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Physical-Chemical Characterization of Cocoa Pod Husk for Possible Use in the Making of Chipboards

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Abstract

In Colombia, cocoa husk is considered a non-reusable waste. For this reason, it is not used in the manufacturing of a product that represents an economic benefit, in addition, the inadequate handling of these residues generates environmental impacts and become sources of diseases for farmers. In accordance with the foregoing, this research studies the physical-chemical properties of the CN 51 cocoa pod husk. For this purpose, tests were carried out on the residues to determine the lignocellulosic components; as well as thermo-gravimetric scanning and electron microscopy tests. The chemical composition results showed higher proportion values of lignin, followed by cellulose, and hemicellulose. In the thermal analysis there was an initial peak associated with evaporated moisture in addition to four fragmentation stages, which correspond to the residue's primary components. On the other hand, a porous surface was observed in the microstructure, micropores and cell walls were present. In general terms, the contribution of this research allowed to conclude that these wastes are a viable alternative of raw material from renewable sources in the agricultural sector for the manufacture of chipboards with industrial applications.

Keywords: Agribusiness, use of resources, characterization, industrial processes.

I. INTRODUCTION

Industrial development has led to the uncontrolled generation of waste, causing an economic and environmental problem for companies that must bear the costs of their final disposal [1-2]. In accordance with the above, more efficient processes are being implemented, these allow creating alternatives for the use of such organic waste, and by doing, so these natural resources become a source of raw materials for the manufacture of industrial elements [3].

Colombia produces 54,785 tons of dry cocoa beans per year, corresponding to 23% of the pods used for the production of chocolate, 77% of that corresponds to the husks, which is equivalent to 183,410 tons/year of residue in the country where the department Santander is the largest producer with 22,177 tons per year [4].

In the cocoa farm, only the seed is economically used, which represents approximately 10% of the fresh fruit's mass. The by-products generated, the husk and the pulp, when deposited on the soil are considered a breeding ground for the spread of a fungus belonging to the Phytophora spp genus, which is the main cause of economic losses from cocoa activity [5]. On the other hand, these wastes cause a major environmental impact, due to the release of methane gas that occurs naturally by the decomposition of organic substances in oxygen-poor environments, becoming a more powerful agent responsible for global warming than carbon dioxide [6].

A way has been sought to provide a sustainable use of agro-industrial waste derived from cocoa production, as has been done in the manufacture of pectins, obtaining biogas, polyurethane foam, adsorbents, production of activated carbon and paper pulp [7-10]. Similarly, the cocoa pod husk has been tested for use as an adsorbent for the processing of contaminated waters [10] and also in the production of activated carbon for wastewater treatment [11].

In the literature, investigations have been reported using agroindustrial residues for the elaboration of chipboards. Self-bonded laminates were prepared from fibers of the banana leaf's central vein in which variables such as pressure and temperature in the agglomerate pressing process were evaluated [12]. With the rachis fiber of the African palm, self-adhered boards were made through a thermo-compression process [13]. The sugarcane bagasse for the production of hybrid chipboards using urea resins in formaldehyde and melanin in formaldehyde has had the mechanical properties of the chipboards made evaluated [14]. The mechanical, thermal and acoustic properties were studied for different mixtures of rice husk residues with different proportions of cork granules and recycled rubber. The results suggest solutions from these compounds, in particular with the thermal and acoustic performance that could be used in construction materials for buildings [15].

In accordance with the above, it is very important to seek new alternatives for the use of agro-industrial waste. Thus, research's the central axis is oriented to the physical-chemical study of the CCN 51 cocoa husk. Among the contributions made, the chemical composition's analysis was carried out, it found the fractions of cellulose, lignin and hemicellulose. Similarly, the thermal properties were evaluated using the thermogravimetry (TGA) technique. In addition, the study of the microstructure was carried out through scanning electron microscopy (SEM). The results obtained from the characterization outline the cocoa husk residues as a potential material for the manufacture of chipboards, however, pre-treatments are recommended to improve compatibility with the binder.

II MATERIALS AND METHODS

II.I SAMPLE PREPARATION

The cocoa husk residues (CPH) were collected in the municipality of San Vicente de Chucuri in the department of Santander and are part of a variety of cocoa called clone CCN 51, shown in Fig. 1.

Fig 1. Variety of cocoa clone CCN 51
Source: The author

The CPH residues were initially treated in an oven at 50°C for more than 72 hours to remove moisture. Subsequently, they were taken to a raw material reclaimer, to carry out a millimeter scale size reduction, followed by grinding to obtain fine particles. The product obtained is sieved for 15 minutes, until obtaining proportions that oscillate between millimeters and micrometers. Knowing the waste grain size plays an important role in the variables of the thermoforming process and also the particles' homogeneity allows to make more compact chipboards with better mechanical properties. For the physical-chemical characterization, residues with #30 sizes were chosen as evidenced in Fig.2.

Fig. 2. Reduction and sieving process.
Source: The author

II.II CHEMICAL CHARACTERIZATION

The chemical characterization of residues was carried out under standardized norms. Regarding the ash content and extractables, the ASTM standard (American Society for Testing and Materials) was used, while the determinations of lignin, cellulose, hemicellulose and solubility in NaOH are carried out under the TAPPI standard (Technical Association of the Pulp and Paper Industry) as mentioned in Table 1.

Table 1. Standardized rules for the chemical characterization of CPH waste.

PARAMETER	STANDARD
Cellulose	TAPPI 17 m-55
Hemicellulose	TAPPI 19-wd-71
Lignin	TAPPI 13-os-54
NaOH solubility	TAPPI T212 om-12
Ash	ANSI/ASTM D1102-56
Extractable	ANSI/ASTM D1105-56

Source: The author

II.III PHYSICAL CHARACTERIZATION

The moisture determination was carried out on a PRECISA XM60 model scale, with a sample weight of approximately 1 gr, which is heated up to 105°C.

The thermal properties were analyzed through the thermogravimetry technique (TGA), in a model SDT-Q600 equipment from TA Instruments. The TGAs were carried out with samples of 10 mg by weight in a temperature ranging from 25°C to 620°C, at a heating rate of 10°C/min in an argon atmosphere with a flow of 100 ml/min.

The morphology was analyzed using a TESCAN model MIRA 3 FEG-SEM scanning electron microscope, previously coated with a micrometric layer of gold to improve the sample's electrical conductivity.

III. RESULTS AND DISCUSSION

Knowing the chemical composition of the cocoa husk (CPH) is of vital importance, because of the information it provides on the fractions that constitute this waste. Consequently, chemical analysis in triplicate tests were carried out to determine the amounts of cellulose, lignin, and hemicellulose for the samples prepared from CPH obtaining the average values, standard deviation, and variance as shown in Table 2.

Table 2. Determination of CPH's chemical composition.

CHEMICAL COMPOSITION (% P/P)	Average	Deviation	Variance
LIGNIN	43,6	1,04	0,72
CELLULOSE	34,4	0,55	0,20
HEMICELLULOSE	11,75	0,28	0,05
EXTRACTABLES	2,43	0,12	0,01
NaOH SOLUBILITY	47,51	0,47	0,15
ASHES	1,11	0,11	0,01

Source: The author

According to the previous table's results, lignin represents the highest percentage of CPH's residues chemical composition with 43.6%, followed by 34.4% associated with the amount of cellulose and well below it is hemicellulose with 11.75%. The content of lignin concentrated in the residue represents a significant contribution to the plant's mechanical properties, providing rigidity to the cocoa husk. Similar studies experienced different stages of maturity in the walnut husk residue and consequently a better tensile behavior was observed in the wastes with longer times due to the increase of lignin during the amorphous phase [16]. On the other hand, the cellulose that constitutes the crystalline phase is fundamental in the resistance that the cell wall must withstand [17]. These values are shown in the CPH's waster chemical composition, because they determine, in a certain way, the mechanical behavior of the agglomerated material when it is subjected to different loads according to its application.

The solubility of the residues in 1% sodium hydroxide, [13]; was calculated for the cocoa husk obtaining values that comprise 47.51%, which means that they are substrates that can be exposed to degradation by fungi. Finally, the extractables and ash content does not exceed 3% of CPH's waste chemical composition.

In Figure 3, the results of moisture determination in CPH residues are presented, yielding an average value of 14.6%. According to the standard for wood particle board ASTM-D-1552-10, the humidity for the elaboration of chipboard must be kept at a maximum of 13% [18]. In addition, it is observed that from minute 60 the variation in mass loss is minimal and remains constant until minute 90. According to these results, drying pre-treatments are suggested before pressing the CPH grains to adjust the humidity percentage according to the one stipulated in the standard.

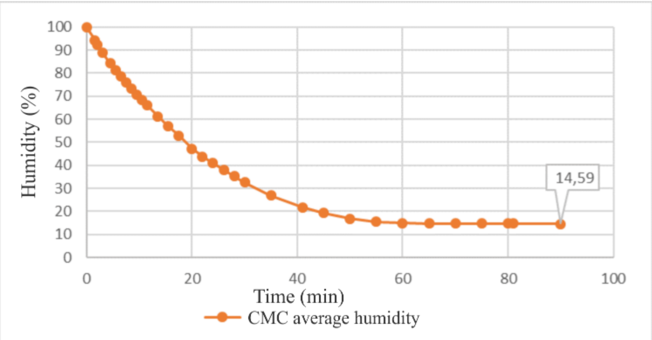

Fig. 3. CPH's Average humidity
Source: The author

The evaluation of humidity in CPH waste is a fundamental variable in the making of chipboards due to different factors that include water absorption and swelling in thickness, these being physical properties that show the dimensional stability of fiber boards. Such properties provide us with information about the boards when they come into contact with moisture [19].

Studying the thermal behavior of CPH waste is important due to the information it provides, both in the variables related to the manufacturing process and in the material's thermal stability at high temperatures. In Figure 4, the TGA (mass loss Vs temperature) and DTG (first derivative of the TGA Vs temperature curve) curves for organic waste are shown.

As can be seen in the thermograms, in the TGA curve, a mass loss is initially evidenced between 50°C and 120°C corresponding to the evaporation of the water contained in the CPH study material, with a percentage of 15, 63%, very similar to that obtained in the moisture analysis test. This percentage demonstrates the hygroscopic nature of CPH residues and consequently the particulate material has the capacity to store large liquid contents. This phenomenon would represent an increase in the absorption and swelling properties of the agglomerated material. Subsequently, a drastic fall is observed between 200°C and 400°C that shows the disintegration of the primary components such as cellulose, lignin and hemicellulose, with a loss of mass of 41.93%

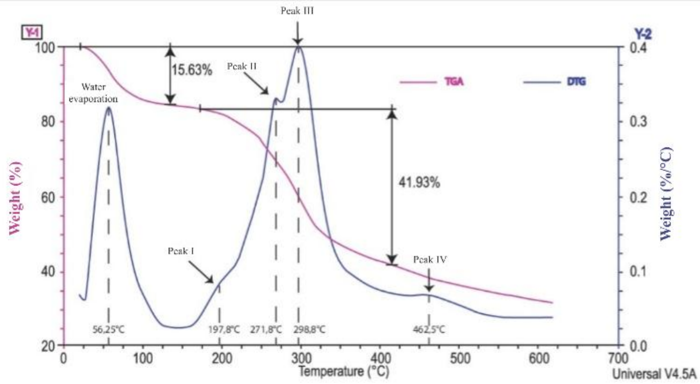

Fig. 4. CPH's TGA/DTG thermograms
Source: The author

The DTG curve is more accurate in terms of analyzing the degradation temperature ranges of the primary microconstituents. An initial jump of great magnitude related to the elimination of moisture is observed. At higher temperatures there are four decomposition peaks associated with the relaxation of the structure. A first peak, around 197.8°C, which represents the loss of extractables, fatty acids, oils and resins. Followed by a second peak, at 271.8°C, which corresponds to the degradation of hemicellulose. Subsequently, a maximum is shown on the curve, around 298.8°C, linked to the depolymerization of cellulose. Finally, a fourth peak is evidenced at 462.5°C corresponding to the rupture of the chains that make up the lignin. Navas et al. [20], evaluated the thermal properties of olive husks residues in wet by TGA, dry, along with the grape stems in the production of wine. The DTG results yielded similar results, with four states of degradation of the structure and one related to the evaporation of the retained liquid.

The morphological evaluation of the cocoa husks residues was carried out by using the SEM scanning electron microscopy observation technique, to identify the CPH's the microstructure.

According to Figure 5, an amorphous irregular structure is observed with particle sizes ranging between 100 and 300 microns. Similar surfaces with SEM images are reported in research carried out by other authors [21-22].

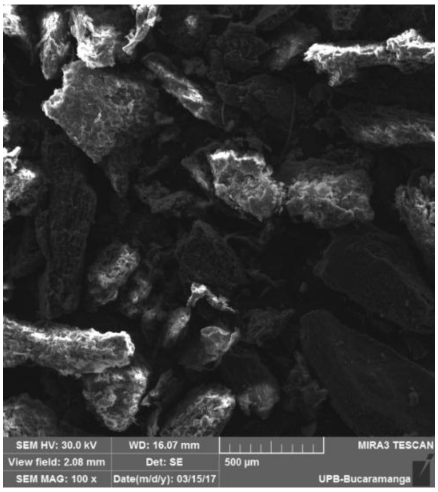

Fig. 5. Irregular amorphous structure of cocoa husk residues
Source: The author

In Figure 6, different grains that correspond to the cell wall with an average thickness of 5 µm are observed, these are associated with the primary components of cellulose and lignin, these have the high contents of cellulose and lignin presented in the chemical composition. Likewise, the micrographs show a micro-pore structure and a middle lamella that divides the grains from each other in the cell wall. Some authors mention the conformation of structures that contain cell walls of great thickness separated by the middle lamella in their studies of plant species with natural fibers [23-24].

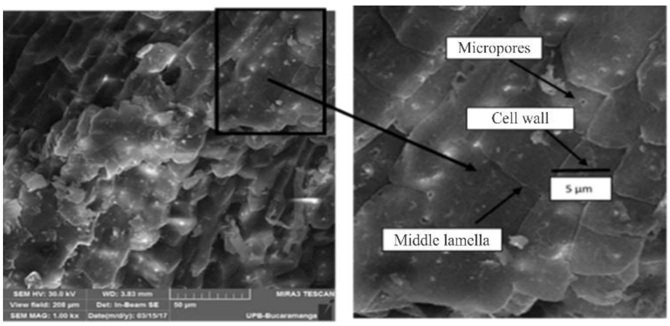

Fig. 6. CPH's Microporosity
Source: The author

IV CONCLUSIONS

According to the chemical composition, there are high percentages of lignin, cellulose and hemicellulose, in the residues, and therefore promise an agglomerated material with good performance in service.

According to the thermal analysis results, it is necessary to carry out a drying pretreatment to the waste as a consequence of its high hygroscopic capacity, in order to prevent a high absorption of moisture and swelling of the agglomerate.

The residues of cocoa pod husk, CCN 51 variety, are presented as an economically viable and environmentally sustainable alternative to be used in the elaboration of chipboards.

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