Cocoa (*Theobroma cacao L.*) Husk Potential for Biogas and Biofertilizer Production

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Abstract: In the context of the transition to renewable energy sources, the valorization of agro-industrial waste is fundamental. Cocoa husk, in particular, emerges as a promising biomass, whose utilization can mitigate environmental impacts and foster a circular economy. The objective of this work is, therefore, to evaluate the potential of cocoa husk for the generation of biogas and biofertilizers. Despite technical challenges, such as its high moisture content, the conversion of this residue into energy can contribute significantly to the diversification of the national energy matrix. The research was conducted based on physicochemical analyses of samples collected in the municipality of Presidente Tancredo Neves - BA, covering parameters such as the determination of moisture content, total solids, volatile solids, ash, pH, cellulose, lignin, and heating value. This study contributes to the implementation of sustainable solutions and highlights the relevance of waste valorization in the transition to a clean energy matrix.

Keywords: Biomass; Cocoa husk; Bioenergy; Characterization.

1. Introduction

The increase in energy demand on a global scale, driven by both technological advancement and world population growth, has intensified the search for renewable and environmentally sustainable energy sources [1]. Still in the 21st century, the global energy matrix remains heavily dependent on fossil fuels, which contributes significantly to the worsening of global warming and climate change. in this scenario, the diversification of energy sources becomes strategic, with biogas being a promising alternative as it allows for the use of organic waste [2].

In Brazil, there is a variety of biomass with potential for energy conversion, such as corn husks, sugarcane bagasse, and rice straw. Specifically in the state of Bahia, the husk of the cocoa fruit stands out as a relevant resource in this context [2]. According to Mariachi et al. [3], this husk corresponds to about 76% of the total weight of the fruit, being the main residue generated in the cocoa processing process.

Despite its wide availability, this residue is often improperly discarded, which can result in negative impacts, such as the spread of agricultural diseases, for example, Witches' Broom and Brown Rot, in addition to soil imbalances, due to its high potassium content [4].

Considering the urgency for complementary and renewable sources and the potential of this agricultural byproduct for the generation of biogas and biofertilizers, the objective of this work is to study the characteristics of cocoa husks to understand how they can be better used in the production of biogas and biofertilizers. Seeking to show that, in addition to reducing environmental impacts, this residue can be transformed into a source of renewable energy and a useful product for agriculture.

2. Agro-industrial Residues

Agro-industrial residues are byproducts generated, for the most part, from the processing of food produced on a large scale. Among the main examples are bagasse, husks, seeds, and other organic materials discarded in large volumes. Despite often being treated as waste, these residues have a high potential for energy recovery [5].

Biomass from agricultural production has enormous potential to be converted into raw materials used in the production of biofuels, biopolymers, biomaterials, biofertilizers, and biopesticides. The use of this biomass, aligned with the principles of the bioeconomy, promotes environmental and social benefits, while at the same time boosting the economic sustainability of production chains [6].

3. Origin and Availability of Cocoa Husks

The cocoa tree (Theobroma cacao L.) is a perennial, tree-sized plant that develops well in shaded environments, such as undergrowth and sparse forests. Currently, the states of Bahia and Pará account for about 96% of the national production of cocoa beans, making them the main producing hubs in the country [7].

The cocoa tree varieties are grouped into three main types: Criollo, Forasteiro, and Trinitário, each with distinct characteristics regarding flavor, yield, and resistance [7].

According to the Brazilian Institute of Geography and Statistics (IBGE), in 2023 Brazil produced 296,145 tons of cocoa, of which 139,011 tons came from the state of Bahia, confirming its prominent position alongside Pará, which together account for a large part of the national production. It is estimated that approximately 236,916 tons correspond to cocoa husks, a high-volume residue with underutilized potential [8].

Historically, the husk has been discarded directly in the plantations or used as organic fertilizer. However, the improper disposal of the husk on the ground has contributed to the spread of fungi and diseases, representing a phytosanitary challenge in the plantations [9]. This situation has sparked scientific and technological interest in the search for alternative ways to utilize the cocoa husk, whether as an input for bioenergy, an agricultural substrate, or a raw material for compounds of higher added value.

4. Energetic Potential of Cocoa Husks

In the state of Bahia, cocoa cultivation stands out as one of the main agricultural activities, generating a significant amount of byproducts. Among these residues, the husk of the cocoa fruit represents one of the largest volumes, yet it remains underutilized.

Both the husk and the cocoa bran have high potential for reuse and can be converted into energetic and agricultural inputs, such as biogas, biofertilizers, briquettes, and even substrates for the production of industrial enzymes.

The cocoa husk has physicochemical characteristics that qualify it as a promising biomass for energy purposes. Table 1 shows the energetic potential of various raw materials used as biomass, allowing for a comparison of the energy performance of cocoa husks with other sources.

Table 1. Higher Heating Value (HHV) of different biomass sources

Raw Material	HHV (MJ/Kg)
Firewood [10]	19,10
Cocoa husk [11]	16,23
Sugarcane bagasse [12]	18,04

The data indicate that cocoa husk has an amount of energy similar to that of sugarcane bagasse. Although it is lower than firewood, which has the highest value among the sources analyzed, cocoa husk presents itself as a viable and sustainable option, especially as it is a residue produced in large quantities and is seldom used. Furthermore, the use of energy from biomass can help reduce dependence on fossil fuels, promote the use of renewable waste, and reinforce sustainability in cocoa production.

5. Methodology

In this study, an experiment was conducted in triplicate with biomass samples from cocoa husks. The samples were collected from two distinct agricultural properties located in the municipality of Presidente Tancredo Neves - BA (13° 26′ 56″ S, 39° 25′ 12″ W). One of the collection areas corresponded to a cloned cocoa plantation (variety PS 1319), as illustrated in Figure 1, while the other was a common cocoa plantation (Forasteiro), represented in Figure 2.

Figure 1. Cloned cocoa in its natural state

Figure 2. Common cocoa in its natural state

After collection, the samples were properly stored and sent for analysis. The physicochemical and energetic characterizations of the biomass were carried out in two laboratories: at the Energy Laboratory (LEN) of the Federal University of Recôncavo da Bahia (UFRB) and at the Energy Laboratory at Senai Cimatec, in Salvador - BA. The sample preparation was performed based on the protocols recommended by the National Renewable Energy Laboratory - NREL, ensuring the standardization and reproducibility of subsequent analyses [13]. First, the samples underwent a size reduction and homogenization process; the fresh husks were manually cut into small particles using pruning shears.

5.1. Determination of total solids and moisture content

The determination of total solids and moisture content was performed in triplicate for both types of cocoa (cloned and common). 10 g of biomass from each type were used, weighed on an analytical balance, and transferred to previously identified crucibles.

The samples were kept in a Limatec brand drying oven at a temperature of 105 ± 3 °C for a period of 18 hours. After this period, the crucibles were removed, cooled in a desiccator, and weighed to determine the dry mass. The ratio between the dry mass and the initial sample mass was used to calculate the total solids content (Equation 1). Moisture was calculated by the difference between the wet mass and the dry mass (Equation 2).

$$Total\ solids\ content\ (\%) = \frac{Dry\ biomass\ mass}{Wet\ biomass\ mass} \times 1 \quad (1)$$

$$Moisture\ content\ (\%) = 100 - Total\ solids\ content \quad (2)$$

5.2 Determination of the Heating Value

To calculate the Higher Heating Value (HHV), 10 g samples of each biomass type, which were previously ground and sieved through a 100-mesh screen, were sent to SENAI CIMATEC. The specialized technical team conducted the analysis using bomb calorimeters with heads cod. 3 and 4, in addition to an analytical balance, cod. 83823, and following the ASTM D240-19, DIN 51 900, and ASTM D5865 standards.

The Lower Heating Value (LHV) was determined from the HHV by subtracting the energy related to the vaporization of water produced during the combustion of the hydrogen contained in the sample. To find the hydrogen content, Equation 3 was used [14].

Styles for table title, table head, and table text are provided. Tables could be in one or two columns, and be placed near their first mention in the body. Tables, figures and graphics need to be placed on separate pages at the back of the manuscript.

$$\%H = 10,72 + 2,43 \times log_{10}(MV) \quad (3)$$

5.3 Determination of ash content

After the drying process in a Limatec brand drying oven at 105 ± 3 ºC, the biomass samples reached a constant mass and were then considered moisture-free, from which point the ash content could be calculated. For the determination of ash content, the dry samples were weighed in previously tared crucibles on an analytical balance and then subjected to incineration in a muffle furnace at 575 ± 25 ºC for a period of 15 minutes (Figure 3).

After this time, the crucibles were cooled in a desiccator and weighed again with the aid of an analytical balance. The ash content was calculated based on the difference between the mass of the dry sample and the residual mass after incineration.

Figure 3. Determination of ash content: biomass in crucibles after drying and incineration. a) Cloned cocoa husk and b) Common cocoa husk.

a)

b)

5.4 Determination of volatile solids

To determine the volatile solids, it was necessary to calculate the difference between the dry mass of the biomass and the ash mass; for this, the raw material had been pre-treated and subjected to a muffle furnace at 575 ºC. This content indicates the combustible organic compounds that turn into vapor during the sample's combustion process.

5.5 Determination of pH

To determine the pH, 10 g of the fresh sample were diluted in 100 mL of distilled water. The mixture was stirred and, after a resting period, the pH was measured using a calibrated pH meter.

5.6 Cellulose content

Three 1 g samples of dry biomass were prepared from each type of husk, and the material was transferred to a 250 mL Erlenmeyer flask. A 25 mL aliquot of a solution of nitric acid (90 mL) and glacial acetic acid (732 mL) was added, and the mixture was refluxed on a hot plate (MA 239 - Marconi) for 25 minutes at 120°C. After cooling, the cellulose residue was vacuum-filtered through filter paper and washed with 500 mL of distilled water and 25 mL of ethanol. Subsequently, the material was dried in an oven at 100 ± 5°C to a constant weight. After cooling in a desiccator, the filter paper containing the residue was weighed.

6. Results and Discussion

The results of this study allow for a comparison between the biomass of cloned cocoa husk (PS 1319) and common cocoa, highlighting their physicochemical properties and potential for energy use. The analyses performed included the determination of solids content, moisture, ash, heating value, and pH, providing essential information about the composition of this biomass and its implications for use as a biofuel. Taking into account the significant cocoa production in the Lower South region of Bahia, samples from this area were chosen for the research.

In the visual and gravimetric physical characterization of the cocoa samples, it was observed that the fruits of the cloned cocoa PS 1319 have a predominantly reddish color, a thicker husk, and a significantly higher mass of 520.74 g, when compared to the fruits of the common variety, which have a yellowish color, a thinner husk, and a lower mass of 398.6 g. This difference indicates that the cloned cocoa has a greater volume and density, which can directly influence the yield of biomass originating from the husk. The physicochemical and energetic analyses of the cloned and common cocoa husk samples resulted in the average values presented in Tables 2 and 3.

Table 2. Average Physicochemical and Energetic Properties of Common Cocoa Husk

Parâmetro	**Cacau Forasteiro**	**Desvio Padrão**
Umidade (%)	83,13	0,53
Sólidos Totais (%)	16,87	0,53
Sólidos Voláteis (%)	90,13	0,32
Cinzas (%)	10,03	0,32
PCS (MJ/kg)	17,45	0,26
PCI (MJ/kg)	14,05	-
Celulose (%)	22,08	0,83
pH (%)	5,2	-

It is noted that the moisture content was 83.13%, with a standard deviation of 0.53%, which demonstrates good consistency in the measurements. This high level of moisture is a determining factor, as it directly decreases the Lower Heating Value of the biomass and compromises combustion efficiency. Therefore, it is necessary to apply pre-treatment processes, such as drying, to enable its energetic use.

The total solids represented a percentage of 16.87%, of which 90.13% were volatile materials. This indicates that the biomass has a high potential to release combustible gases during the thermal process.

However, the ash content, which is 10.03%, may suggest an increase in the accumulation of solid residues after burning, which affects equipment maintenance and process efficiency.

The HHV was 17.45 MJ/kg, a value that is in line with other lignocellulosic biomasses. On the other hand, the Lower Heating Value was 14.05 MJ/kg, indicating a significant energy loss due to the high moisture content.

In addition to these parameters, the cellulose content found was 22.08%, its presence positively influences the heating value, as the thermal decomposition of cellulose releases combustible gases and contributes to the formation of char with high energy value. However, since cocoa husk also has a high moisture content, part of this energy potential is compromised, reinforcing the need for pre-treatments to enable its use in processes such as direct combustion or gasification.

Table 3 presents the average results of the physicochemical analysis of the cloned cocoa husk, offering essential information to evaluate its viability as an energy source.

Table 3. Average Physicochemical and Energetic Properties of Cloned cocoa husk

Parâmetro	**Cacau clonado (PS 1319)**	**Desvio Padrão**
Umidade (%)	86,96	0,78
Sólidos Totais (%)	13,04	0,78
Sólidos Voláteis (%)	91,48	0,29

Cinzas (%)	8,68	0,29
PCS (MJ/kg)	17,03	0,12
PCI (MJ/kg)	13,63	-
Celulose (%)	21,76	0,56
pH (%)	5,2	-

From the data presented in Table 3, it is observed that the moisture content was 86.96%, slightly above that recorded for the common cocoa husk. This indicates that the biomass was even more humid and, consequently, had more restrictions for direct energy use. The standard deviation of 0.78% indicates good consistency in the results among the analyzed samples.

The total solids content was only 13.04%, indicating a reduced amount of dry material available for combustion. Even so, the majority of the dry material is composed of volatile substances (91.48%), indicating the possibility of releasing combustible gases during heating.

On the other hand, the ash content was 8.68%, slightly below that found in the common cocoa husk, which may indicate a lower production of solid residues after burning.

The Higher Heating Value was 17.03 MJ/kg, and the Lower Heating Value was 13.63 MJ/kg, demonstrating how the high moisture content negatively affects the energy efficiency of the biomass.

In the case of PS 1319, the cellulose content was 21.76%, a value very close to that found in the Forasteiro cocoa. This similarity indicates that, regardless of the variety, cocoa husk has a considerable cellulose content, which contributes to its potential as a lignocellulosic biomass.

Both biomasses have high levels of volatile solids, exceeding 90%, which suggests a high energy potential due to the release of combustible gases during combustion or thermochemical processes.

Both the Forasteiro and the PS 1319 cocoa husks presented a pH of 5.2, indicating a slightly acidic character. This value is relevant in the context of energy conversion, as pH can influence chemical stability, corrosivity, and microbial efficiency.

In the anaerobic digestion process, for example, the indicated pH for the activity of methanogenic microorganisms ranges between 6.7 and 7.5 [15]. Values below this range, such as the one obtained in this study, can compromise the yield of biogas production, requiring a prior pH correction through the addition of alkalizing agents.

7. Conclusion

This study highlights the energetic potential of cocoa husk, from both the common (Forasteiro) and cloned (PS 1319) varieties, as a renewable source of biomass. The physicochemical characterization revealed a high content of volatile solids in both samples, reinforcing their capacity to release combustible gases.

The PS 1319 variety stood out for its greater mass, favoring the energy yield per unit of volume and its use on an industrial or decentralized agro-energy scale. Despite the high moisture content, which reduces the LHV, this challenge can be overcome through pre-treatments such as drying. The pH indicates a need for alkalizing corrections for applications in biodigesters or biofertilizers.

In conclusion, cocoa husk is technically and energetically viable, with the potential to be integrated into waste valorization chains and to contribute to the environmental sustainability and economic development of producing regions.

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