g^{-1}$)	52.10 ± 4.72	89.15 ± 5.88

three main aspects: surface chemistry, morphology and swelling [49]. Although parenchymal cells have a higher capacity to absorb water, due to their smaller cell wall thickness and larger lumens [14], and the higher swelling ability of the fines [50], the absorption value of the rind paper has approximately double the water absorption of the core paper. For both papers the surface chemistry is similar, and since swelling is a time-dependent effect [49], the greater compaction of the core papers and the consequent presence of fewer voids explains this apparent discrepancy.

The greater presence of fibers in the bleached rind pulp would allow a wider range of products since this material could undergo refining processes. While the refining of the core pulp is limited by its drainage ability, the refining of the rind pulp could promote an improvement in the mechanical properties of the produced papers. The high Schopper-Riegler degree of the core pulp should also make the paper formation difficult [9].

When compared to commercial papers, it can be seen that the paper produced from the rind and core fractions of sugarcane exhibit mechanical and physical property values in the same range. Thus, the different properties of the rind and core paper sheets allow using each one for the most adequate purpose. Despite that, the core fraction may not be suitable for paper production, considering the current technology. Hence, this fraction could be used as raw material for different applications in a sugarcane biorefinery, like the production of second-generation ethanol, chemicals or thermo-energy. Therefore, not only these materials, but mainly the processes to produce these fractions, should be considered as possible strategies in a sugarcane biorefinery context.

4 CONCLUSIONS

A simple fractioning process of the sugarcane plant was verified as a potential step in a biorefinery. The two distinct pulps and correspondent paper sheets presented different physical and mechanical properties, whose values were comparable to that of commercial papers and other papers reported in the literature from many cellulosic sources.

The higher amount of parenchymal cells in the sugarcane core fraction resulted in a pulp with lower drainage ability and denser and stiffer paper sheets. The core paper had a low air permeability, which is associated with the presence of parenchymal cells that can be better compacted, resulting in a material with a lower amount of voids.

The lower amount of fines and parenchymal cells of the rind pulp produced more porous paper sheets, which resulted in higher air permeability and water absorptions. Although mechanical properties of this paper had common values, the greater amount of fibers allows its potential use both as is and after a refining process.

Although the degree of polymerization of the cellulose from the two physical fractions had very different values, the tensile strengths of the fiber had very similar results.

Considering the results obtained in this work, physical fractioning can be a promising route to opening up new possibilities for the valorization of sugarcane. Also, the contrasting properties of the pulps and paper sheets of both fractions allow their use for different application domains, and can be considered products of a sugarcane biorefinery.

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