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Phytochemical Characterization and Fixed Carbon by Ignition of two Varieties of Cocoa Husk (*Theobroma cacao* L.) for Sustainable Use of the Residue

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One reality for Colombia is that the government has considered cocoa production to be of great economic importance and plans to progressively increase the areas under cultivation. In this context, only the seed, which represents approximately 10 % of the weight of the fruit, is used for cocoa production. The waste generated consists of the husk or pod, which is a focus for the propagation of pathogens of the Phytophora spp. genus, the main cause of economic losses in cocoa farming. Therefore, this project evaluated the potential use of cocoa pods of ICS-95 and CCN-51 clone based on bromatological, phytochemical, volatile material, and fixed carbon analyses of harvest residues. Laboratory tests were carried out at the Fundación Universitaria Agraria de Colombia - UNIAGRARIA, in the Nutrition and Animal Feeding laboratories, as well as in the Phytochemistry laboratory. The bromatological analysis and preliminary phytochemistry were carried out under the Colombian technical standard, while moisture was determined with the use of standard D3173-87, volatile matter with standard D3175-89 (02), ash with standard D3172-89 (02) and fixed carbon ignition with standard 3172- 89 (02); The latter, considered as the part that is not volatile and burns in solid state of the lignocellulosic material, establishing the difference between the sum of residual moisture, moisture, ash and volatile material and 100. The analysis of the data was carried out in the IBM SPSS Statistics package using a simple analysis of variance and a multiple range test for comparison of means. The comparative analysis of the variables shows a statistically significant difference in fixed carbon content according to the variety under study, but greater than 20% in both cases. The above results agree with those indicated for the % moisture, the response variables of the bromatological analysis, the phytochemical results, and the content of volatile compounds.
Keywords: Agricultural, plant fisiology, by-products, agribusiness.

1. Introduction

A reality of our days in the Colombian context arises around the national and international prospects of the cocoa agro-chain. In this sense, cocoa cultivation has a positive impact on the quality of life of farmers, allows the reduction of greenhouse gas (GHG) emissions caused by increasing deforestation and positions Colombia in the international chocolate market as a producer of high-quality raw material (Meza-Sepulveda et al., 2020). At the same time, wastes, throughout the development of the agro-chain, have aroused international interest among scientists and industrialists, due to their poor disposal and scarce use, before and during the transformation process (Arcos-Pazmiño, 2022). Within this framework, this research led to the analysis of the potential use of (cocoa pod) from its preliminary phytochemical composition and its capacity as a source of

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energy, the latter being a potential option given the high volumes of waste generation and the growing trend towards the generation of clean energy (Suárez-Rivero et al., 2021). Thus, from the application of the principles of the circular economy, the Colombian cocoa sector could benefit from the results obtained in the development of this project given the valorisation of the by-products generated and their potential inclusion as a source of raw material for other production chains.

2. Material and methods

The raw material came from cocoa crops from Pauna, Department of Boyacá, Colombia. Cobs of two varieties (ICS95 and CCN51) were analyzed at the Phytochemistry Laboratory and Biofuels Pilot Plant of the *Fundación Universitaria Agraria de Colombia* - UNIAGRARIA. This is located at 170 No 54A -10, Bogotá DC (Colombia), with coordinates 4°45'70''N and 74°03'12''W, an elevation of 2650 m above sea level, relative humidity of 94 % and an average annual temperature of 14 °C.
The characteristics of the two clones under study can be reviewed in the article published by Quintana Fuentes et, al. (2015).

2.1. Preliminary phytochemical analysis

For the preliminary phytochemical analysis, the methodologies proposed by Rojas, Jaramillo and Lemus (2015) in their text "Analytical methods for the determination of secondary metabolites" were used. The tests that were performed are:

- Unsaturations
- 2, 4 Dinitrophenyl Hydrazine (Test for aldehydes and ketones)
- Phenols and Tannins
- Sterols and Triterpenes
- Flavonoids
- Carbohydrates
- Coumarins Test
- Lactones Test

2.2. Determination of moisture content

To demonstrate this indicator, the protocol established in D3173-87 was followed, evidencing the loss of moisture from a known sample mass, which is heated in a stream of nitrogen in an oven maintained at a temperature between 105 °C y 110 °C, where the sample was equilibrated for the first time in atmospheric laboratory conditions, the result is the percentage of humidity calculated by the loss of mass.

2.3. Ash Content Establishment

The ashes were determined under Standard D3172-89 (02). Thus, a sample of known mass was taken, which was subjected to heating in air up to 500 °C for 30 minutes and subsequently going from 500 °C to 815 °C for 60 to 90 minutes until a constant mass was obtained. The amount of ash in the dough is a measure to determine the portion of minerals it contains and was established by weight difference.

2.4. Determination of volatile content

For this process, Standard D3175-89 (02) was used, which established the content of volatile materials, considered as gaseous detachments of organic and inorganic matter during heating. In a sample of estimated mass, the portion was heated to 900 °C without friction with the air for a certain time (7 minutes), as it was heated, the gaseous and liquid elements that contained it emanated (mainly water, hydrogen, carbon dioxide, carbon, carbon monoxide, methane, among others).

2.5. Determination of fixed ignition carbon content

The fixed ignition carbon was established following Standard 3172-89 (02). This is the part that is not volatile and burns in a solid state. It is the difference between the sum of residual moisture, ash, volatile material and 100, as it appears in equation 1:

$$\text{Fixed carbon (FC)} = 100 - (\text{Rh} + \text{A} + \text{Vm}) \quad (1)$$

Where:

Rh= moisture content
A= ashes
Vm=Volatile Material

2.6. Statistical analysis

Taking as a starting point the tests described above, and analyzing each sample in triplicate for its behavior with respect to each of the variables, the statistical analysis was carried out. An analysis of variance (ANOVA) was performed between the averages of the samples per treatment at a confidence level of 95 % (α = 0.05) to establish whether there are differences, as well as a multiple range test to establish the level of significance (Suárez-Rivero, 2011). Both tests are used using the Statgraphics 5.1 PLUS statistical software.

3. Results and discussion

3.1. Preliminary phytochemical analysis

Phytochemical analysis is used to identify bioactive substances that come from the secondary metabolism developed in plants, mainly as a defense mechanism (protection), adaptation and to improve the absorption of nutrients; they also have high commercial value for their use in industries such as pharmaceuticals, cosmetics, among others. The qualitative analysis of the ethanolic extracts of the two clones under study can be observed in Table 1. This analysis allowed us to identify, preliminarily, the presence of aldehydes and ketones, sterols and triterpenes, carbohydrates, as well as coumarins and lactones. Given the molecular structure of the compounds, by means of a chemical reaction, positive tests were observed by means of color changes or precipitation of the sample.

Table 1: Results of preliminary phytochemical analysis of ethanolic extracts of cocoa husk from two clones (CCN51 and ICS95).

Qualitative analysis	CCN51	ICS95
Unsaturations	**-**	**-**
2,4 Dinitrophenyl Hydrazine (Test for Aldehydes and ketones)	**++**	**+**
Phenols and Tannins	**-**	**-**
Sterols and Triterpenes	**++**	**+**
Flavonoids	**-**	**-**
Carbohydrates	**++**	**++**
Coumarins Test	**+**	**++**
Lactones Test	**++**	**++**

The tests that yielded positive results evidence a marked potential of the raw material for use in the pharmaceutical and cosmetic industry (Hernández-Alvarado et al., 2018). However, the tests that yielded negative results do not allow us to definitively conclude the non-existence of such metabolites in the raw material evaluated, as these types of results may be due in part to the low sensitivity of the test to characterize small concentrations of substance or to the interference of other compounds in the recognition reaction.

3.2. Moisture and Ash content

The results for the percentage of moisture in the cocoa husk (cob) are similar for both varieties, being 13.75 % and 13.86 % for clones CCN51 and ICS95, respectively, with no significant differences between the samples evaluated. These results agree with those shown by Suárez-Rivero et al. (2021) and Romo et al. (2011), who point out that when this type of variable is determined in biomass or residues of this woody type, moisture content should be expected to be lower than that of sugarcane bagasse, whose moisture content is close to 50%. Possessing low moisture content in this raw material gives it an advantage in terms of combustion, since a high moisture content reduces the efficiency of this process, since part of the energy of the raw material must be consumed by evaporating the contained moisture (Suárez-Rivero, 2017). The results presented show that this material could be dried in the environment, by exposure to sunlight, tending to lose moisture quickly, as stated by Correa-Méndez et al. (2015), coinciding with Suárez-Rivero et al. (2023).
As for Ash content, like moisture content, very low ash values were observed without significant differences between them for both clones, with a report of 1.4 % and 1.1 % for clones CCN51 and ICS95, respectively. In this sense, the determination of ash content indicates whether the biomass can achieve near-total combustion, since the lower the moisture and ash content, the better its utilization. According to Cigasova et al. (2016),

tropical plants normally have a high ash content compared to temperate forest species, which is reported for stems, but a low content is observed in the pericarp (cob) of the cocoa fruit.

3.3. Volatile content

The percentage of volatiles represents the amount of gas that is eliminated when performing a heating process (Oliveros et al., 2017). For Guo et al. (2014), establishing that the higher the percentage of volatiles, the lower the non-volatile matter, thus improving the combustion process. This is how Figure 1 evidence significant differences between the two clones, presenting higher percentage of volatiles the Clone ICS95 with 65.9 %, while the clone CCN51 presented 55.5 %.

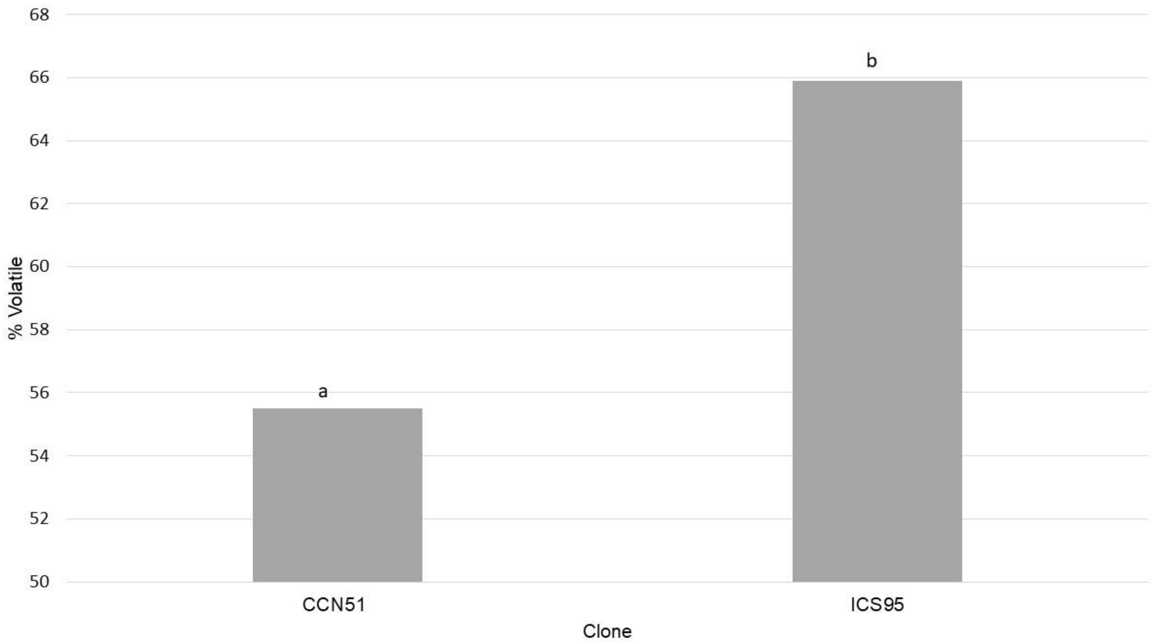

Figure 1: Expression of the % of volatiles present in the samples studied (Equal letters show no significant differences between treatments and different letters show significant differences between treatments)

In accordance with the above, Ruiz et al. (2013) state that during drying processes other processes such as gasification, pyrolysis, oxidation, and reduction commonly occur, stressing the importance of the elimination of water from the biomass during drying. They also point out that pyrolysis produces thermal degradation or volatilization of the material in the absence of oxygen if temperatures close to 200 °C are reached, thus obtaining a solid material (charcoal) and condensable fluids that give rise to fuels; concluding in his studies that cellulose and hemicellulose are the main sources of volatiles in plant material

3.4. Fixed carbon content of ignition

Figure 2 shows the behavior, according to the two clones studied, of the content (percentage) of fixed carbon determined by ignition. In this sense, with values ranging from 19.13 % (Clone ICS95) to 29.38 % (Clone CCN51), there are significant differences between the two clones.

The results obtained for the husks of the cobs in the two cocoa clones indicate that the evaluated residues are generally suitable to be used in a boiler for energy generation, since the number of solid residues can be the minimum possible, thus avoiding the pre-treatment of the raw material. According to Nova (2013), unlike the content of volatile material, the fixed carbon is a crucial characteristic in the composition of the raw material, thus becoming a limiting factor of the biomass to be used as fuel, since it represents the major source of heat during its combustion.

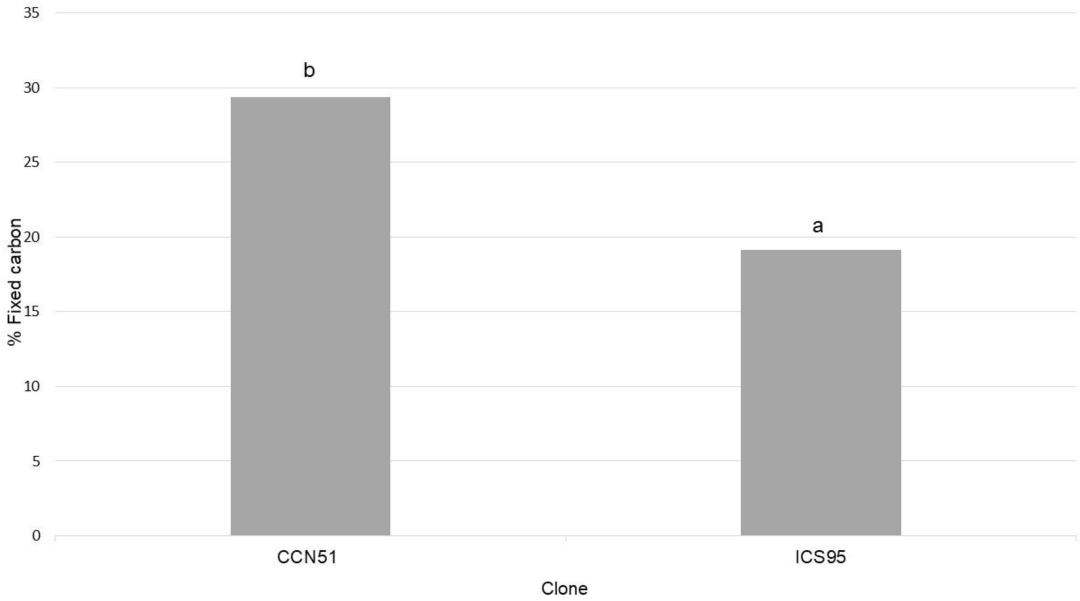

Figure 2: Expression of the % of fixed carbon by ignition in the studied samples (Equal letters show no significant differences between treatments and different letters show significant differences between treatments).

4. Conclusions

Cocoa (*Theobroma cacao* L.) is one of the agroindustrial crops of tropical origin with the greatest penetration in the international market and its exports in beans have represented a competitive factor in the phenomenon of illicit crop substitution in Colombia, a situation derived from the high benefit promoted by the chocolate industry and its derivatives. The preliminary phytochemical characterization revealed the presence of traces of compounds such as aldehydes and ketones, sterols and triterpenes, carbohydrates, as well as coumarins and lactones. It should be noted that these compounds have a high value for the pharmaceutical and cosmetic industries, but they are also gaining popularity due to their antimicrobial capacity and possible inclusion in disease management plans for agricultural crops.

The cocoa residues (cocoa pods or cocoa shells) studied showed energetic and moisture properties that allow affirming that they can be used for the manufacture of pellets for energy purposes. In this order of ideas, the highest contents of fixed carbon, related to the energetic properties of the biomass, were presented in Clone CCN51 (29.38 %) and the lowest content of volatiles (55.5 %), differing significantly from clone ICS95. Regarding moisture content, the two clones showed similar results without statistical difference, very close to 13 %.

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