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Thermoanalytical study of inner and outer residue of coffee harvest

Applications on biomass

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Abstract The better use of agricultural residues is expected, when they are mostly disposed of improperly and it is often burned in the natural environment. This study of the thermal decomposition of residues was performed from the coffee crop for energy purposes and in this case was used thermal analysis techniques for such assessment. The TG/DTG and DSC curves showed that the thermal decomposition occurs in four consecutive events and it is predominantly exothermic. The first mass loss evidenced in TG/DTG curves has an endothermic peak in DSC curve, which it can be associated with the water liberation of the material. This first thermal event also can be related to the liberation of volatile compounds present in the sample, which is also corroborated by the endothermic peak. The other events of mass loss are related with the thermal decomposition of the material. This decomposition has an exothermic behavior, which is positively applied to the main aim of this scientific research: the coffee straw use like biomass energy font. The thermoanalytical techniques were satisfactory in the characterization of this material.

Keywords TG/DTG · DSC · Coffee straw · Biomass

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Introduction

Several materials such harvest residues and crops or even leftovers of processed products are improperly disposed in the rural environment. These materials are contributing for the pollution and degradation of soils and waters, which facilitates the proliferation of disease vectors. This factor implies directly into the non-exploitation of this soil as a source of extra income. This does not serve as a raw material for other products.

Much of the residual organic matter is improperly treated and it is contributing in an undesirable way in the biosphere changes, especially in low-income countries where the reuse of organic waste is not a common practice, while large amounts of these products are burned in the fields or are used as a domestic fuel.

Of several agricultural cultures in the Brazil, the coffee planting is distinguished by its large scale production, since Brazil is the world's largest producer, with an average value of 30% of production [1].

Many studies have been conduced to evaluate the potential of using agricultural byproducts proceeding from the processing of coffee, transforming them into raw materials as an alternative to avoid environmental disorders [2–9]. Several works with the coffee straw has been studied in Brazil in order to add value to this residue [9–16].

Studies indicate that 55% of dried fruits represent the grains, 29% the pulp, 12% the bark, and 4% the mucilage. Therefore, 45% of production of a determined area is considered as waste [17]. The implementation of a good use of the organic residue of the coffee crops contributes to minimizing the negative aspects in the environment and creates energy alternatives for the country.

In this scientific investigation, the thermal behavior of the inner, the outer, and the mixture of inner and outer

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straw of coffee was carried out to evaluate the potential use of this material as biomass energy. The thermal behavior was obtained by the thermal analytic techniques: Thermogravimetry/Derivative Thermogravimetry (TG/DTG) and Differential Scanning Calorimetry (DSC) that it has been widely used for characterization of several biomasses [18, 19].

Materials and methods

The selected biomass for this study is proceeding from the region of *Três Pontas*, located in the state of Minas Gerais-Brazil, whose city is considered the Capital of the World Coffee [20]. The material was packed in bags, manually homogenized, and the samples were taken randomly.

The TG/DTG curves [21] were performed in a thermobalance TGA-51, Shimadzu, using a dynamic atmosphere of air with a flow rate of 50 mL min^{-1}, temperature range between 25 and 900 °C, with heating rate (β) of 10 °C min^{-1} and sample mass of 25 mg. The DSC curves [22] were obtained in a DSC 50 cell, Shimadzu, using dynamic atmosphere of nitrogen (N_2) with a flow rate of 100 mL min^{-1}, temperature range from 25 to 550 °C, with β of 10 °C min^{-1} and sample mass of 2 mg.

Results and discussion

The coffee straw in nature is a mixture of the inner and outer parts. The grain has a light color wrapper (inner straw), which is coated with a dark color layer and it is defined as outer straw. At the beneficiation stage of coffee grains, the outer straw is also known as the heaviest part, while the inner straw is lighter color, more brittle, and lighter.

In order to characterize the layers isolated, the inner and the outer straw was manually separated (Fig. 1).

Fig. 1 Photo of the Inner coffee straw (*light*) and outer coffee straw (*dark*)

Table 1 Mass loss/% and decomposition range of temperature/°C of each thermal event in the coffee straw

$[T_i–T_f]$/°C	Δm/%		
	Outer	Inner	Mixture
25–150	10.04	8.55	11.18
150–400	43.19	51.20	44.15
401–580	27.83	34.95	32.35
581–900	5.08	2.08	2.46
25–900	86.13	96.77	90.15
Residue[a]	13.87	3.23	9.85

[a] After 900 °C

Table 2 Enthalpy variation/J g^{-1}, onset and peak temperatures/°C of endothermic event

Sample	T_{onset}/°C	T_{peak}/°C	ΔH/J g^{-1}
Outer	27.0	64.5	223.4
Inner	20.0	54.3	317.5

Table 1 shows the mass loss and the respective temperature range for each thermal event. Table 2 has the enthalpy data, onset temperature, and peak temperature of the endothermic event, which was related to the dehydration of the material under study. These data were obtained from the TG/DTG and DSC curves of the samples mentioned above (Figs. 2, 3).

Inner straw

The TG/DTG curves of the inner straw sample (Fig. 2a) show a thermal decomposition in five consecutive steps, while the third and the fourth are concomitants. Similarly to the outer straw sample, the first event of mass loss (up to 150 °C) may be related to the dehydration of the material under study, which is associated with a variation of 8.6% of mass. This event also can be associated with the thermal liberation of volatile compounds. The second and third mass losses are related to the thermal decomposition of the material under study, with a total variation of 86.2%. The third thermal event occurs in two consecutive and concomitant steps: before the end of the third thermal decomposition, the fourth event of mass variation starts. The inner straw decomposes almost completely, remaining a residual mass of 3.2% of the original mass. It is notorious the increase of mass loss percentage in the event that is supposed to be the thermal decomposition of the organic matter (second, third, and fourth thermal events). In contrast, a decrease in the residual mass observed, which was associated to the existence of an inorganic material, due to the final temperature value (900 °C).

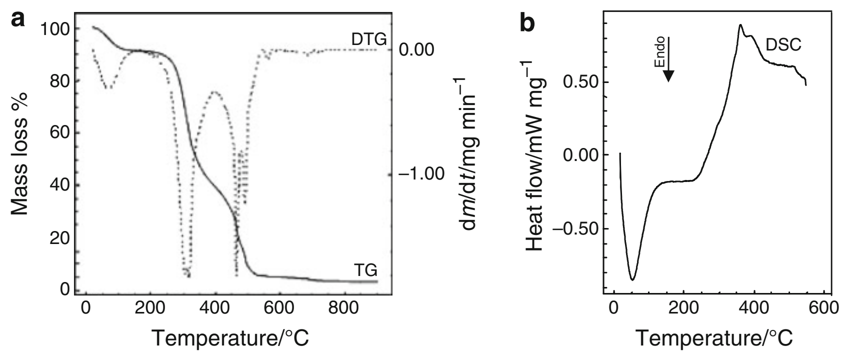

Fig. 2 **a** TG/DTG curves of inner coffee straw. **b** DSC curve of inner coffee straw

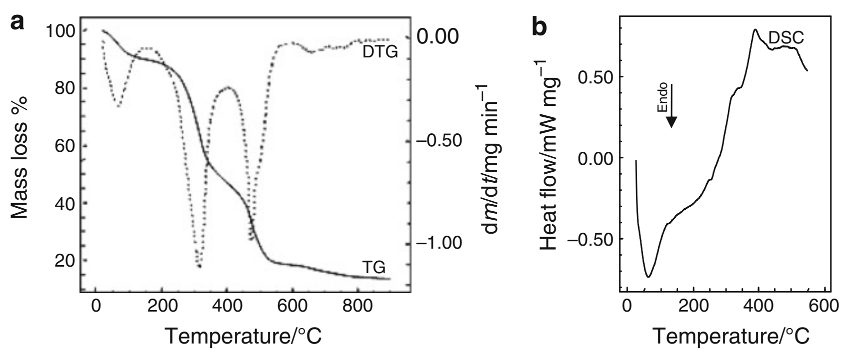

Fig. 3 **a** TG/DTG curves of outer coffee straw. **b** DSC curve of outer coffee straw

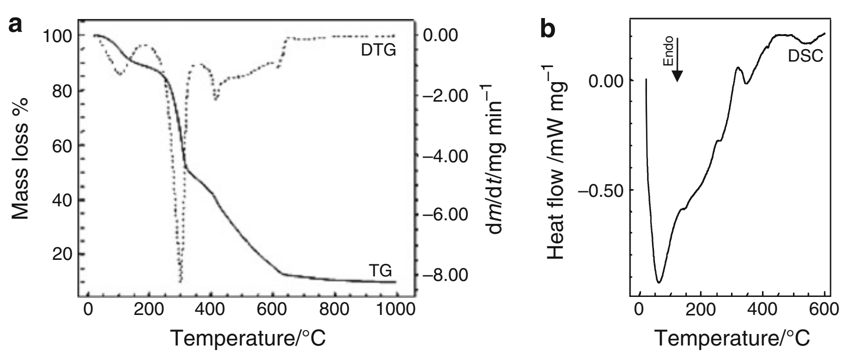

Fig. 4 TG/DTG (**a**) and DSC (**b**) curves of the mixture of outer and inner coffee straw

The DSC curve of the inner straw sample (Fig. 2b) has the same profile of the outer straw sample and evidences an endothermic event at the beginning, followed by consecutive and concomitant exothermic events. This event corroborates the data obtained from TG/DTG curves for the first event of thermal decomposition confirming a possible dehydration of the material.

Outer straw

The analysis of TG/DTG curves (Fig. 3a) allowed to infer that the thermal decomposition of the outer straw sample occurs in four consecutive stages. The first event of mass variation (up to 150 °C) is related to the release of water or sample dehydration, which is associated with 10% of mass loss. The following events are related to the thermal decomposition of the material. The second and third events are related to the thermal decomposition of the organic matter present, totalizing 71% of mass loss. However, it can be suggested that the fourth thermal event, which starts at 580 °C and which is related to the thermal decomposition of some inorganic compound present in the sample. This hypothesis is based on the fact that at 500 °C a few organic compounds are thermally stable and also because the decomposition represents only 5% of the initial mass. The decomposition of this material is not complete until the temperature of 900 °C, i.e., the presence of a residue of approximately 14% of original mass is observed. Since this residual mass does not decompose until this temperature, it is suggested the presence of inorganic material. This

Table 3 Enthalpy variation/J g^{-1}, onset and peak temperatures/°C for a mixture of inner and outer samples

Event		ΔH		T_{onset}/°C	T_{peak}/°C
Number	Characteristic	Type	Value/ J g^{-1}		
1°	Dehydration	Endothermic	353.0	23.7	62.1
2°	Decomposition	Exothermic	249.0	280.7	494.2

greater amount of inorganic material on the outer straw allows the material to resist more to the tension, characteristic presented by its hardness.

The DSC curve of the outer straw sample (Fig. 3b) shows an endothermic event at the beginning (up to 110 °C, approximately), after this endothermic peak the curve only shows an exothermic events of thermal decomposition. The endothermic peak is associated with the sample dehydration corroborating the data from the TG analysis. The thermal decomposition of the material occurs, in energetic terms, in an exothermic form with consecutive and concomitant events.

Inner and outer straw mixture

The TG/DTG curves of the inner and outer straw coffee mixture (Fig. 4a) show successive events of mass variation, some of which are consecutive while others are concurrent. The first mass loss observed is related to the release of water present in the sample, as discussed before. From the DSC curve of the sample (Fig. 4b) was made an estimative of the enthalpy variation found in the process of thermal decomposition of the sample. It was an estimated by the fact that it has its decomposition process to a temperature higher than 600 °C observed by the thermogravimetric technique. The experimental value obtained was 249.0 J g^{-1} with $T_{onset} = 280.7$ °C. This onset temperature can be associated with the start of the thermal decomposition of organic material present, in others words, with the start of the carbonization of the sample. In the TG/DTG curves, this event is evidenced in the second mass loss, amounting to 40.5% in mass.

Table 3 shows the values obtained from the DSC curve of the mixture of the inner and outer samples. The value for enthalpy of decomposition is a value close to the real one because after the analyzed temperature part of the sample even is being decomposed.

Conclusions

The TG/DTG curves allowed inferences about the amount of water present in the samples, as well as to discuss the residual mass. Regarding to the "hardness" from inner and outer coffee straw, it can suggest a correlation with the organic and inorganic material present in each sample. The DSC curves corroborated with TG data for the thermal dehydration of the material under study. From these curves, it can be concluded that the thermal decomposition of the material is exothermic and it is indifferent whether it is the inner or the outer part of the coffee straw.

The value for the enthalpy of decomposition for the mixture is a value close to the real one because after the analyzed temperature part of the sample even is being decomposed. From the viewpoint of the mixture, a DSC analysis up to 600 °C obtains a value of the heat released in the process of thermal decomposition of the sample close to the real one, which is essential to establish a correlation between the studied material and its possible application as biomass. This value showed the coffee straw as an important precursor, since it has a high enthalpy value (249.0 J g^{-1}).

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