



# Pyrolysis of açai stems (*Euterpe oleracea* Mart.) and cocoa husks (*Theobroma cacao* L.) residues for the generation of added-value products in rural areas

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## Abstract

Generally, agriculture activities represent the main economic income of rural areas, and during these, huge amounts of biomass are generated. This biomass is considered as garbage due to its high storage cost. However, energy and added-value products can be recovered from biomass. Within this context, açai stems and cocoa husks were collected from different rural areas of Bolivia due to their high importance in the local and international markets as two of the most available products of the country. The preliminary study will contribute in the field of green energy recovery and resource management. Thus, in this study, both residues were tested as renewable feedstocks for the generation of added-value products from pyrolysis at 500 °C for 30 min. Açai stems were found to be more suitable to biochar based with yields up to  $49.1\% \pm 2.4\%$ , but also for biogas production ( $33.9\% \pm 2.0\%$ ). Cocoa husk was also found to be more suitable for biochar production ( $38.1\% \pm 1.7\%$ ) but also for bio-oils ( $33.6\% \pm 17.6\%$ ). Both resulting biochars had basic pH (between 10 and 12) and low density ( $287.2 \text{ kg/m}^3$  and  $401.7 \text{ kg/m}^3$ ). Additionally, the lack of heavy metals on the surface makes both biochar products good candidates for soil amendment applications. Furthermore, the bio-oil composition is complex and varied, and products such as Maltol, 2-methyl furane, and D-allose have direct applications in the food industry. Moreover, the presence of phenolic compounds and hydrocarbons with more than five carbons in the structure makes the obtained bio-oils suitable for upgrading processes for biofuel production. Finally, the obtained biogases can be applied for local electricity generation, or to reduce the energy requirements for the pyrolysis reactor.

**Keywords** Biomass pyrolysis · Açai stems · Cocoa husk · Amazonas · Rural areas · Biochar

## Highlights

- Açai stems and cocoa husk residues were pyrolyzed to get added—value products.
- The obtained biochar has good properties for soil amendment applications.
- Açai stems are more suitable for biogas and biochar production.
- Cocoa husks are more suitable for bio-oil and biochar production.
- The obtained bio-oil can be improved to produce fuels and chemicals.

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## 1 Introduction

Agriculture is the main activity in rural areas, and this leads to a residue generation problem. The amounts of generated biomass during the harvesting process can reach up to 85% depending on the biomass source. Biomass is a problem mainly due to its low density, making the accumulation of bulky residues a big problem. Different regions in Bolivia have experienced problems with biomass accumulation, and the huge amounts of residues gathered in one place do not only occupy a lot of space but also contribute to promoting unhealthy spaces full of plagues such as rats. However, biomass can be converted into added-value products and green energy through thermochemical processes. One of the most studied processes is pyrolysis, which offers flexibility in the obtained products by changing the operation parameters such as temperature, residence time, and feedstock composition [1]. During pyrolysis, biomass is subjected to

elevated temperatures in an inert atmosphere, resulting in the partial decomposition of cellulose, hemicellulose, and lignin forming a variety of products with different characteristics (bio-oils, biogases, and biochar) [2, 3]. Factors such as the moisture content, the ash content, extractives (organic matter such as fats, waxes, resins, sugars, and other soluble in solvents), and the chemical structural composition (lignin, cellulose, and hemicellulose content) are important to define the final properties of the products, and ultimately to define the final application for the biomass feedstocks [4–6].

The potential benefits of biomass are even more relevant in the context of rural areas where agricultural and forestry activities usually represent a main source of income [7]. Generally, rural areas are far from main cities, and in some cases, the access to these regions is limited due to geographical constraints. Therefore, electricity and energy tend to have higher prices, in these places [8, 9]. South America has one of the most diverse ecosystems in the world, with a variety of flora and human activity offering different types of biomass residues spread all around the continent. Nevertheless, the availabilities of particular residues depend on the location. As a consequence of the differences in weather conditions and geography, different agricultural products are favored in different regions. For example, in the Amazon in the north of Bolivia (Pando), one of the most popular products is açai (*Euterpe oleracea* Mart.), from which the seeds and stems are obtained as biomass residues during the harvesting season. Açai consumption is widely spread around the world due to its antioxidant and anti-inflammatory properties [10]. Another example can be found in the rainforest in the north-west region of Bolivia (Yungas) where cocoa (*Theobroma cacao* L.) is produced, and cobs and husks are obtained as biomass residues. Cocoa is one of the most consumed agricultural products worldwide because it is the key ingredient for chocolate production. In the other hand, açai can also be found in Brazil and Colombia, while cocoa is also produced in Ecuador, Brazil, Ivory Coast, and Nigeria, among others countries. Although this study was conducted with samples provided by local producers in Bolivia, it is also possible to find açai and cocoa residues in different countries. Within the Bolivian context, açai and cocoa are two of the most important products both in the national and international markets. The production of both is well spread along the amazonic and tropical region of the country.

Therefore, in this study, açai stems and cocoa husks were selected to set the base for further studies about how to use these residues as a source of clean energy and added-value products. Both samples were found interesting since they are common in certain areas of Bolivia, and because as far as we know, these biomass residues are under-researched. Moreover, the use of local biomass resources positively contributes to reducing the use of fossil fuels in Bolivian rural areas by increasing the share between renewable and fossil. Furthermore, the use of accumulated biomass improves the resource management in the area, impacting also in the economy of the place by adding value to bulky residues (garbage) such as biomass.

## 2 Experimental

### 2.1 Samples collection

Two different agriculture residues were used in this study; açai stems and cocoa husk. The açai stems were collected from the Amazon rainforest located in Pando, Bolivia. The açai farm was in the community of La Trinchera in El Porvenir region, located at a latitude of  $-11.083^{\circ}$ , and a longitude of  $-68.90^{\circ}$  in the southern hemisphere. The cocoa husk samples were collected from Condor Industries, a chocolate food producer in La Paz, Bolivia. The cocoa was produced in the region of Caranavi located at a latitude of  $-15.84^{\circ}$ , and a longitude of  $-67.57^{\circ}$  in the southern hemisphere. In both cases, the samples were collected randomly from a pile of biomass residues which had been exposed to different storage times, temperature, and different levels of humidity (see Table 1).

The storage conditions difference between both samples is important because they introduce variability in biomass properties and will influence the overall pyrolysis behavior, including product yields and properties. To avoid this, pre-treatments such as drying, grinding, and improving storage conditions will be necessary. Long storage time, different humidity levels, and the place where the biomass is stored can enhance partial degradation due to microbial activity, leading to reducing product yields and reducing the quality of the final product (e.g. lower biochar porosity) [11, 12].

**Table 1** Biomass collection conditions

| Sample     | Location                                                | Season | Storage conditions                                                             |
|------------|---------------------------------------------------------|--------|--------------------------------------------------------------------------------|
| Açai stems | El Porvenir, La Trinchera community, Pando, Bolivia     | Autumn | 35 °C -High humidity—Long storage time (more than 2 months) – outdoors storage |
| Cocoa Husk | Chocolates Condor Industries, Caranavi, La Paz, Bolivia | Summer | 15 °C – Low humidity—Short storage time (1 week) – indoor storage              |

## 2.2 Biomass characterization

Proximal analysis (moisture content, the amount of volatile organic compounds (VOC), fixed carbon, and ash content) of the biomass samples was conducted with a Thermogravimetry instrument (TG) NETZSCH Instrument STA 449 F3 Jupiter. The samples were treated with a multi-step heating program. As a first step, the temperature was increased from 25 to 100 °C, at a heating rate of 10 °C/min under inert nitrogen flow (50 mL/min). The temperature was kept at 100 °C for 20 min. After that, the temperature was increased up to 600 °C and kept for 40 min, under the same gas flow and heating rate conditions. Finally, to combust the fixed carbon fraction, the gas composition was changed to oxidative conditions (1:1 nitrogen:air) at the same temperature, 600 °C. The temperature was kept for 30 min until no further changes were observed during the thermal decomposition process. Each experiment used about 30 mg of biomass. The heating conditions and steps were based on the procedure described by Dayton et al. [13]. Additionally, the ash content was also measured by following the TAPPI standard t211 om-02 [14] due to the relevance of the ash content in the overall pyrolysis behavior. Ash content strongly influences the product yield distribution and, also influences the cracking mechanisms modifying the bio-oil composition and increasing the gas fraction [5].

Extractives content was quantified by following the TAPPI standard t204 cm-97 [15]; to do this, 10 g biomass was weighed and dried overnight at 105 °C. The mass of the sample was constantly monitored until no further mass changes were observed. After drying, the sample was introduced to a Soxhlet extraction system to eliminate most of the solvent-extractable substances from biomass. The extraction was performed with a benzene-ethanol mixture (3:1 v/v) at 100 °C for 5 h ensuring that the total number of cycles was 24. After the extraction, the biomass filtered, collected, and dried overnight. The extractives content was then quantified by comparing the final mass with the initial mass. This

procedure ensures that the lignin, cellulose, and hemicellulose content will not be affected for further quantification procedures.

To estimate the lignin, cellulose, and hemicellulose content in the biomass samples, a series of thermal decomposition experiments was performed at different heating rates. To avoid interference from the extractives, this fraction was removed before the TG studies. The analysis was carried out with 30 mg of each sample. The furnace was heated from 25 °C up to 1000 °C in a single step under nitrogen flow (50 mL/min). Five heating rates were studied (2, 5, 10, 15, and 20 °C/min). The results were analyzed and compared in a similar way to the methodology described by Díez et al. [16]. The obtained TG results were processed through signal deconvolution where the shape and intensity of the signals were compared to the reference [16]. Additionally, insoluble lignin and  $\alpha$ -cellulose were quantified by following the TAPPI standards t222 om-02 and t203 cm-99 respectively [14, 17]. These were performed to support the TG results.

## 2.3 Experimental setup: pyrolysis reactor

The pyrolysis tests were performed in a horizontal batch reactor with a Proportional-Integral-Derivative (PID) system to control the temperature (see Fig. 1). Immediately after the stream outlet, three impinger bottles (the first and second filled with Isopropanol, and the third with water) were connected to rapidly condense the bio-oils and to breakdown possible aerosols formed during the condensation as described by Pouyas et al. [18] After the impinger bottles, a silica gel column was installed to eliminate any remaining moisture from the gas stream. Finally, the gas output was connected to an online gas analysis system to quantify the CO and CO<sub>2</sub> concentrations. However, the pyrolysis system was not able to collect all the gases generated during the pyrolysis; thus, the analyzed gas composition was limited to a ratio between CO and CO<sub>2</sub> as mentioned above.

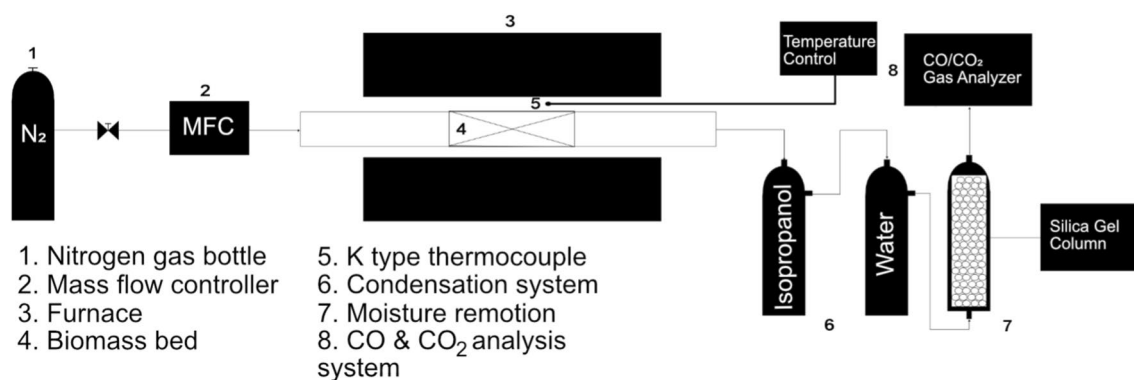


Fig. 1 Pyrolysis setup schematics

## 2.4 Pyrolysis experiments conditions and product characterization

The biomass samples were dried overnight at 100 °C as a strategy to prolong the storage time by avoiding bacterial or fungal contamination. A ceramic boat with approximately 1 g of pre-dried biomass was placed inside the pyrolytic reactor at 500 °C for 30 min. The pyrolysis experiments were performed under inert conditions with nitrogen (200 mL/min). Three types of products were biochar obtained, bio-oils, and biogases.

After the pyrolysis was complete, the gas flow was increased to cool down the furnace before weighing the biochar. The biochar yield was quantified by comparing the final weight with the initial biomass weight. Properties such as pH and density were measured according to the European Biochar Certificate (EBC) [19]. Regarding the bio-oil fraction, the yield was quantified by registering the mass difference of the impinger bottles. Immediately after quantifying the yield, an aliquot of the bio-oil in isopropanol was taken to the gas chromatography (GC) instrument to analyze the main components present in the isopropanol fraction. An analogous analysis was performed with oil directly condensed in a separated system and then diluted in isopropanol to identify the water-soluble compounds. It is important to identify the main products such as furans, phenolics, and long-chain hydrocarbons because these can be treated afterwards to produce biofuels and other added-value products. The GC analysis was performed in an Agilent Gas Chromatographer 7890B coupled with a Mass Spectrometer 5977A MSD as a detector. The pH and the density of the bio-oils were measured with different condensation systems,

avoiding the use of solvents. Finally, the biogas yield was estimated from the biomass mass balance. The CO and CO<sub>2</sub> composition was recorded with the gas analysis system.

Scanning electron microscopy (SEM) was used to study the morphology and the textural properties of the samples before (biomass) and after (biochar) the pyrolysis. The samples were crushed and dried at 105 °C for 48 h. A double-sided carbon tape was used to fix the samples in alumina stubs. The images were collected with a Thermo Fisher Scientific Apreo 2 s LoVac SEM with a field emission gun, coupled to an energy dispersive spectroscopy (EDS) system. The images were taken with an average working distance of 7 mm at different magnification levels. Elemental qualitative analysis was also performed by using EDS as a detector. The applied voltage and current were 20 kV and 26 nA, respectively. By using SEM–EDS, it is possible to observe changes in the porosity and the elemental composition of the biochar; this is important because biochar can be applied as a soil amendment agent.

## 3 Results and discussion

The results of the study are presented as follows.

### 3.1 Proximal analysis

The thermal decomposition curves of açai stems and cocoa husk are shown in Fig. 2. The green region shows the experimental procedure under inert atmosphere, and the red one, the moment where the atmosphere was changed to an oxidative one. The green lines show the different regions observed

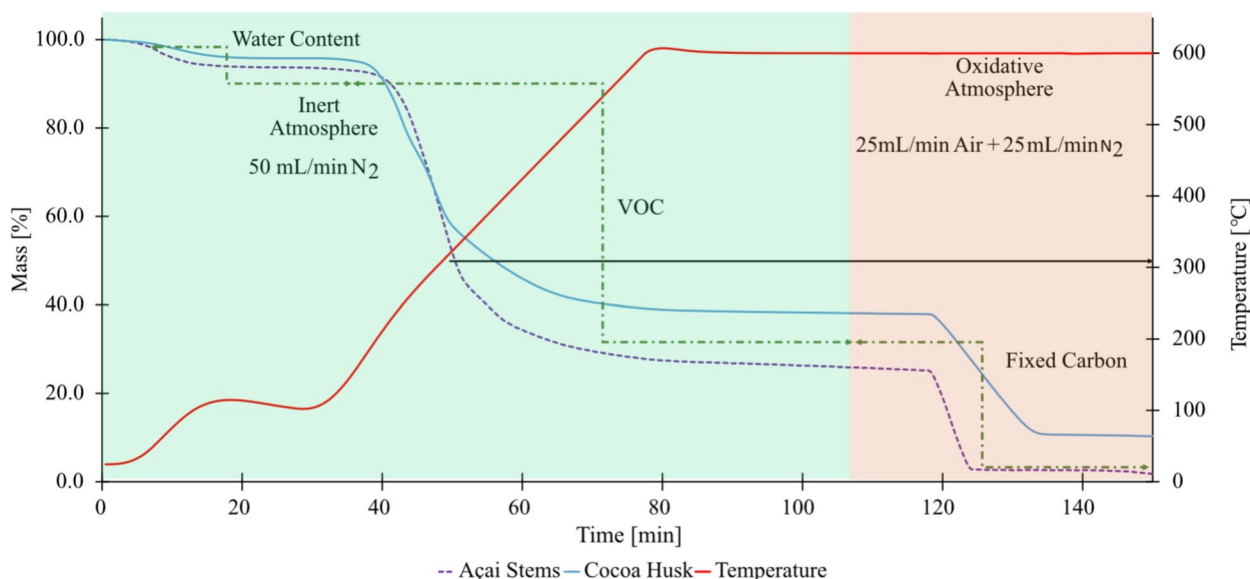


**Fig. 2** TG curves for proximal analysis quantification

along the experiment representing the changes related to water, volatile fraction, and fixed carbon elimination, respectively. The proximal analysis is an important step to quantify the amount of water in order to sufficiently dry the biomass before introducing it into the pyrolysis reactor. Additionally, it is important to know the fraction of fixed carbon from the biomass that will define the maximum amount of biochar to be produced. This becomes important during the application of the products. Knowing the fixed carbon content is necessary to design the pyrolysis process to get the highest biochar yield. Also, by controlling the operation parameters, it is possible to promote higher porosity and basic pH that are good parameters to treat different soil types.

The proximal analysis results from TG in Table 2 show that both cocoa husk and açai stems are within similar ranges of moisture, and volatile matter content. Regarding the fixed carbon, the açai stems have higher values, which means that the expected biochar yield should be higher for açai stems than for cocoa husk. However, the most significant distinction lies in the ash content, where the açai stems have about twice the amount of ash compared to the cocoa husk. The obtained results show a broad distribution that is common for agricultural and lignocellulosic biomass [20, 21]. Due to the variation in the storage conditions and the non-homogeneity of the raw materials, the values are reported as ranges.

In both cases, the ash content is higher than conventional biomass sources [22]. When the results are compared to

other biomasses types such as rice straw, and corn stover the levels of ashes are within a reasonable range. However, for açai stems, have a considerably higher quantity of ash. Depending on the final application of the products, the high ash content might be problematic. For bio-oil recovery, a high ash content in the raw material will reduce the heat capacity of the obtained bio-oil [23]. However, the high ash content might be beneficial for the biochar properties, especially in the nutrient content as long as the biochar does not release heavy metals [24].

### 3.2 Cellulose, hemicellulose, and lignin content

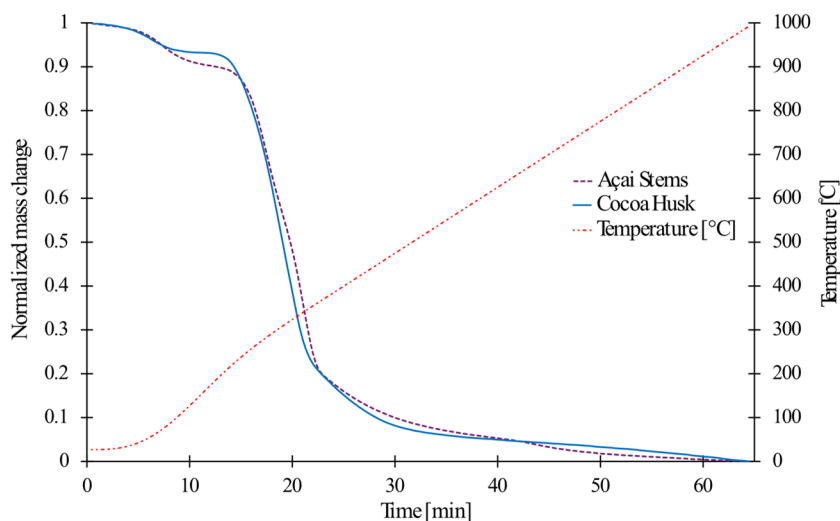
After the remotion of the extractives, the thermal decomposition curves of açai stems and cocoa husk were obtained at different heating rates (2, 5, 10, 15, and 20 °C/min) to estimate the cellulose, hemicellulose, and lignin content. Figure 3 shows the normalized TG curves of a single-step heating process from 25 to 1000 °C at a heating rate of 15 °C/min.

To properly observe the mass changes and to estimate the composition of the different fractions, the derivative thermal gravimetric analysis (DTG) results were processed with the software OriginPro 2023. DTG curves were fitted into five signals through a deconvolution process shown in Fig. 4. The pseudo component (PC 1) was assigned to water elimination due to it appearing at a low-temperature range

**Table 2** Proximal analysis summary for cocoa husk, açai stems, and reference biomass values

| Properties            | Cocoa Husk | Açai Stems | Brazil Nut<br>Endocarp [21] | Rice Straw [20] | Corn Stover [20] |
|-----------------------|------------|------------|-----------------------------|-----------------|------------------|
| Moisture [%]          | 2.2–4.1    | 4.4–6.7    | 8.5                         | 4.2–6.0         | 5.3–7.4          |
| Volatile fraction [%] | 55.6–58.4  | 51.8–62.4  | 40.2                        | 71.6–92.8       | 86.5–96.8        |
| Fixed Carbon [%]      | 25.0–25.5  | 20.8–32.9  | 59.1                        | 14.5            | 16.9             |
| Ashes Content [%]     | 11.5–15.3  | 25.9–31.9  | 0.8                         | 8.2–16.0        | 4.2–6.3          |

**Fig. 3** TG curves of açai stems and cocoa husk for cellulose, hemicellulose, and lignin quantification



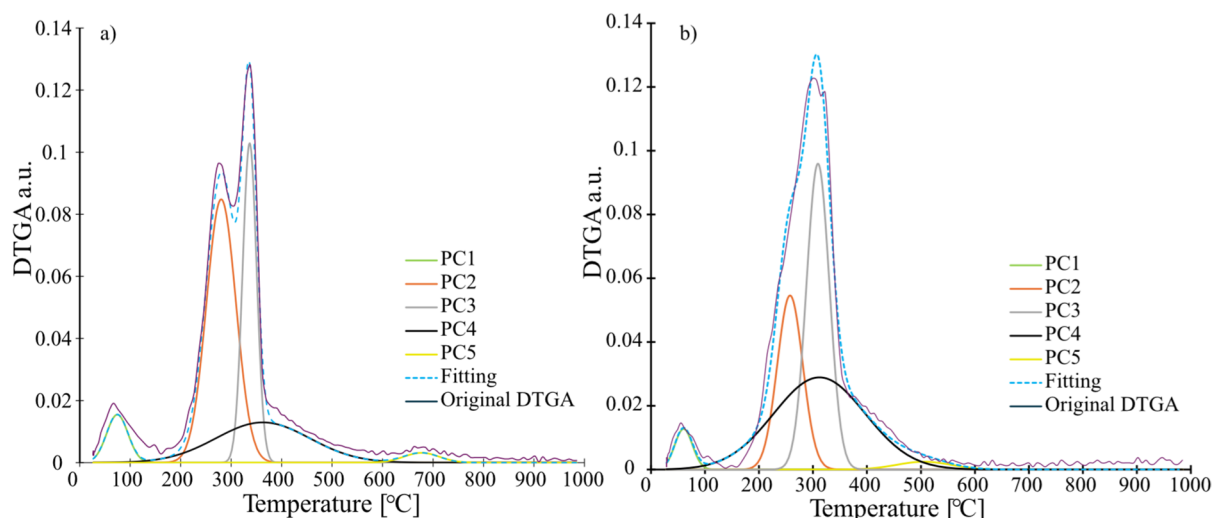


**Fig. 4** Deconvoluted DTG curves. **a)** Açai stems, and **b)** cocoa husk

(below 120 °C). PC 2 and PC 3 appeared between 200 °C and 400 °C indicating rapid decomposition, that resulted in sharp signals compared to the other signals. This behavior is common for cellulose and hemicellulose [3]. Consequently, the combined signals will be represented as the holocellulose fraction. Finally, PC 4 and PC 5 were assigned to lignin due to a lower decomposition temperature (PC4) and broad signals, indicating a slow decomposition rate. It is known that the presence of lignin will reduce the pyrolysis rate and it will increase the fraction of biochar [2]. All the signal assigning was performed by comparing the shape and the temperature range with the reported results by Díez et al. [16].

The structural composition was estimated by integrating the area of each deconvoluted signal shown in Fig. 4. The extractives, holocellulose, and lignin content are summarized in Table 3. In both biomass samples, the lignin content is the major individual component reaching values of 25% for açai stems, and 32% for cocoa husk. The lignin content is relevant for the production of bio-oils because it comprised of phenolic and aromatic compounds [25]. Regarding the soluble lignin content, it is worth to mention that cocoa husk has higher content (22%); this is interesting because soluble lignin contributes in the formation of more bio-oil. In the case of açai, the insoluble lignin is higher (16%); therefore, this contributes to producing higher biochar yields [26], which will mainly contribute to biochar formation while the soluble lignin generates bio-oil. It will be necessary to separate or upgrade the phenolic compounds to reduce the reactivity of the bio-oil [25]. Even though the samples have different cellulose and hemicellulose content, the overall holocellulose content is in the same range: 32% and 38% for açai stems and cocoa husk, respectively. Also, the  $\alpha$ -cellulose content is pretty similar for both biomass

**Table 3** Biomass fraction composition, extractives, cellulose, hemicellulose, and lignin content

| Biomass             | Açai Stems | Cocoa Husk | Rice Straw [20] | Corn Stover [20] |
|---------------------|------------|------------|-----------------|------------------|
| Extractives [%]     | 0.8        | 4.4        | N.A             | N.A              |
| Holocellulose [%]   | 32         | 38         | 56              | 64               |
| $\alpha$ -Cellulose | 7.4        | 8.1        | N.A             | N.A              |
| Cellulose [%]       | 12         | 28         | 32              | 38               |
| Hemicellulose [%]   | 20         | 10         | 24              | 26               |
| Lignin [%]          | 25         | 32         | 18              | 19               |
| Insoluble lignin    | 15.9       | 9.2        | N.A             | N.A              |
| *Soluble lignin     | 9.1        | 22.8       | N.A             | N.A              |

The total percentage obtained from the chemical structural composition analysis excludes water and ash content

\*The soluble lignin content was calculated by subtracting the insoluble lignin from the total lignin content

samples. The main contribution of holocellulose is the formation of volatile matter, free sugars, aldehydes, ketones, and other non-aromatic compounds [3].

### 3.3 Biomass pyrolysis and product characterization

Table 4 summarizes the overall product yield distribution and some physicochemical properties of each product. The biochar yields are similar for both samples, with approximately one third of the initial biomass having been transformed into biochar. Considering the high lignin content (see Table 3), it was expected to have these biochar yields. The lignin is the main contributor to the solid fraction with

**Table 4** Pyrolysis products distribution and properties

| Product  | Properties         | Cocoa Husk   | Açaí Stems   | Units             |
|----------|--------------------|--------------|--------------|-------------------|
| Biochar  | Yield              | 38.1 ± 1.7   | 33.9 ± 2.0   | %                 |
|          | Density            | 401.7 ± 28.3 | 287.2 ± 37.3 | kg/m <sup>3</sup> |
|          | pH                 | 10.1–10.8    | 10.5–11.6    | -                 |
| Bio-oil  | Yield              | 33.6 ± 17.6  | 17.0 ± 0.8   | %                 |
|          | Density            | 0.24 ± 0.03  | 0.31 ± 0.02  | g/mL              |
|          | pH                 | 2.2–3.0      | 3.1–3.9      | -                 |
| Biogases | Yield              | 28.1 ± 17.6  | 49.1 ± 2.4   | %                 |
|          | CO/CO <sub>2</sub> | 0.46 ± 0.01  | 0.76 ± 0.09  | mol/mol           |

minor contributions of secondary reaction between the volatile matter with the surface [3, 27]. However, considering the insoluble lignin content, it was expected to get higher biochar yields with açaí stems than with cocoa husks. The main reason behind this behavior lies in the high ash content of açaí stems (up to 32%), as mentioned above higher ash content promotes higher gas yields [5, 26]. The combination of low-density with the basic nature of the biochar obtained (high pH) suggests that the biochar can be suitable for soil amendment applications [28].

Regarding the biogas fraction, the yields are significantly different for the two types of biomass samples. The high biogas yield for açaí stems was promoted by the higher ash content (up to 32%) [5]. Furthermore, the obtained gases

from açaí stems would have a higher combustion heat capacity than the ones obtained from the cocoa husk due to higher yields with a higher CO/CO<sub>2</sub> ratio. The combustion of pyrolysis gases is a way to reduce the dependence on fossil fuels in rural areas and also contributes in the environmental aspect considering that pyrolysis products are neutral carbon emission processes [29]. Nevertheless, to get energy from pyrolysis gases, some treatments are necessary to avoid emissions, particulate matter, and other problems [29].

The main components identified from the bio-oil fraction with the GC/MS instrument are summarized in Table 5. It can be noticed that the overall oil composition is primarily based on oxygenated compounds (sugars, ketones, alcohols, and others); this is the main reason behind the acidic pH and the highly reactive nature of bio-oils [30, 31]. The majority of the obtained compounds are also commonly found in different biomass pyrolysis studies, products such as phenol, p-cresol, catechol, benzenediol derivatives, and others are reported in different literature sources [32–35]. However, less common compounds offer a wide range of potential applications due to their diversity. For example, maltol, D-Allose, 2-methyl furan, and benzoic acid are generally used in the food industry, as flavoring substances, or flavor enhancers (maltol). Compounds such as hydroquinone, acetamide, and 2-pentanone are used as solvents, or as pain relieving additives. Additionally, considering the relative proportions from the reported peak areas, açaí stems have

**Table 5** Bio-oil components detected using a GC/MS instrument

| Biomass | Cocoa Husk |                                |               | Açaí Stems |                           |               |
|---------|------------|--------------------------------|---------------|------------|---------------------------|---------------|
| Peak #  | RT [min]   | Compound                       | Peak Area [%] | RT [min]   | Compound                  | Peak Area [%] |
| 1       | 3.01       | 1-hydroxy-2-Propanone          | 13.6          | 3.00       | 1-hydroxy-2-Propanone     | 11.7          |
| 2       | 4.33       | Tetrahydro-3-furanol           | 2.0           | 3.49       | Propanoic acid            | 4.1           |
| 3       | 5.57       | Furfural                       | 4.6           | 4.01       | Pyridine                  | 1.1           |
| 4       | 6.03       | 2-Furanmethanol                | 2.1           | 4.47       | Acetamide                 | 1.7           |
| 5       | 6.07       | 2-Pentanone                    | 3.4           | 4.60       | 2,3-Butanediol            | 1.7           |
| 6       | 6.33       | 1-(acetyloxy)-2-Propanone      | 2.5           | 5.24       | 2-methyl-Pyridine         | 1.7           |
| 7       | 6.55       | 2-(1-methylethoxy)-Ethanol     | 6.5           | 5.56       | 2-methyl-Furan            | 1.9           |
| 8       | 7.57       | 1,2-Cyclopentanedione          | 3.1           | 6.07       | 2-Furanmethanol           | 4.3           |
| 9       | 8.94       | Phenol                         | 29.4          | 7.25       | Butyrolactone             | 3.1           |
| 10      | 9.91       | 3-methyl-1,2-Cyclopentanedione | 3.5           | 8.46       | 2,4-Dimethylfuran         | 2.0           |
| 11      | 11.03      | p-Cresol                       | 1.3           | 8.93       | Phenol                    | 2.8           |
| 12      | 11.34      | 2-methoxy-Phenol               | 8.3           | 11.81      | Maltol                    | 1.4           |
| 13      | 13.00      | Benzoic acid                   | 1.2           | 13.73      | Catechol                  | 8.6           |
| 14      | 13.56      | Creosol                        | 1.3           | 14.97      | 3-methoxy-1,2-Benzenediol | 1.6           |
| 15      | 13.68      | Catechol                       | 3.5           | 15.42      | Hydroquinone              | 1.3           |
| 16      | 14.95      | 3-methoxy-1,2-Benzenediol      | 3.7           | 15.58      | 4-methyl-1,2-Benzenediol  | 1.8           |
| 17      | 15.32      | 4-ethyl-2-methoxy-Phenol       | 1.4           | 16.69      | 2,6-dimethoxy-Phenol      | 2.3           |
| 18      | 16.68      | 2,6-dimethoxy-Phenol           | 5.9           | 19.19      | D-Allose                  | 1.8           |
| 19      | 24.91      | Caffeine                       | 1.0           | 24.93      | Caffeine                  | 37.2          |
| 20      | 25.31      | Theobromine                    | 1.7           | 25.39      | Theobromine               | 8.1           |

37.2% of caffeine (from the extractives content) which might be worth extracting due to its importance as a precursor for some pharmaceutical drugs. For all these compounds, an extra treatment will be necessary to isolate and properly get valuable products. One of the most used techniques to separate high value compounds is successive extraction with different solvents and purification steps. The use of solvents such as water, ethers, dichloromethane, and others allows the purification of interesting compounds [36].

Another application of the bio-oils can be biofuel production by catalytic upgrading, which is performed to reduce the oxygen content. Considering that most of the compounds identified in the bio-oil have five or more carbon atoms, it will be possible to get a biofuel with higher stability and to increase the octane number due to deoxygenation, hydrogenation, and isomerization reactions during the catalytic process [30, 37]. To perform the upgrading of the bio-oil, the samples are treated at high pressures (up to 40 MPa) and high hydrogen concentrations. The bio-oil reacts with the metallic sites and the oxygenated functional groups are

removed from the molecules (the bond cleavage depends on the active metal site) [38, 39]. By reducing the oxygen content, the bio-oil stability will increase, and other properties such as viscosity, pH, and density will also get improved [38, 39].

Figure 5 shows the cocoa husk before and after the pyrolysis process. Before pyrolysis, the biomass exhibits surface porosity, with two distinct shapes observable. Although the main structure can still be observed after the pyrolysis, there is a noticeable increase in surface porosity. The fixed carbon keeps mostly the overall structure, and the degradation of the volatile fraction produces the new porosity [40, 41]. This behavior is typical for biochar samples of lignocellulosic biomass. To properly compare the morphology and the surface of both samples different magnification degrees were applied.

Figure 6 shows the SEM images of açai stems before and after the pyrolysis process. The major changes discussed for cocoa husk were also observed for açai stems indicating that the thermal treatment increased the overall surface porosity

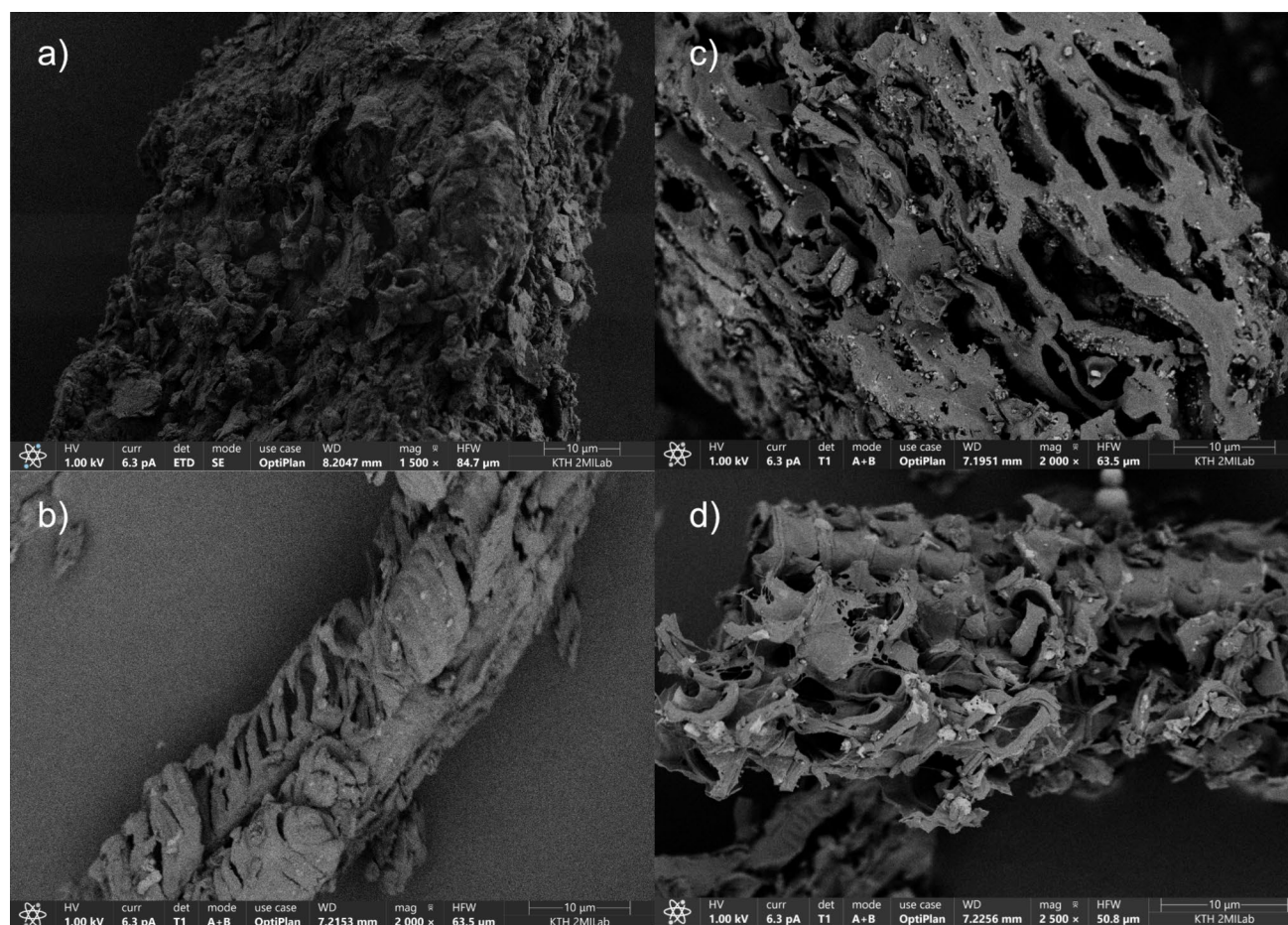


**Fig. 5** SEM Images of cocoa husks before (a–b) and after (c–d) pyrolysis a) cocoa husk magnification 1500×, b) cocoa husk magnification 2000×, c) cocoa husk biochar magnification 2000×, and d) cocoa husk biochar magnification 2500×

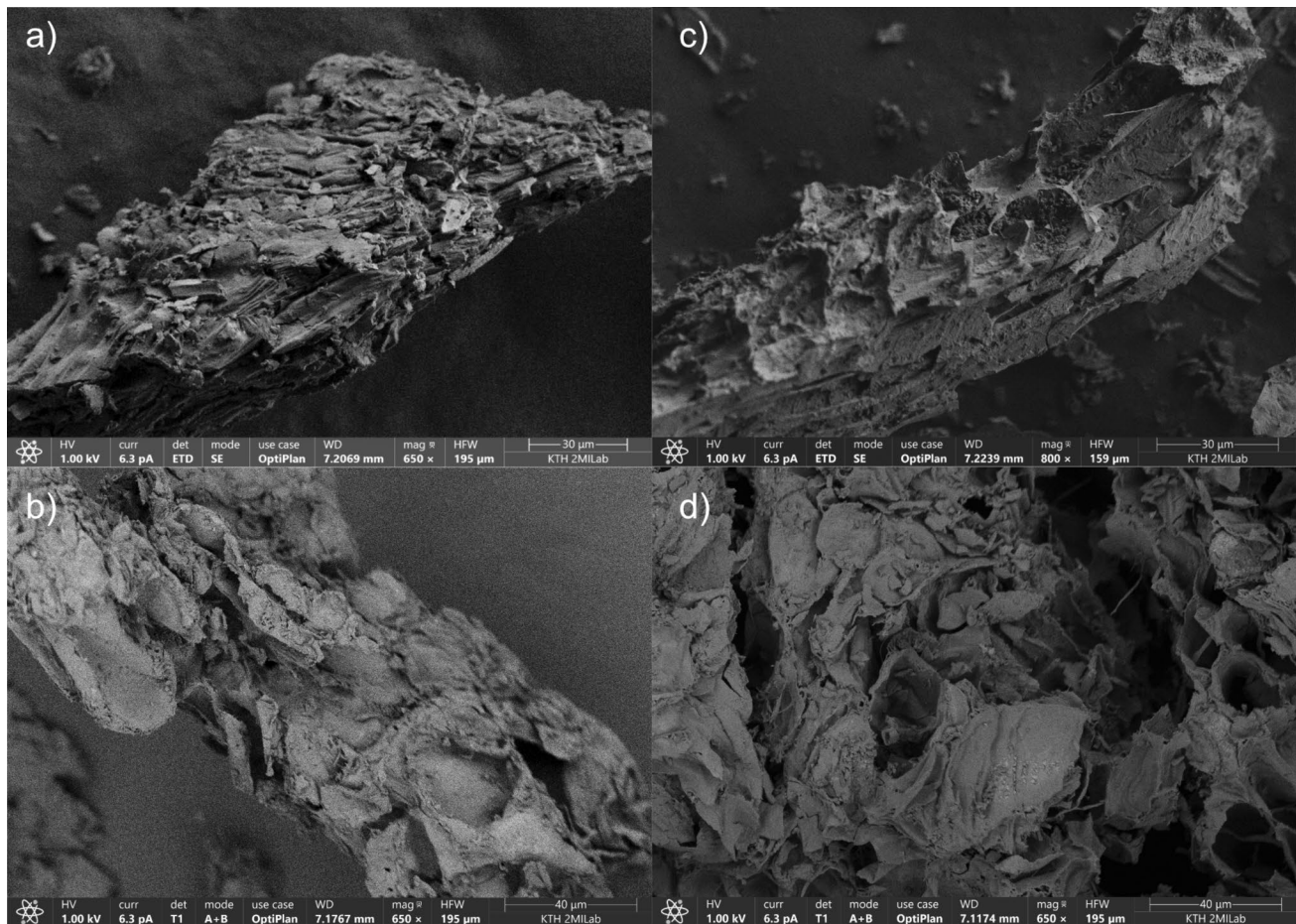


**Fig. 6** SEM Images of açai stems before (a–b) and after (c–d) pyrolysis. **a)** açai stems magnification 650×, **b)** açai stems magnification 800×, **c)** açai stems biochar magnification 650×, and **d)** açai stems biochar 650×

keeping the same shape and morphology. Therefore, both açai stems and cocoa husk show morphological changes after the pyrolysis as expected [40, 41].

The biochar obtained, and the raw biomass samples were studied with a SEM–EDS instrument to compare the changes in the morphology and surface qualitative elemental composition before and after the pyrolysis tests. Carbon, potassium, phosphorus, and magnesium were the major elements found in the cocoa husk biochar as shown in Fig. 7. Additionally, other elements such as calcium, and silica were detected in minor proportions (from elemental mapping). Regarding the açai stems biochar carbon, calcium, phosphorus, and silica were the detected elements with the highest concentration (see Fig. 8). Additionally, phosphorus and magnesium were found on the surface of the biochar obtained.

The EDS results show the presence of potassium, phosphorus, magnesium, and calcium, which are commonly reported as beneficial for the soil properties due to their properties as nutrients during the growing stage of the plants [42, 43]. Moreover, it is important to mention that no harmful or heavy metals were

found on the surface of the obtained biochar. The measured properties of the obtained biochar samples strongly suggest that it is possible to apply them for soil amendment. Higher surface porosity is related to an increase in the water-holding capacity and nutrients retention on biochar [44]. Moreover, the basic pH is good for acid soils treatment. Also, the lack of heavy metals is a good indicator to show that the biochar is suitable for soil amendment [45]. However, to properly do this, further research is needed. Considering the environmental aspect, applying biochar can contribute by absorbing CO<sub>2</sub> and CH<sub>4</sub> [46]. Moreover, its application as carbon credits can also be beneficial in the economic aspect, contributing to the development of rural areas [47].

## 4 Conclusions

Açai stems and cocoa husk were tested under pyrolysis conditions to explore various applications for these residues that are commonly generated in different regions of

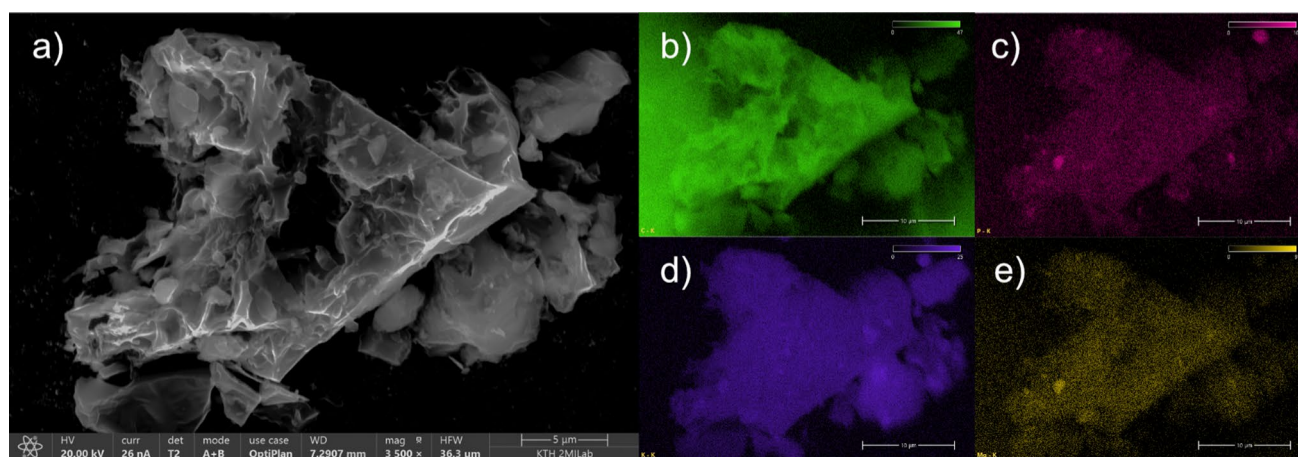


**Fig. 7** Cocoa Husk biochar elemental composition with EDS. **a)** Cocoa Husk biochar SEM photo magnification 3500×, **b)** carbon image mapping, **c)** phosphorus image mapping, **d)** potassium image mapping, and **e)** magnesium image mapping

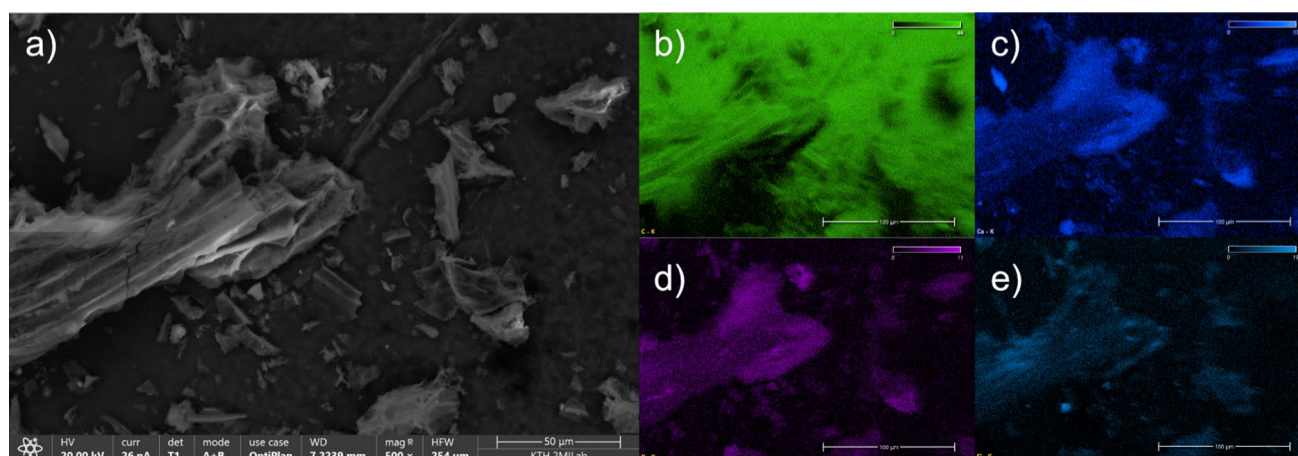


**Fig. 8** Açai Stems biochar elemental composition with EDS. **a)** Açai Stems biochar SEM photo magnification 500×, **b)** carbon image mapping, **c)** calcium image mapping, **d)** potassium image mapping, and **e)** silicon image mapping

South America. The proximal analysis results show a low moisture content for both samples and a relatively high ash content. The biochar obtained has a high pH (above 10) and low density, making the biochar suitable for its application in acidic soils. SEM images show that the main particle morphology was kept after the pyrolysis and an increment in the overall porosity was also observed. Moreover, the EDS results show that there are no harmful elements on the surface of the biochar samples. The combination of these properties makes the biochar suitable as a soil amendment agent. Furthermore, the use of biochar in soils can absorb  $\text{CO}_2$  and  $\text{CH}_4$  improving the quality of the air and fixing more carbon into the soil. Another advantage of applying biochar is that the carbon is fixed in the soil avoiding further emissions; therefore, it can be used as carbon credits, contributing to the economy of the region (in this case the rural areas).

If the desired application of the pyrolysis process is biofuel production, the minerals present in the biomass should be removed to avoid stability problems or catalyst deactivation. Moreover, due to the presence of alcohols, ketones, acids, and aromatic compounds, the bio-oil fraction will require a catalytic upgrading step to reduce the concentration of oxygenated compounds in order to improve the stability and quality of the final biofuel. Other treatments can also be implemented to get valuable products from the obtained bio-oil fraction. The use of solvents to perform successive extractions is a way to get valuable compounds such as maltol, benzoic acid, D-allose, tetrahydro-3-furanol (found in the bio-oil). However, considering the source of the biomass, it will be more interesting to aim towards bio-fuels production to reduce the rural areas dependence on fossil fuels, producing cleaner energy and using residues that nowadays are just getting accumulated

in the fields. Finally, the obtained CO/CO<sub>2</sub> ratios show that açai stems biogas is more suitable for electricity generation than cocoa husk, due to higher CO concentration in the obtained biogas. The use of pyrolysis gases as a source of cleaner energy also contributes to reducing the dependence on fossil fuels.

In summary, açai stems and cocoa husk were successfully tested as renewable resources for the production of added-value products such as biochar, bio-oils and pyrolysis gases. The biochar has characteristics to be applied as soil amendment agent due to its properties, while the bio-oil requires catalytic upgrading processes to produce bio-fuels. Finally, the pyrolysis gases can be applied for electricity generation. Therefore, both biomass samples are suitable materials to positively contribute to the economy of rural areas while reducing the environmental impact of fossil fuels, and at the same time provide the opportunity of transforming underutilized resources. Further research will enhance our understanding of the feasibility of scaling up the process and getting added-value products from these biomass residues.

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## Declarations

**Competing interests** The authors declare no competing interests.

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