

Physicochemical characterization of coffee parchment of species *Coffea arabica* variety Castillo®

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ABSTRACT

Coffee parchment is one of the most abundant wastes from coffee processing in Colombia, representing 5.8% of the dry weight of the berry. This waste has been scarcely characterized, which is a fundamental requirement to generate new value-added usages. Therefore, the aim of this work is to study the coffee parchment of the species *Coffea arabica* variety Castillo® in compositional, chemical, thermal, crystallinity, morphological, and granulometric aspects. The coffee parchment composition was studied, determining the fractions of cellulose (49%), hemicellulose (21%), lignin (28%), and inorganics (3 %) presented. Also, Fourier Transform Infrared (FTIR) spectroscopy was made to explore the different functional groups of the constituent molecules and confirm their presence, likewise the thermal profile was determined to confirm the composition and explore the thermal stability of this waste. Crystallinity was determined by the Segal method using XRD. A morphological analysis by SEM and a granulometric analysis of this raw material is also presented. All these analyses are important for proposing alternative uses of coffee parchment and make it a promising source for obtaining crystalline cellulose.

Key words: Coffee parchment; Compositional analysis; FTIR; XRD; TGA.

1 INTRODUCTION

Within the environmental problems there is a growing impact caused by the waste generated. Specifically, the food and green wastes make a 44% of wastes all over the world. In Latin America, the disposal of these and other wastes are mainly open dumps and landfills, causing environmental damage (Kaza et al., 2018). The problems associated with this type of wastes are not because of hazard, but for the big volume generated (Thassitou; Arvanitoyannis, 2001). For instance, the agro-industry is responsible for an important quantity of wastes, and lignocellulosic materials constitute an important part of them (Kaza et al., 2018).

Among these, the coffee industry generates different lignocellulosic wastes through the whole process. Coffee may be processed by either dry or wet method. The dry process generates mainly a waste named coffee husk, while the wet one is carried out through several steps in which different wastes are generated. Wet process is usually carried out in some coffee producer countries such as Colombia (Alves et al., 2017). This country produces 13.9 million bags of green coffee grains annually, 60 kg each (Federación Nacional de Cafeteros de Colombia, 2021), and one of the wastes generated by this industry is the coffee parchment (CP), which represents 5.8% of dry weight of the berry (Fernandez-gomez; Iriondo-dehond; Zhou, 2017).

As many lignocellulosic materials, CP has been used as solid fuel, briquetting it for combustion purposes in diverse industries like cement and artisanal cooking

(Jeguirim; Limousy; Labaki, 2017; Suarez et al., 2003; Wondemagegnehu; Gupta; Habtu, 2019). Another approach is the pyrolysis, and CP has been subjected to this process to obtain substances of energetic interest like biofuels, gas, and carbon (Fernández; Menéndez, 2011; Hughes et al., 2014; Jeguirim; Limousy; Labaki, 2017). Furthermore, CP has been studied for bioethanol production via the saccharification and further fermentation of its constituent carbohydrates by either acid or enzymatic hydrolysis (Hughes et al., 2014; Jeguirim; Limousy; Labaki, 2017).

On the other hand, CP has been explored as livestock feed and dietary fiber ingredient, showing to be a good food and to have hypolipidemic and hypoglycemic effects (Benitez et al., 2019; Franca; Oliveira; Franca, 2009; Souza et al., 2003). Moreover, phenolic compounds, caffeine, and other compounds of cosmetic and food interest have been extracted from CP (Benitez et al., 2019; Mirón-Mérida et al., 2019). Even the antifungal activity of CP has been studied showing inhibition of many fungus (Mirón-Mérida et al., 2019). Lastly, 2.5 – 3 mm particles of CP have been employed for the manufacture of water filters, demonstrating good capacity to retain solids, and ions such as Na⁺ (Io Monaco et al., 2011).

Recently, CP has become a good candidate for cellulose obtention due to its relative high content (near 50%) (Bekalo; Reinhardt, 2010; Reis et al., 2020). The interest in cellulose obtention has also grown, due to its potential applicability in diverse areas (Abdul Khalil et al., 2015; Ahmed; Kanchi; Kumar, 2019; Gao et al., 2020; Gopi et al., 2019; Khattak et al., 2019; Ruso; Messina, 2017; Sharma; Nandal; Arora,

2019). Specifically, cellulose nanocrystals compared with its amorphous counterpart, has shown better mechanical properties, high free hydroxyl groups availability which are of interest in functionalization, lower density, better permeability properties, low thermal expansion coefficient, high aspect ratio, and good optical properties (Abdul Khalil et al., 2015; George; Sabapathi, 2015; Sharma et al., 2019). All these properties have allowed the study of cellulose for multiple applications in thermo-reversible and tunable hydrogels, paper making, coating additives, food packaging, flexible screens, optically transparent films and lightweight materials for ballistic protection, automobile windows, adsorbents for water treatment, filters, reinforcing agent, biological membrane reconstruction like dura mater, the manufacture of synthetic blood vessels, the coating of vascular stents and potential materials for scaffolds fabrication for regeneration of tissues such as skin, eye, bone and liver tissues (Abdul Khalil et al., 2015; Abudula et al., 2019; Gao et al., 2020; Kang et al., 2018; Mo et al., 2015; Sharma et al., 2019; Thompson et al., 2019; Yan et al., 2020).

Despite all the benefits shown by cellulose and thus cellulose obtained from CP, this waste has been scarcely characterized, which is a fundamental requirement to generate new value-added usages such as cellulose obtaining. Addressing this necessity, the aim of this work was to study the CP in compositional, chemical, thermal, crystallinity, morphological, and granulometric aspects to establish the potential use of CP as a source of crystalline cellulose. This, in turn, will enable others to propose new value-added usages based on the physicochemical characteristics of this abundant waste.

2 MATERIAL AND METHODS

2.1 Sample source and preparation

Approximately 20 kg of CP was obtained from A. Laumayer y Compañía Exportadores de Café S.A.S. This sample came from the processing of the species *Coffea arabica* variety Castillo®, from the department of Antioquia (Colombia).

The initial amount of CP was reduced to smaller samples following the quartering process described in ASTM C702/C702M-18, the Standard Practice for Reducing Samples of Aggregate to Testing Size, to maintain the significance of the sample (ASTM, 2018). The process was conducted several times until obtaining a sample of approximately 1 kg. The sample was stored in a sealed 2 L plastic container in a room without temperature or humidity control.

2.2 Compositional analysis of coffee parchment

The compositional analysis of CP was performed following the Laboratory Analytical Procedures (LAP) of the

National Renewable Energy Laboratory (NREL) (Sluiter et al., 2008a, 2008b, 2011)

2.2.1 Determination of total solids

Representative samples of approximately 7 g, obtained in triplicate, were collected following the quartering process described in section 2.1. Following the NREL's LAP (Sluiter et al., 2008a) the samples were weighted directly in aluminum pans, and dried into an oven at 105°C for 4 hours. Then, the samples were cooled into a desiccator for 1 hour and weighted again.

2.2.2 Determination of extractives

The appropriate NREL's LAP was followed (Sluiter et al., 2008b). A representative sample of about 75 g was obtained following the quartering process cited in section 2.1. The samples were sieved using meshes number 20 and 70. The fraction retained by the 70 mesh but passing the 20 mesh was set apart for the extraction process. From this fraction 3 samples of approximately 7 g each were weighted. These samples were subjected to Soxhlet extraction for 12 hours with 250 mL of water. Then, the water with the aqueous extractives was transferred to glass cups and dried into an oven at 105°C until the change in weight was not greater than 0.1 mg. The remaining solids were again subjected to Soxhlet extraction for 24 hours with 250 mL of ethanol 96%. Finally, the ethanol with the ethanolic extractives was transferred to glass cups and dried into an oven at 105°C until the change in weight was not greater than 0.1 mg.

After the extraction process, the remaining solids were set apart for the subsequent determination of structural carbohydrates.

2.2.3 Determination of structural carbohydrates

The free extractives samples obtained in section 2.2.2 were sieved again with meshes number 35 and 70. The fraction retained by the 70 mesh but passing the 35 mesh was separated for the determination of structural carbohydrates. From each of these samples, two samples of 300 ± 10 mg were weighted, then 3 mL H₂SO₄ 72% was added to the samples. The samples were incubated at 30 ± 3 °C for 1 hour with frequent shaking. Then, the H₂SO₄ 72% was diluted to 4% and samples were autoclaved at 120°C for 1 hour. After this, the samples let cooled freely until room temperature (Sluiter et al., 2011).

The hydrolysates were vacuum filtered using glass fiber membranes. The filtered hydrolysates were used for determining the contents of glucose, total reducing sugars and acid soluble lignin. The remaining solids were used to determine the acid insoluble lignin by calcination.

An aliquot of 5 mL was set apart for the determination of acid soluble lignin. The concentration of the sample was determined by UV spectrophotometry at 205 nm.

3 RESULTS

An aliquot of 15 mL was also taken and neutralized with calcium carbonate until pH between 7 and 8. This neutralized sample was used for quantifying the glucose and the total reducing sugars. Glucose quantification was subjected using the reagent Glucose from BioSystems. Total reducing sugars were quantified by the 3,5-Dinitrosalicylic acid method (Miller, 1959).

2.3 Coffee parchment functional groups analysis

CP was analyzed by Fourier Transform Infrared spectroscopy (FTIR) using an IR-Tracer 100 Shimadzu, from 400 to 4000 cm^{-1} , to identify the main functional groups of cellulose, hemicellulose, and lignin, and so, confirm them as the main components of this material. Data was plotted and analyzed using Python Software.

2.4 Coffee parchment thermal profile

The thermal profile of the CP was determined with thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) using a TGA Q500 TA Instruments. Sample was heated from room temperature to 600 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under a flow of nitrogen gas. Data was plotted and analyzed using Python Software.

2.5 Coffee parchment crystallinity analysis

The sample was subjected to powder X-Ray Diffraction (XRD) using a Malvern-PANalytical Empyrean 2012 diffractometer with 3D pixel detector, a Cu source ($\lambda=1.541874 \text{ \AA}$) and voltage and current settings of 40 kV and 40 mA, respectively. A background run was performed, and the result was subtracted from the sample run. The crystallinity index (CI) was determined according to equation (1), using the methodology described by Segal et al. (1959).

$$CI = \frac{I_p - I_v}{I_p} \times 100\% \quad (1)$$

Where, I_p is the intensity of the main peak and I_v is the minimum intensity immediately before I_p .

2.6 Morphological characterization

Three CP samples were analyzed with Scanning Electron Microscopy (SEM) to identify the surface morphology.

2.7 Granulometric analysis

To determine the granulometric distribution of raw material, an appropriate amount of the sample of about 28 g was separated using the quartering process described in 2.1. This was made by quadruplicate. The samples were sieved in a test sieve shaker for 10 minutes using the series of meshes: 4, 8, 14, 20, 40, 60, 80, 100 and 140, and the fraction retained in each mesh was weighted.

3.1 Compositional analysis

Moisture percentage was determined as 3.8%. Ethanolic extractives were established as $13.8827 \pm 2.1866 \%$ of the raw material. Regarding the aqueous extractives, it was determined that they correspond to $3.1445 \pm 0.0736 \%$ of the raw material. The CP composition in an extractives free basis is shown in Table 1.

Table 1: Coffee parchment percentage composition in an extractives free basis.

Component	Percentage
Cellulose	49.5837 ± 1.8444
Hemicellulose	21.4753 ± 1.8227
Lignin	28.3345 ± 0.8666
Ashes	2.9716 ± 0.0067

3.2 Functional groups analysis

Figure 1 shows the FTIR spectrum for CP. The main functional groups presented in cellulose, hemicellulose, and lignin can be identify. The 3325 cm^{-1} band corresponds to hydrogen bonds of cellulose and hemicellulose (Coelho de Carvalho Benini et al., 2017; Kale; Getachew Alemayehu; Gorade, 2020; Lim et al., 2020; Najeeb et al., 2021; Silverstein; Webster; Kiemle, 2005). Symmetric and asymmetric stretching of C-H bonds of methylene groups presented in cellulose and hemicellulose can be seen in 2917 and 2850 cm^{-1} , respectively (Coelho de Carvalho Benini et al., 2017; Kale; Getachew Alemayehu; Gorade, 2020; Lim et al., 2020; Najeeb et al., 2021; Silverstein; Webster; Kiemle, 2005). The band in 1733 cm^{-1} can be assigned to the C=O bond of the acetyl group in the uronic acid of the hemicellulose (Coelho de Carvalho Benini et al., 2017; Kale; Getachew Alemayehu; Gorade, 2020; Lim et al., 2020). The 1640 cm^{-1} band could correspond to stretching vibrations of C=C when conjugated in lignin rings (C=C-C=C) (Silverstein; Webster; Kiemle, 2005). Water trapping in the lignocellulosic matrix can cause the presence of a band in 1595 cm^{-1} (Lim et al., 2020). The presence of the 1455 cm^{-1} band corresponds to C-H bending of methylene groups in rings of lignin (Kale; Getachew Alemayehu; Gorade, 2020; Najeeb et al., 2021; Silverstein; Webster; Kiemle, 2005). The O-H out of the plan bending with wagging coupling of C-H in primary and secondary alcohols presented in cellulose shows bands in 1420 and 1320 cm^{-1} (Silverstein; Webster; Kiemle, 2005). A band near 1370 cm^{-1} can be related with nitrogenous groups such as N-O in lignin (Lim et al., 2020; Silverstein; Webster; Kiemle, 2005). The 1233 cm^{-1} band can be attributed to an asymmetric stretching of an aryl-alkyl-ether of lignin (Najeeb et al., 2021; Silverstein; Webster; Kiemle, 2005). The asymmetrical stretching in C-O-C of cellulose shows a band

in 1155 cm^{-1} . The intense band in 1026 cm^{-1} can be attributed both to the cyclic ether in the glucose units of cellulose, and to the C-O of alcohols in the sugars (Coelho de Carvalho Benini et al., 2017; Kale; Getachew Alemayehu; Gorade, 2020; Lim et al., 2020; Najeeb et al., 2021; Silverstein; Webster; Kiemle, 2005). Finally, the 895 cm^{-1} corresponds to the β -glycosidic bound in cellulose (Coelho de Carvalho Benini et al., 2017; Kale; Getachew Alemayehu; Gorade, 2020; Lim et al., 2020).

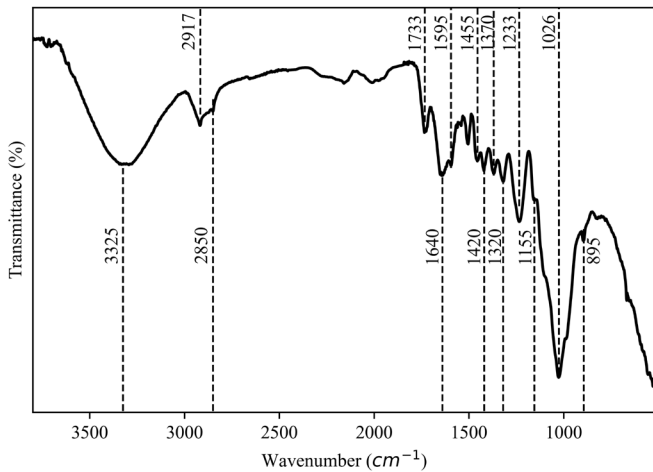


Figure 1: FTIR spectrum of CP. Dotted lines mark the main bands.

3.3 Thermal profile analysis

The thermal decomposition profile of CP and stages of decomposition are shown in Figure 2. The first stage, between room temperature and the onset temperature had a mass losing of 2.9%. Second stage of decomposition, between $148\text{ }^{\circ}\text{C}$ and $312\text{ }^{\circ}\text{C}$, had a maximum degradation temperature of $297\text{ }^{\circ}\text{C}$, and a 23.6% of weight losing. The third stage in the range of $312\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$ has a maximum decomposition temperature of $352\text{ }^{\circ}\text{C}$ and a weight losing of 49.1 %. Finally, at $600\text{ }^{\circ}\text{C}$ there is a remaining amount of material corresponding to the 24.3 %.

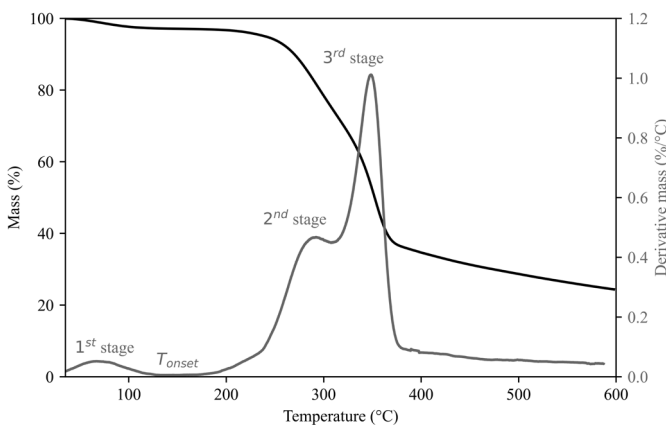


Figure 2. TGA and DTG profiles of CP.

3.4 Crystallinity analysis

The X-ray diffractogram obtained is showed in Figure 3. The XRD data was smoothed and plotted with Python software to appreciate correctly the values required for determining the CI (equation 1). The characteristic peaks of cellulose were observed, at 15.6° and 22° , which represent directions perpendicular to the fiber axis, and a peak at 34.8° representing directions parallel with the fiber axis which are characteristic of the crystal polymorph I β of cellulose (Thygesen et al., 2005). The Segal background at 18° is also presented (Coelho de Carvalho Benini et al., 2017; Lindner et al., 2015; Thygesen et al., 2005). In addition, it can be seen in Figure 3 the characteristic broad hump of raw lignocellulosic materials caused by the amorphous character of lignin, hemicellulose, and some amorphous cellulose (Coelho de Carvalho Benini et al., 2017; Kale; Getachew Alemayehu; Gorade, 2020). A CI of 59.7% was obtained from this assay and it is comparable with similar wastes like rice and arecanut husks, and soy hulls (Flauzino Neto et al., 2013; Islam et al., 2018; Julie Chandra; George; Narayanankutty, 2016).

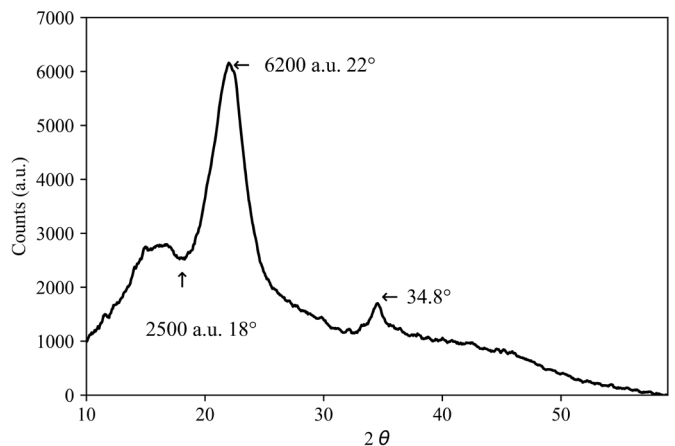


Figure 3: X-Ray diffractogram of raw CP.

3.5 Morphological characterization

Figure 4.a shows a CP flake of approximately $3 \times 4\text{ mm}$ with a 50X magnification. In Figure 4.b and 4.c can be seen parallel structures with high aspect ratio, marked with white arrows. In addition, this SEM analysis revealed a homogeneous surface, suggesting an extremely order lignocellulosic matrix (Figure 4.d).

3.6 Granulometric analysis

It was possible to determine the granulometric distribution of raw CP. Figure 5 shows both the cumulative and differential granulometric analysis. This last showed that the largest amount of raw CP ($45.93 \pm 1.72\%$) has a main diameter of 1.125 mm . The cumulative passing analysis which revealed that $84.11 \pm 0.83\%$ can pass a mesh number 14, that is, a mesh with a passing diameter of 2.38 mm .

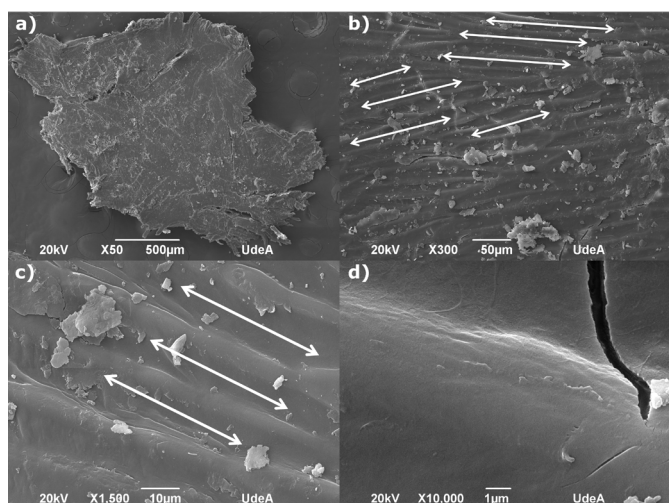


Figure 4: SEM micrographs of CP surface at different magnifications. White arrows in b and c indicate the growing direction of the lignocellulosic matrix.

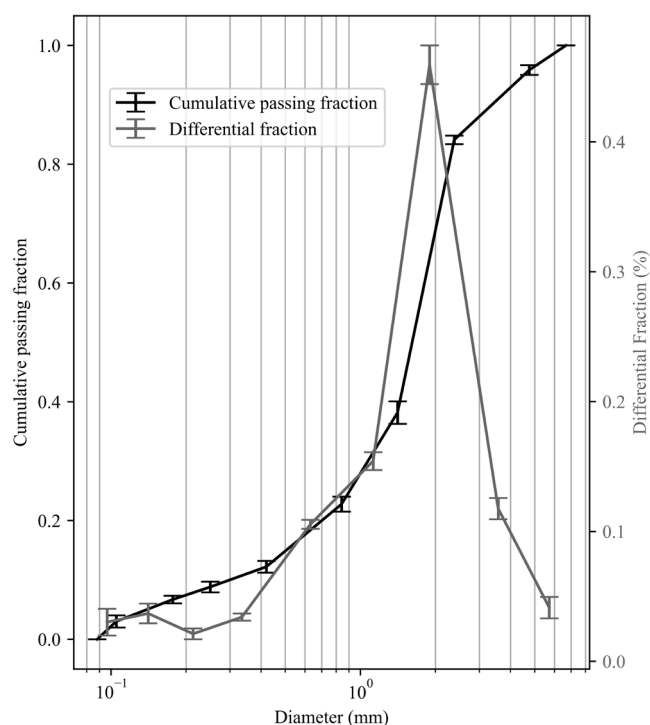


Figure 5: Cumulative and differential granulometric analysis for raw CP. For cumulative analysis, diameter axis corresponds to the passing diameter, for differential analysis, diameter axis corresponds to mean diameter.

4 DISCUSSION

4.1 Compositional analysis

We hypothesize that the extractive content of CP could be rich in essential oils, chlorophyll, and waxes (Sluiter et al.,

2008b; Verran et al., 2014), since most of them were obtained by ethanolic extraction. Nevertheless, it is necessary to study the extractives more thoroughly to establish their precise nature.

Cellulose content turns to be interesting because it can make CP a good candidate for cellulose recovery. This compositional distribution agrees with one reported by (Bekalo; Reinhardt, 2010). They reported contents of cellulose, hemicellulose, lignin, and ashes between 40 – 49 %, 25 – 32 %, 33 – 35 % and 0.5 – 1 %, respectively. Conversely, the composition here determined differs to the one reported by (Reis et al., 2020), who reported amounts of cellulose, hemicellulose, and lignin of 23.70 %, 19.35 % and 57.00 %, respectively. It should be noted that they reported the percentage composition in a basis non free of extractives, but in this study, the corresponding percentages in an extractives free basis have been calculated to be comparable. In this way, here is an important contribution to literature regarding the compositional analysis of CP.

On the other hand, lignin is responsible for lignocellulosic matrix protection in higher plants by inhibiting enzymatic action due to its hydrophobic behavior, and to achieve this function, lignin is highly crosslinked with hemicellulose which interacts with cellulose by hydrogen bonds (Belgacem; Pizzi, 2016; Jawaaid; Paridah; Saba, 2017). Thus, cellulose extraction always implies lignin removal or degradation, so the higher the lignin content is, the more difficult the cellulose recovery is. Considering both the content of lignin (28.3345 %) and hemicellulose (21.4753%) obtained, it can be inferred that the cellulose extraction process should be similar to that of other lignocellulosic materials with similar compositions (Geng et al., 2019; Huang et al., 2019). The compositional analysis mentioned above can be confirmed by FTIR since all bands are associated with bonds in cellulose, lignin, or hemicellulose, as described in the results.

4.2 Thermo profile analysis

The thermal profile analysis allowed to confirm the composition of CP, as hemicellulose, cellulose and lignin decompose at different temperatures due to their significant structural differences (Coelho de Carvalho Benini et al., 2017; Lim et al., 2020). The first stage has been related to moisture and extractives evaporation (Coelho de Carvalho Benini et al., 2017; Kale; Getachew Alemayehu; Gorade, 2020; Lim et al., 2020; Najeeb et al., 2021). The second stage has been mainly reported to be related with hemicellulose decomposition, but it also has been associated with some lignin decomposition (Coelho de Carvalho Benini et al., 2017; Lim et al., 2020). The third stage has been reported to be cellulose decomposition (Coelho de Carvalho Benini et al., 2017; Kale; Getachew Alemayehu; Gorade, 2020; Lim et al., 2020). The remaining amount of material up to 600°C has been reported to be mainly lignin, which exhibits better thermal stability due to

its complex structure (Coelho de Carvalho Benini et al., 2017; Lim et al., 2020). The percentages of mass loss in this thermal analysis agree with the compositional analysis also conducted in this work, supporting the composition shown in Table 1.

4.3 Crystallinity analysis

XRD analysis allowed to state that CP has high crystalline cellulose content, which is desirable due to the enhanced properties achieved compared with its amorphous counterpart. Crystalline cellulose has been shown to have better mechanical properties especially when it is brought to nanoscale. Crystalline nanocellulose has shown higher strengths and modulus, higher surface area, as well as better biomedical properties, compared with its amorphous homologous (Abdul Khalil et al., 2015; Thompson et al., 2019). Thereby, CP could be utilized for crystalline nanocellulose obtention, so giving to this waste a usage with added value.

4.4 Morphological characterization

Considering the way in which plants synthesize the lignocellulosic matrix, that is, they synthesize a cellulose microfibril and coat it with hemicellulose and lignin (Wertz; Bédoué; Mercier, 2010), in Figure 4.b and in Figure 4.c, a clear growth direction of the matrix (marked with white arrows) is identified. Consequently, it would be expected to obtain fibrillated cellulose from CP.

Furthermore, lignin removal would be expected to be a difficult step in cellulose extraction, due to the highly organization of the lignocellulosic matrix indicated for this SEM micrographs. The homogeneity of the surface suggests a reduction of the specific surface area that may affect the penetration rate of the substances utilized for lignin removal or degradation, and therefore, also its removal rate (Awoyale; Lokhat, 2021; Mosier et al., 2005). Moreover, this homogeneity is consistent with a highly degree of crosslinking and an extremely order molecular organization, which also would affect the lignin removal rate (Awoyale; Lokhat, 2021).

4.5 Granulometric analysis

Granulometric analysis result is interesting because having a small size is advantageous. The smaller the size of the material, the greater the surface area, and, therefore, the easier the extraction processes (Mosier et al., 2005). This result also suggests that size reduction for cellulose extraction purposes could be avoidable since a significant quantity of the material already has a small size. However, there is a small fraction of the material with large sizes. Considering that CP is a waste and grinding is expensive, it would be more economical to discard the fraction of CP with large sizes than to reduce its size. This hypothesis is further supported by the cumulative passing analysis, which revealed that the majority of the material has small sizes.

5 CONCLUSIONS

Coffee parchment was characterized in compositional, chemical, thermal, crystallinity, morphological, and granulometric aspects. The results obtained here allow us to propose coffee parchment as an interesting source for fibrillated crystalline cellulose, given its high cellulose content ($49.5837 \pm 1.8444\%$) and the observed crystallinity index (59.7%). The granulometric distribution also supports the CP use as cellulose source since size reduction stages could be avoided. Furthermore, this work can be utilized to suggest alternative uses for this abundant waste.

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7 AUTHOR CONTRIBUTIONS:

Conceptual idea: Campuzano, F.; Escobar, D. M.; Torres L, A. M. Methodology design: Campuzano, F.; Escobar, D. M.; Torres L, A. M; Data collection: Campuzano, F., Data analysis and interpretation: Campuzano, F. and Writing and editing: Campuzano, F.; Escobar, D. M.; Torres L, A. M.

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