



# Assessment of the physical–chemical properties of residues and emissions generated by biomass combustion under N<sub>2</sub>/O<sub>2</sub> and CO<sub>2</sub>/O<sub>2</sub> atmospheres in a Drop Tube Furnace (DTF)

Glauber Cruz<sup>1,2,3</sup> · Paula Manoel Crnkovic<sup>2</sup>

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## Abstract

This study evaluated the gases CO, CO<sub>2</sub>, NO and SO<sub>2</sub> emitted from five *in natura* Brazilian biomasses: pine sawdust, sugarcane bagasse, coffee and rice husks, *tucumã* seed and the residues generated when these biomasses were applied to combustion atmospheres (N<sub>2</sub>/O<sub>2</sub>: 80/20%) and oxy-fuel combustion (CO<sub>2</sub>/O<sub>2</sub>: 80/20%) in a Drop Tube Furnace. The *in natura* samples and residues were evaluated by TG/DTG (thermogravimetry/derivative thermogravimetry), SEM images (scanning electron microscopy) and EDS analysis (energy-dispersive spectroscopy). The SEM images revealed some of the main morphological differences in the *in natura* materials. However, for the residues under both atmospheres, a large part of the lignocellulosic matrix was degraded, indicating the good efficiency of the thermal process. The TG/DTG curves for the *in natura* samples and residues for both thermal processes enabled the quantification of the contents of remaining moisture, total organic materials consumed and ashes produced. The emissions for both atmospheres ranged between 90 and 6200 mg Nm<sup>-3</sup> g<sup>-1</sup> for CO, 5 and 210 mg Nm<sup>-3</sup> g<sup>-1</sup> for CO<sub>2</sub>, 10 and 170 mg Nm<sup>-3</sup> g<sup>-1</sup> for NO and 25 and 870 mg Nm<sup>-3</sup> g<sup>-1</sup> for SO<sub>2</sub> and are directly related to the chemical composition of the lignocellulosic materials, oxidizing atmospheres and furnace conditions. The O<sub>2</sub> consumption (6–77 mg Nm<sup>-3</sup> g<sup>-1</sup>) inside the furnace for the oxidizing atmospheres and different biomasses exhibited an 80% CO<sub>2</sub> > 80% N<sub>2</sub> trend. The chemical composition (EDS) for the *in natura* samples and residues under both atmospheres revealed different proportions of organic, inorganic and metallic elements in the samples and that the individual behavior of the biomass is a consequence of the diversity of its properties.

**Keywords** Renewable sources · Energy production · Lignocellulosic materials · Metallic parts

## Introduction

The several agricultural cultures in Brazil have been characterized by its large-scale production, presenting in its vegetation a wide variety of lignocellulosic materials, which can be used as feedstock sources for bioenergy production. In terms of using alternative sources of energy, Brazil has a privileged position compared to other countries [1, 2].

Several materials such as harvest residues and energy crops or even the leftovers of processed products have been discarded in rural environments. These materials negatively contribute to pollution and degradation of the soil and water, facilitating the proliferation of diseases and venomous animals [1]. An alternative to avoid the burning of agricultural residues in fields, which causes emissions of pollutant gases into the atmosphere, is to use them as fuel

✉ Glauber Cruz  
cruz.glauber@ufma.br

<sup>1</sup> Department of Mechanical Engineering, Process and Thermal Systems Laboratory, Federal University of Maranhão, Avenida DOS Portugueses 1966, São Luís, Maranhão 65080-505, Brazil

<sup>2</sup> Department of Mechanical Engineering, Thermal Engineering and Fluids Laboratory, Engineering School of São Carlos, University of São Paulo, Avenida Trabalhador São-Carlense 400, São Carlos, São Paulo 13566-590, Brazil

<sup>3</sup> Post-Graduate Program in Mechanical Engineering, Department of Mechanical and Materials, Federal Institute of Education, Science and Technology of Maranhão, Avenida Getúlio Vargas 04, São Luís, Maranhão 65030-005, Brazil

feedstock in thermal conversion processes, such as biomass combustion for bioenergy production [2].

Bioenergy from biomass is a clean technology, safe and renewable resource and is considered as a potential alternative to partially replace fossil fuels, which may possibly present a decreased trend in the future [3]. The replacement of fossil fuels by renewable sources, as well as biomass, for a clean energy production has gained great concern. These fuels are responsible for most of the gaseous emissions into the atmosphere and have caused several problems to the environmental, animals and humans [1–3].

Second Wang et al. [4] discussed that thermochemical and biochemical processes are used to convert biomass in energy useful forms. Due to high efficiency in the conversion into solid, liquid and gaseous products, technology of biomass conversion has found wide application under specific thermal conditions. Some researchers [5–8] have conducted studies to elucidate what occurs with the main constituents of the biomass in thermal degradation steps (mass loss thermal events) during the several thermal conversion processes.

For example, the conventional combustion process of biomasses comprises the burnout in an ambient rich in oxygen or air, which considers types and fuel properties, particle size, air flow rate and fuel moisture. Such characteristics affect directly combustion, reaction rates and generation and heat transfer [9, 10].

According to Yang et al. [11], the main constituents of the biomass (hemicellulose, cellulose and lignin) present mass loss thermal events, which occur in determined temperatures and specific thermal conditions, because each one of them has its particularities. During the direct combustion processes, hemicellulose, cellulose and lignin have its reactivity influenced directly by chemical differences between them. Knowledge of the each component amount is important to predict the efficiency of the biomass thermal conversion processes [12].

Other combustion process well actually addressed in this study involves clean energy technologies by the use of high CO<sub>2</sub> concentrations generated in the fossil fuel power plants. In case of the oxy-fuel combustion, where the fuel is burnt in a mixture of pure oxygen and recycled flue gases. Because nitrogen is eliminated from the oxidizing atmosphere, the flue gas leaving the combustion chamber is highly enriched in CO<sub>2</sub>, which means that the combustion process takes place in a CO<sub>2</sub>/O<sub>2</sub> atmosphere. Partial recycling of flue gas helps to control the flame temperature in the combustion chamber [13] or Drop Tube Furnace [14].

Although many characteristics of the combustion processes and pollutant formation (CO, CO<sub>2</sub>, NO and SO<sub>2</sub>) are known, some details still lack for the oxy-fuel combustion process and their emissions gaseous in a DTF. Within the context presented, this study evaluated the gases CO, CO<sub>2</sub>,

NO and SO<sub>2</sub> emitted from five *in natura* Brazilian biomasses: pine sawdust, sugarcane bagasse, coffee and rice husks, *tucumã* seed and the residues generated, when the biomasses are applied to conventional combustion atmospheres (N<sub>2</sub>/O<sub>2</sub>: 80/20%) and oxy-fuel combustion (CO<sub>2</sub>/O<sub>2</sub>: 80/20%) in a Drop Tube Furnace (DTF). The *in natura* samples and residues generated in these processes also were evaluated by TG/DTG curves (thermogravimetry/derivative thermogravimetry), SEM images (scanning electron microscopy) and EDS analysis (energy-dispersive spectroscopy).

## Materials and methods

### Biomass origin

The five *in natura* biomass samples used in this study were collected from different regions of Brazil, namely sugarcane bagasse; pine sawdust; coffee husk samples (São Paulo State, southeast region); rice husk (Maranhão State, northeast region); and *tucumã* seed (Pará State, north region). It is interesting to note that each country region exhibits vegetation and climate has been clearly defined and differentiated. These features facilitate the plantation of several native species, which require very specific natural conditions.

### Biomass preparation

The samples have been received *in natura* from their respective regions and underwent pre-treatments that comprised: washing in running water to remove impurities, grinding in laboratory knives mill to decrease particle size and subsequent sieving for separation in the required granulometric range. The biomass samples *in natura* have been pulverized using a household blender and thereafter sieved. For all the biomass samples, average sizes of 0.46 mm particles were selected. The biomass samples used in this research were prepared and established by standard ASTM (D 2013-72) [15].

### Biomass samples characterization

#### Elemental analysis and calorimetry

An equipment of the Instruments brand (Elemental Analyzer) and EA1110-CHNS-O model was used. The moisture and ash content was determined by thermogravimetry (TG curves) under oxidizing atmosphere (carbon dioxide) and controlled temperature  $\approx 600$  °C [16]. The High Heating Value (HHV) of the samples was measured in an

adiabatic oxygen bomb calorimeter IKA C 200 model, according to the standard ASTM E-711 [17].

Table 1 shows details of the physical–chemical properties of the biomasses, which can be used for the biofuel or bioenergy production. Such properties are ultimate analysis, moisture and ash contents, and High Heating Value (HHV) of the samples.

### Thermal analysis (TG/DTG curves)

The TG/DTG curves for the *in natura* and residues samples were carried out using Shimadzu analyzer, TGA-50H model. The oxidizing atmosphere was promoted by synthetic air (80% N<sub>2</sub>/20% O<sub>2</sub>) with a dynamic flow rate of 100 mL min<sup>-1</sup>, which was kept constant during the experiments. For these experiments, the constant heating rate utilized was of 10 °C min<sup>-1</sup> from room temperature up to 700 °C. The mass of the samples used was 10.0 ± 0.5 mg and crucible of alumina. The tests were carried out in duplicate, and the mean values and standard deviations were considered.

### Scanning electron microscopy (SEM images)

The morphological analysis of all the biomass samples *in natura* and residues was analyzed by means of images produced in a scanning electron microscopy (SEM); it was obtained with a scanning electron microscope equipment, LEO 440 model, with amplitude of 1000 times.

### Energy-dispersive spectroscopy (EDS analysis)

The *in natura* samples and residues were prepared by sintering for the best adherence on the surface of the aluminum support for the EDS analysis, which was also performed under a scanning electron microscope, LEO 440 model. No metallization type (gold or graphite bath) was used for this analysis, as it may hide or show regions of some elements (organic and inorganic) more common in lignocellulosic materials.

**Table 1** Percentages of moisture and ash contents, elemental compositions and high heating values of the *in natura* biomass samples

Samples	Moisture/%	Ash/%	C/%	H/%	N/%	S/%	O*/%	HHV/MJ kg <sup>-1</sup>
Sugarcane bagasse	6.4 ± 0.2	4.8 ± 1.9	45.05	5.57	0.25	N.A.	37.93	17.5 ± 0.1
Pine sawdust	7.2 ± 0.1	1.2 ± 0.1	46.60	6.17	0.40	N.A.	38.43	18.3 ± 0.2
Coffee husk	8.2 ± 0.3	8.3 ± 2.8	43.13	5.93	1.55	0.67	32.22	16.8 ± 0.1
Rice husk	7.1 ± 0.4	11.2 ± 2.4	39.11	4.91	0.31	0.59	36.78	15.4 ± 0.1
<i>Tucumã</i> seed	5.3 ± 0.3	5.3 ± 0.1	48.83	6.71	0.88	N.A.	32.98	20.8 ± 0.1

\*Difference at 100%; N.A.—not available

### Combustion and oxy-fuel combustion in a Drop Tube Furnace (DTF)

A Drop Tube Furnace (DTF) electrically heated (3.5 kVA maximum power) (Fig. 1a, b) was used for the biomass thermal processes, *i.e.*, combustion and oxy-fuel combustion. The basic dimensions of the experimental apparatus are 60 mm outer diameter, 400 mm uniform zone and 200 mm heated zone. The biomass particles were introduced into the combustion reactor (DTF) by means of a feeding system, which has a vibratory mechanical transport and controlled via PWM (Pulse Width Modulation), where the optimal rotational velocities and frequencies were achieved for each lignocellulosic material. The sample mass used was 3.0 ± 0.5 g for a 10-min experiment. An air primary flow rate of 1.5 L min<sup>-1</sup> with 20% oxygen concentration was applied to keep the biomass particles in suspension, during the combustion process in DTF. After burning at 950 °C and under atmospheric pressure (≈ 1 atm), the residues generated in thermal processes were collected from the oven bottom and evaluated by TG/DTG curves, SEM images and EDS analysis.

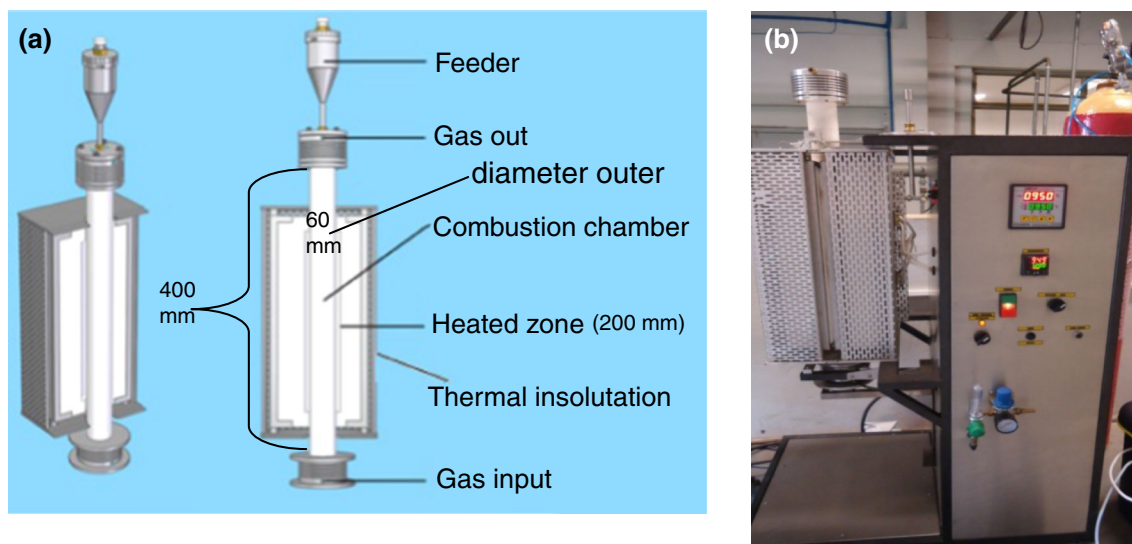
### Gases analyzer

Equipment of the SICK brand (GMS 810 model) was able to detect and capture the emitted concentrations by main atmospheric pollutants, during combustion and oxy-fuel combustion of biomasses in a DTF, such as SO<sub>2</sub>, CO, NO and H<sub>2</sub>O measured in ppm and CO<sub>2</sub> and O<sub>2</sub> in %. It was used a computational program—*SOPAS Engineering Tool*—coupled to the gases analyzer for communication, data capture from gaseous emissions and equipment calibration.

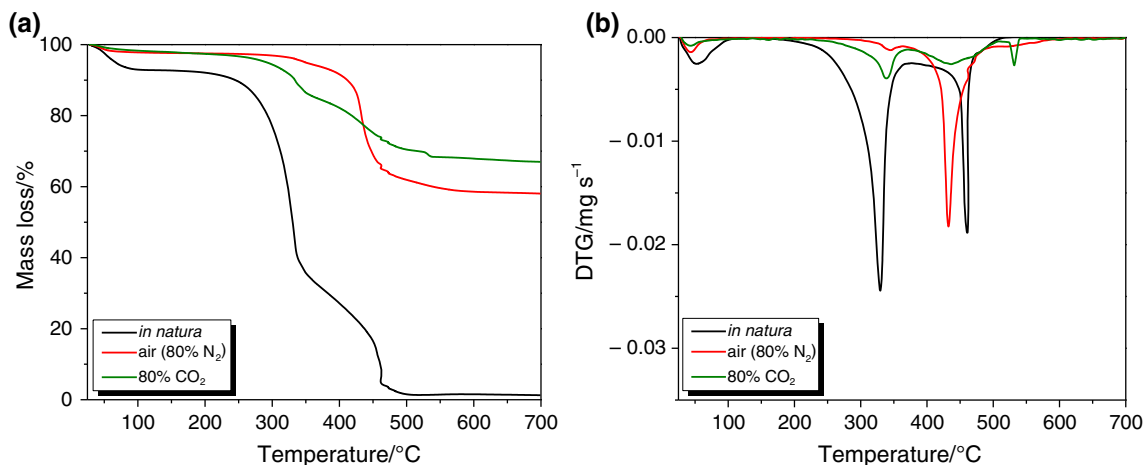
## Results and discussion

### Thermal analysis (TG/DTG curves)

Figures 2–6 present the TG/DTG curves for the *in natura* samples and residues generated from biomasses evaluated



**Fig. 1** **a** Schematic representation of the Drop Tube Furnace (DTF) and **b** DTF reactor and feeding system for the biomass combustion at two atmospheres



**Fig. 2** **a** TG and **b** DTG curves of the *in natura* samples and pine sawdust residues after conventional combustion (80% N<sub>2</sub>) and oxy-fuel combustion (80% CO<sub>2</sub>) in DTF. Experimental conditions: 25 up

700 °C; heating rate: 10 °C min<sup>-1</sup>; sample mass: 10 mg and 100 mL min<sup>-1</sup> of synthetic air flow rate

after conventional combustion (80% N<sub>2</sub>) and oxy-fuel combustion (80% CO<sub>2</sub>) processes.

Figure 2a, b shows TG/DTG curves *in natura* pine sawdust and residues generated after different thermochemical processes (conventional and oxy-fuel combustion) in DTF.

DTG curve (Fig. 2b) of the *in natura* sample displays peaks well defined at 328 and 460 °C, which correspond to maximum combustion rates and can be attributed to thermal decomposition of holocellulose and residual lignin. Thin peaks and elongated are a strong characteristic of crystalline samples [7, 18].

In both thermoconversion processes, pine sawdust residues presented low moisture contents ( $\approx 2\%$ ) according to

the previous studies, which affirmed that woody material residues after thermal processes present moisture content below 5% [4, 7, 18]. For the conventional combustion, it was observed original structure loss, *i.e.*, mainly the holocellulose was totally degraded in thermal process, and the presence of a small intensity peak around 340 °C confirms such information, but still remained residual lignin and this effect can be proved for a high intensity peak being displacement for 434 °C. For the residues under oxy-fuel combustion atmosphere, it was verified a wide oxidation of biomass organic materials, but still exists some remaining material, mainly residual lignin, which can be confirmed by the peaks at 340 and 532 °C.

Comparing the TG/DTG curves profiles of the residues for both atmospheres, it was perceived a higher difference in the maximum decomposition rate of the main constituents of biomasses between 200 and 500 °C.

TG/DTG curves (Fig. 3a, b) of the sugarcane bagasse residues after different oxidative processes (combustion and oxy-fuel combustion) were similar, *i.e.*, showed the same thermal profile. In general, it was observed a wide consumption of the total organic materials (hemicellulose, cellulose and lignin). The *in natura* sugarcane bagasse sample (Fig. 3a) presented a “shoulder” around 310 °C, which is indicative of high hemicellulose content [18] and also that hemicellulose and cellulose are decomposed simultaneously [19]. For the residues after conventional combustion and oxy-fuel combustion (Fig. 3b), this “shoulder” was not identified. For the *in natura* samples, other peak was observed at 445 °C, which is attributed to the residual lignin decomposition. However, for the residues under both atmospheres this event was not observed.

Orsini et al. [1] stated that high amount of inorganic compounds in the coffee husks, mainly potassium element, made them more resistant to the deformations and, consequently, combustion processes. This affirmation is agree with observations made in this study, because evaluation of the residues showed that inside of their particles not presented complete burning process or was deficitary, but only carbonization in more external regions. In comparison to residues under both atmospheres, the difference more pronounced was observed under 80% CO<sub>2</sub> atmosphere. DTG curve (Fig. 4b) presented only one thermal event at 432 °C, probably caused by the presence of residual lignin and/or inorganic materials oxidation not burned at relatively lower temperatures  $\approx$  1000 °C, such as K, S, Cl among other elements, which can conduct to the formation

of corrosive species and environmentally dangerous [1, 6, 20].

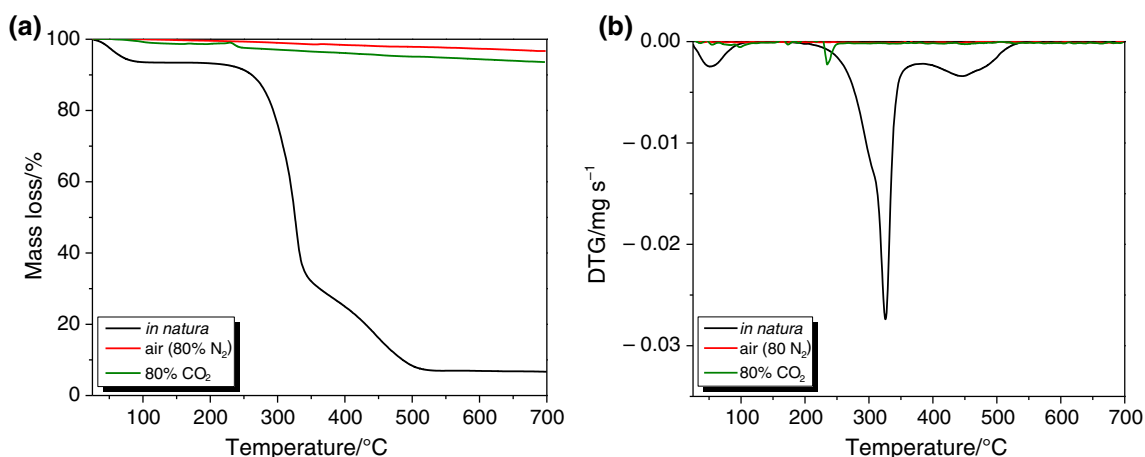
TG/DTG curves (Fig. 5a, b) for the rice husk residues generated after tests carried out under synthetic air (80% N<sub>2</sub>) and dioxide carbon (80% CO<sub>2</sub>) atmospheres showed a degradation almost that total of the organic materials (holocellulose and lignin) present in the biomasses. Such information can be made with base in the ash contents presented in the final TG curves, resulting in average value around  $\approx$  90%.

From TG/DTG curves (Fig. 6a, b) for the *in natura* tucumã seed, it was possible to observe three events well defined of mass loss. The first, with peak in around 185 °C, is due to release of lighter volatiles [21] or by the fast thermal decomposition of fatty compounds present in oil-seed between 150 and 200 °C [22]. The maximum combustion rate was observed in  $\approx$  300 °C for the thermal degradation of holocellulose and at 450 °C for the residual lignin decomposition. However, DTG curves (Fig. 6b) for the residues in both combustion processes exhibited events of mass loss between 220 and 512 °C, with mass loss maximum in  $\approx$  290 °C. *Tucumã* seed samples not presented satisfactory yield in the different thermal processes, possibly, because these samples presented a high oiliness content, which was harmful to feeding system and, consequently, to the burning process.

### Scanning electron microscopy (SEM images)

Figures 7–11 show the SEM micrographics for the *in natura* samples and residues generated after thermochemical processes.

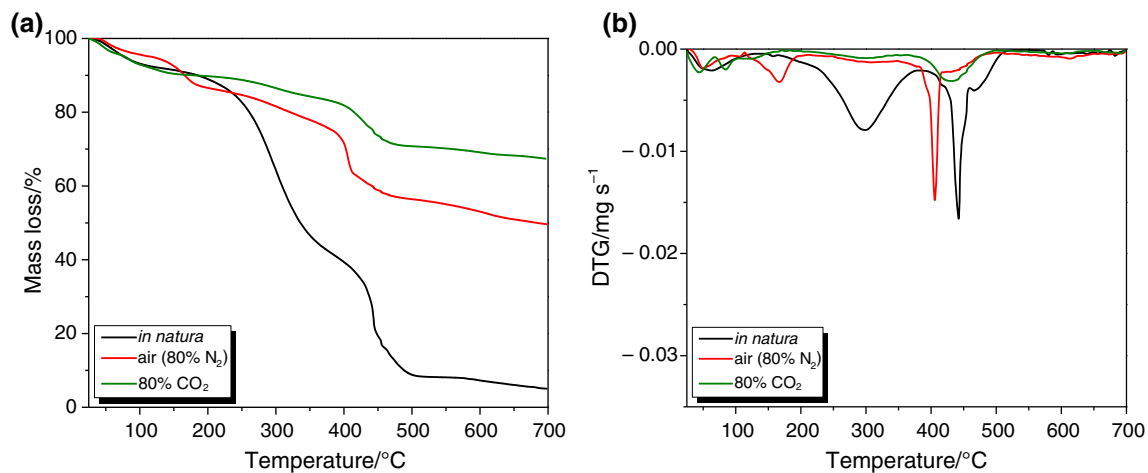
Figure 7a–c shows the SEM images for the *in natura* pine sawdust and residues generated in DTF, after different thermochemical processes. It was noted that morphological



**Fig. 3** a TG and b DTG curves of the *in natura* samples and sugarcane bagasse residues after conventional combustion (80% N<sub>2</sub>) and oxy-fuel combustion (80% CO<sub>2</sub>) in DTF. Experimental

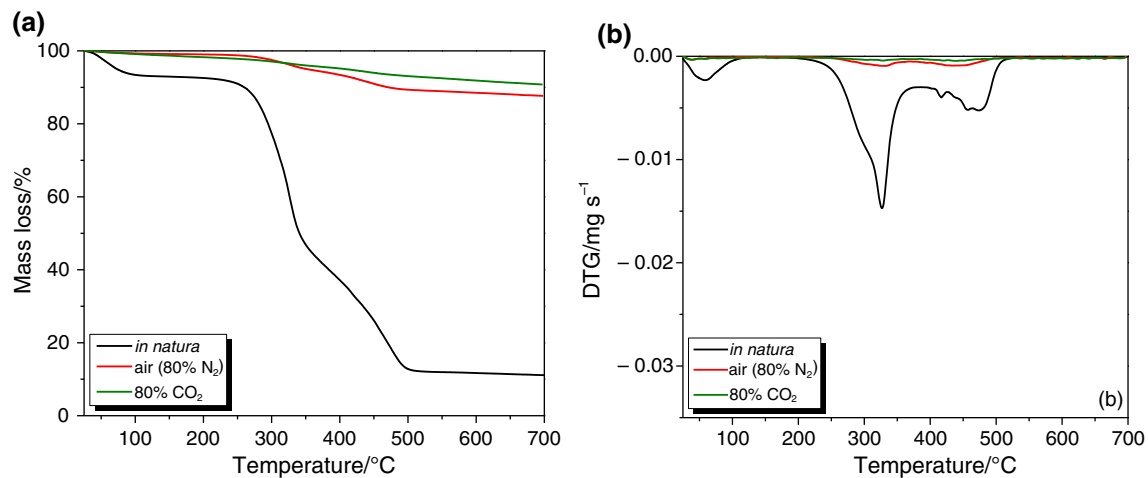
conditions: 25 up 700 C; heating rate: 10 C min<sup>-1</sup>; sample mass: 10 mg and 100 mL min<sup>-1</sup> of synthetic air flow rate





**Fig. 4** a TG and b DTG curves of the *in natura* samples and coffee husk residues after conventional combustion (80% N<sub>2</sub>) and oxy-fuel combustion (80% CO<sub>2</sub>) in DTF. Experimental conditions: 25 up

700 C; heating rate: 10 C min<sup>-1</sup>; sample mass: 10 mg and 100 mL min<sup>-1</sup> of synthetic air flow rate



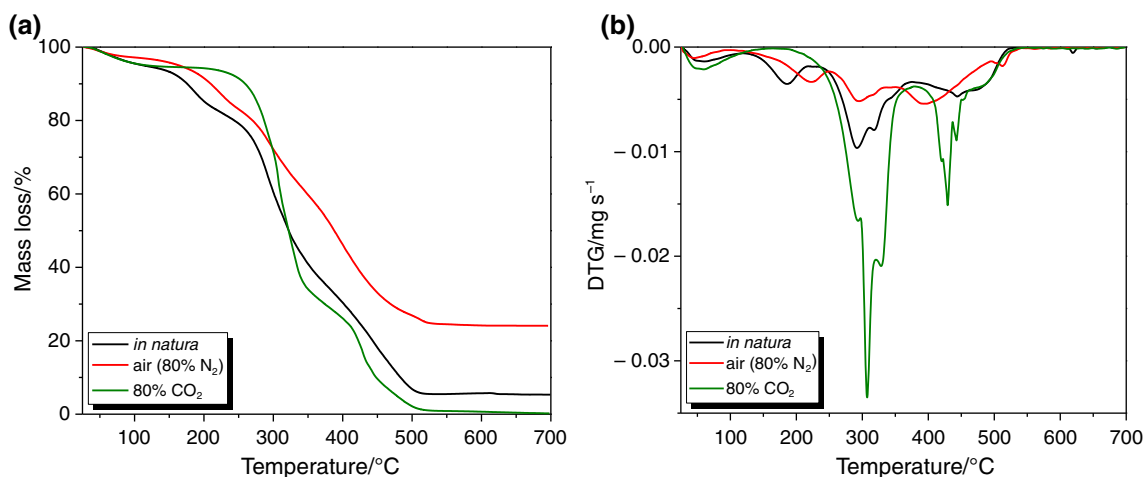
**Fig. 5** a TG and b DTG curves of the *in natura* samples and rice husk residues after conventional combustion (80% N<sub>2</sub>) and oxy-fuel combustion (80% CO<sub>2</sub>) in DTF. Experimental conditions: 25 up

700 C; heating rate: 10 C min<sup>-1</sup>; sample mass: 10 mg and 100 mL min<sup>-1</sup> of synthetic air flow rate

structure of the pine sawdust residues after 80% N<sub>2</sub> atmosphere (Fig. 7b) in comparison with *in natura* sample (Fig. 7a) presented agglomerate of particles, structures that seem cenospheres [23] and particles shrinkage [24]. However, for the 80% CO<sub>2</sub> atmosphere (Fig. 7c), it was verified the presence of some particles with diameters higher, broken structures and a pattern of reticulated type or nanowhiskers [23]. By means of the distinct structural characteristics observed for the pine sawdust residues in different atmospheres, it is understood that each thermal process employed affected the biomass morphology in specific ways.

Figure 8a–c presents the SEM images for the *in natura* sugarcane bagasse and generated residues in DTF after 80% N<sub>2</sub> and 80% CO<sub>2</sub> processes.

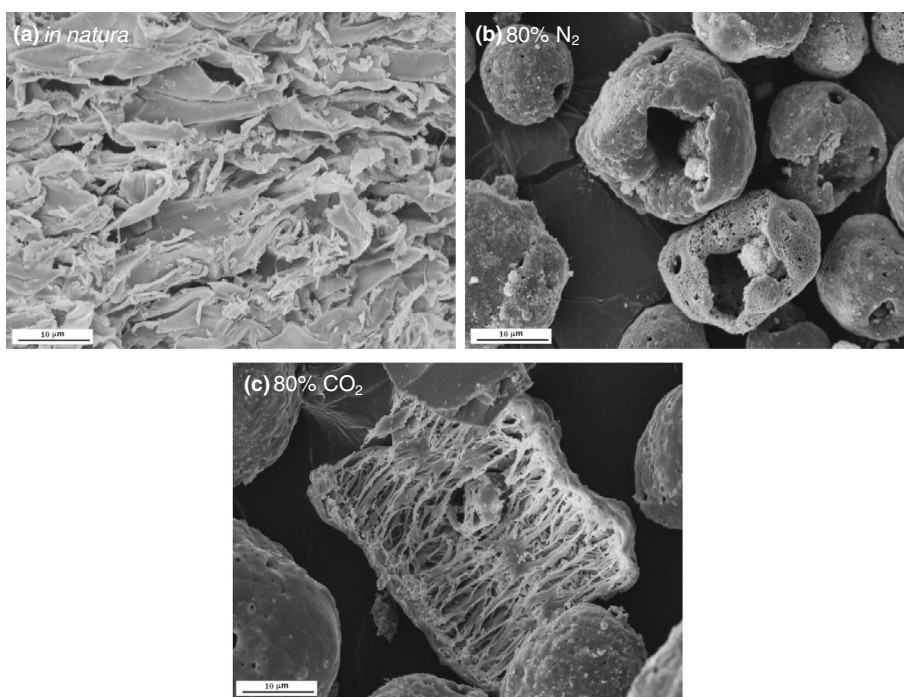
The sugarcane bagasse residues presented morphological structures different from the *in natura* samples (Fig. 8a), mainly with regard to the loss of fibrous characteristics, tubes, marrow and lamellae. It was noted that for the samples under containing CO<sub>2</sub> atmosphere (Fig. 8c), the particles presented a crystalline format, which is the characteristic of the presence of silicon oxides or iron oxides [25] and confirmed by Fig. 12b. Already in sample under synthetic air atmosphere (Fig. 8b), it can also be noted the presence of crystalline and spongy structures. According to Cruz [26], spongy structures are indicative of possible deficiency in the burning process, where part of the samples were undergoing the devolatilization process, *i.e.*, fast volatile release, and other



**Fig. 6** **a** TG and **b** DTG curves of the *in natura* samples and tucumã seed residues after conventional combustion (80% N<sub>2</sub>) and oxy-fuel combustion (80% CO<sub>2</sub>) in DTF. Experimental conditions: 25 up

700 C; heating rate: 10 C min<sup>-1</sup>; sample mass: 10 mg and 100 mL min<sup>-1</sup> of synthetic air flow rate

**Fig. 7** SEM micrographics of the pine sawdust: **a** *in natura* samples and residues generated under typical atmospheres: **b** conventional combustion (80% N<sub>2</sub>) and **c** oxy-fuel combustion (80% CO<sub>2</sub>), with magnitude of 1000 times



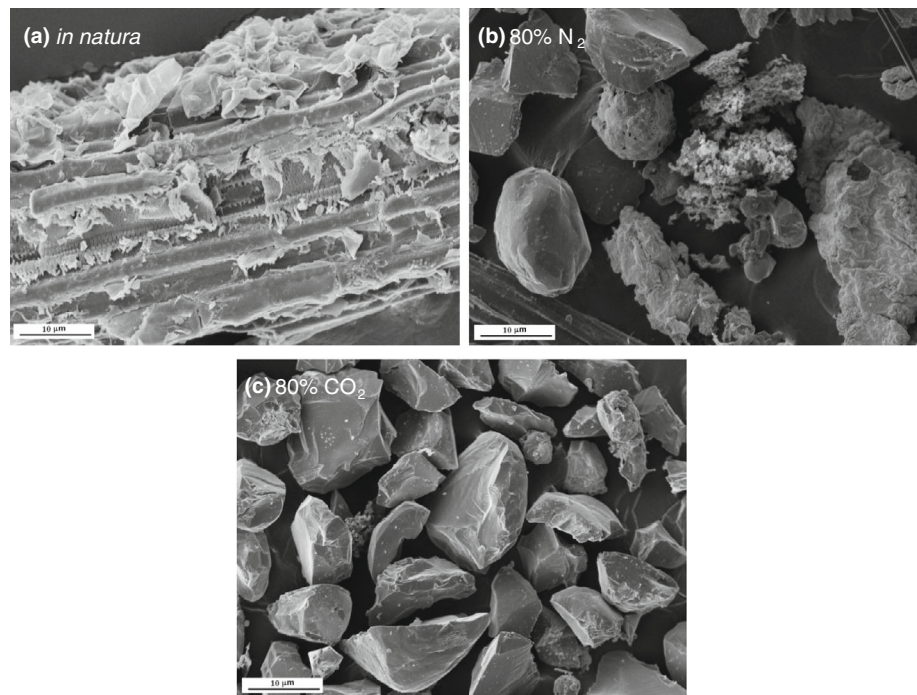
gases, which are trapped inside samples, therefore, not reached the complete combustion.

Figure 9a–c shows the SEM images for the *in natura* coffee husk and residues generated in DTF after conventional combustion and oxy-fuel combustion processes. For the combustion processes of coffee husk, it was observed that both residues (Fig. 9b, c) exhibited a disruption in relation to the *in natura* sample (Fig. 9a) and presented several breaks, meso- and micropores superficial. The formation of these structures was due to high volatile materials release, which for this biomass is around 75%, during the combustion process.

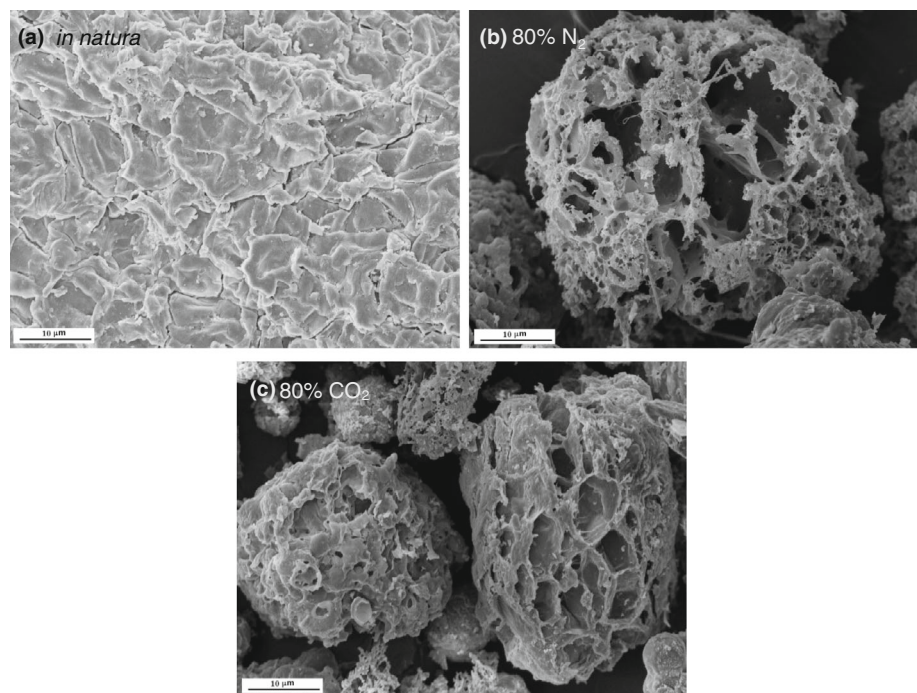
Figure 10a–c shows the SEM images for the *in natura* rice husk and residues generated in DTF after conventional combustion and oxy-fuel combustion processes.

For the rice husk samples, it was observed that remaining residues from several thermochemical processes under both atmospheres presented differences with regard to the *in natura* material (Fig. 10a). Both residues (Fig. 10b–c) showed highly porous structures (mesopores and macropores), and apparently, without any possibility of distinction between them. These presented structures with ruptures of the initial condition, but also maintained part of the original lignocellulosic matrix.

**Fig. 8** SEM micrographics of the sugarcane bagasse: **a** *in natura* samples and residues generated under typical atmospheres: **b** conventional combustion (80% N<sub>2</sub>) and **c** oxy-fuel combustion (80% CO<sub>2</sub>), with magnitude of 1000 times



**Fig. 9** SEM micrographics of the coffee husk: **a** *in natura* samples and residues generated under typical atmospheres: **b** conventional combustion (80% N<sub>2</sub>) and **c** oxy-fuel combustion (80% CO<sub>2</sub>), with magnitude of 1000 times



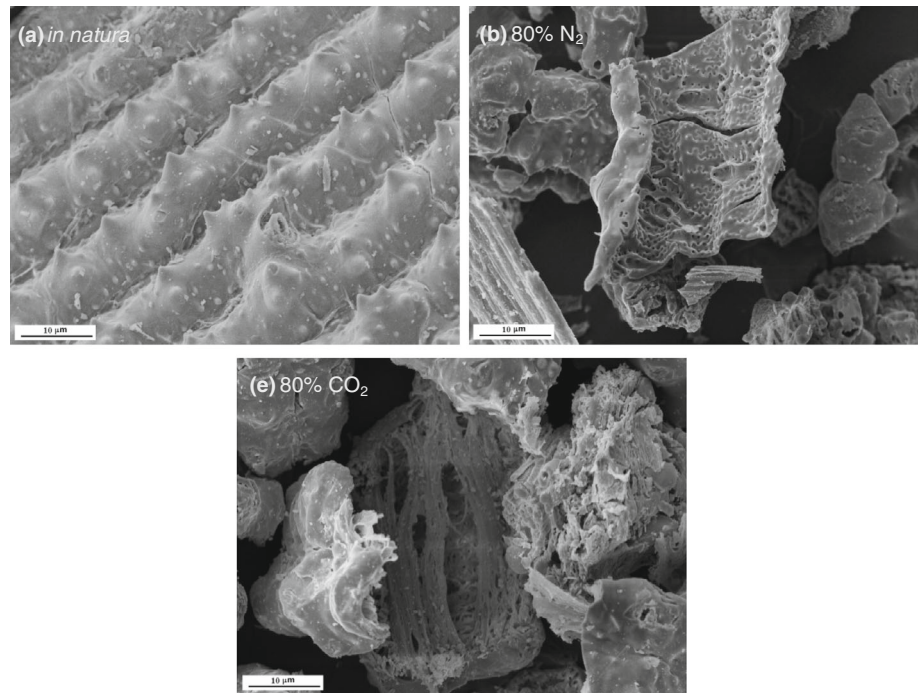
According to Luan et al. [24], the thinner particles deposited on the rice husk samples after conventional combustion processes can be mainly alkali aluminum silicate compounds and/or alkaline chlorides.

It was noted that *in natura* *tucumã* seed structure is composed of a set of axial and radial microchannels, which appear to cross its entire structure (Fig. 11a), whereas for the other *in natura* biomasses, the prevalence of a more

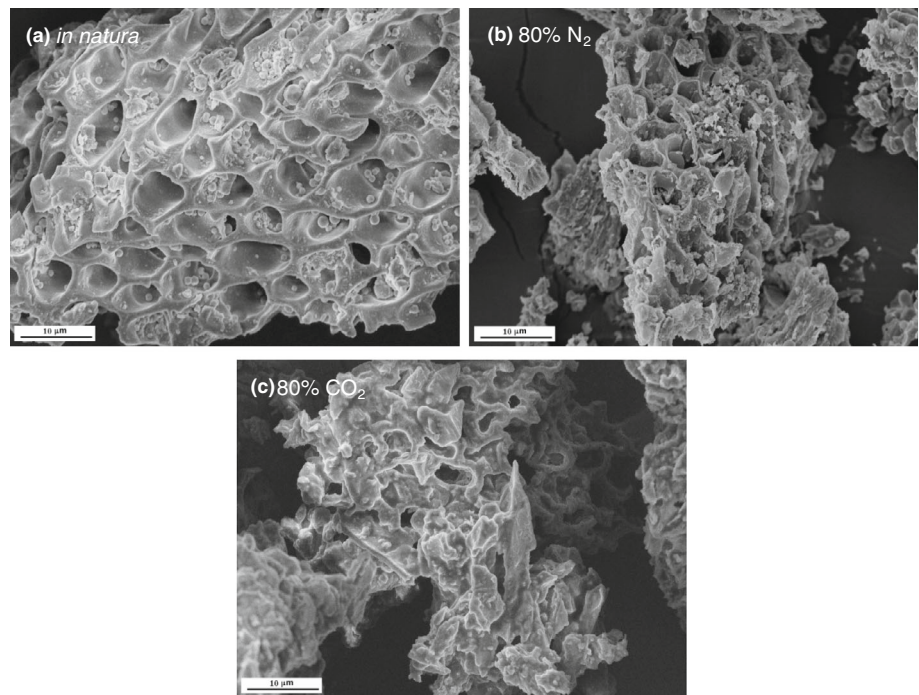
fibrous structure is observed. After submitted to the several thermal processes, *tucumã* seed residues maintained some of its physical characteristics and still presented the microchannels and apparently no disruptions in relation to *in natura* sample, which also differ from other biomasses and can be due to the effect of its rigidity and hardness [26].



**Fig. 10** SEM micrographics of the rice husk: **a** *in natura* samples and residues generated under typical atmospheres: **b** conventional combustion (80% N<sub>2</sub>) and **c** oxy-fuel combustion (80% CO<sub>2</sub>), with magnitude of 1000 times



**Fig. 11** SEM micrographics of the *tucumã* seed: **a** *in natura* samples and residues generated under typical atmospheres: **b** conventional combustion (80% N<sub>2</sub>) and **c** oxy-fuel combustion (80% CO<sub>2</sub>), with magnitude of 1000 times

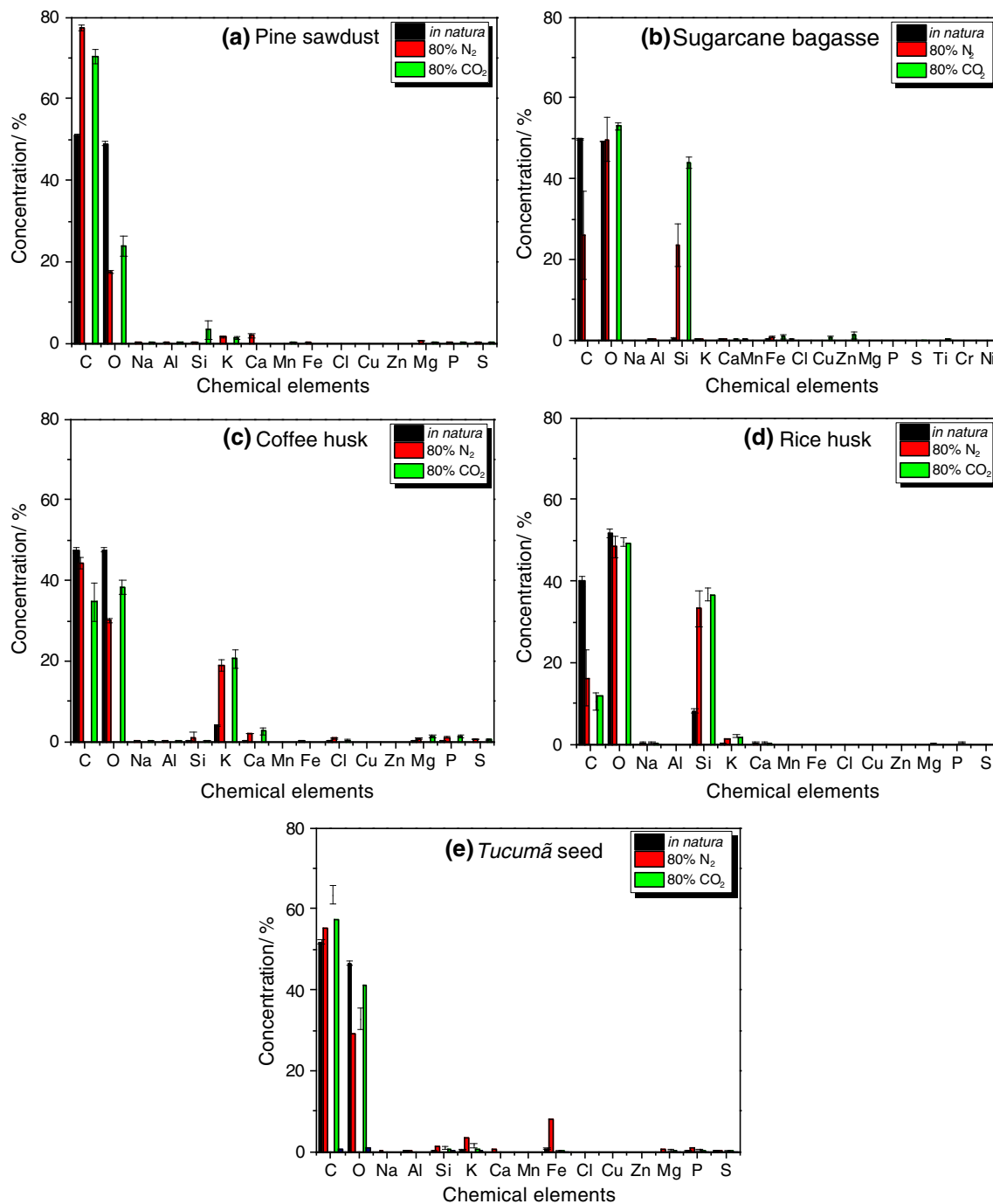


### Energy-dispersive spectroscopy (EDS analysis)

Figure 12 shows the EDS analysis in terms of mass percentage or concentrations for the *in natura* samples and residues generated for the two thermochemical processes. This technique was used to determine the samples elemental composition and compare its compositional evolution in thermal processes, in order to predict the possible

impacts caused by the use of these biofuels in combustion equipments.

According to Fernández et al. [27], chemical elements such as sodium (Na), potassium (K), magnesium (Mg), phosphorus (P) and calcium (Ca) among others, which are present in biomass samples forming oxides, hydroxides and carbonated of alkaline metal and earth alkaline and, are



**Fig. 12** Elemental composition obtained by EDS analysis of the *in natura* biomasses and generated residues under conventional combustion (80% N<sub>2</sub>) and oxy-fuel combustion (80% CO<sub>2</sub>) atmospheres: **a** pine sawdust, **b** sugarcane bagasse, **c** coffee husk, **d** rice husk and **e** tucumã seed

problematic constituents in the combustion process, avoiding the good functioning of the thermal power plants.

Senneca [10] related that biomasses are a biofuels' special class, because it contains less aluminum (Al), iron (Fe) and titanium (Ti) and more silicon (Si), potassium (K) and sometimes more calcium (Ca) than coal. The nitrogen, chlorine (Cl) and metal content also ranges significantly among biomasses. These compounds are directly

related to the NO<sub>x</sub> emissions, corrosion and ash deposition in thermal systems, which also exists a great variation in the biomass elemental composition.

After burning under 80% N<sub>2</sub> atmosphere, pine sawdust residues presented 77.5% of carbon in its composition, while *tucumã* seed 55.2%. These samples presented the higher carbon contents in its residues, regarding the other biomasses, *i.e.*, an indicative that for these samples there

was a lower efficiency in the burn process. In addition, oxygen contents for both samples also were lower, 17.5 and 29%, respectively.

It was verified that sugarcane bagasse residues generated under 80% CO<sub>2</sub> atmosphere not exhibited carbon contents (Fig. 12b), a strong clue that all organic materials were consumed in this process, which can be confirmed by SEM images (Fig. 8c). The high Si presence in sugarcane bagasse residues is not due to their *in natura* composition, but contamination by impurities incorporated in harvest process of the sugarcane or storage of the sugarcane bagasse, after juice extraction, mixing it with land or sand [28]. For the *in natura* samples, rice husk presented in average 8.1% of Si and sugarcane bagasse 0.4%. After burning under 80% CO<sub>2</sub> atmosphere, the sugarcane bagasse showed average values of 44.5% for Si content, while for 80% N<sub>2</sub> atmosphere 23.5%. The rice husk residues in both atmospheres presented Si average content of 34.8%; this increase in silicon indicated a large exposition of this component in the samples and a good efficiency of the thermochemical processes employed.

Another element present in the *in natura* biomasses in quantity that deserves to be mentioned or highlighted is the potassium (K), mainly in the *in natura* coffee husks, which for this study was detected around 4% (Fig. 12c), forming primarily potassium oxides (K<sub>2</sub>O) and located in the ashes, and that may difficult the burning process, but for the other biomasses this content was lower at 0.5% and not offering greater damage to the combustion or thermal power systems [29].

According to Akinrinola et al. [29], K concentrations in biomasses superior 30% decrease the combustion temperature of the volatile materials and char, indicating high fuels' reactivity. However, for this work the K contents in biomasses were lower than 5%, not being possible to establish a correlation between K concentration and samples' reactivity.

Potassium present in ashes is a main precursor in slurry formation, agglomeration and incrustation in thermal systems [20]. After conventional combustion in DTF, K content in the coffee husk residues was in average 18.9%, *i.e.*, 367% superior in relation to the *in natura* biomass. For the residues under both atmospheres, the quantities of this chemical element ( $\approx 20\%$ ) present in the coffee husk were intensified by means of superficial broken and exposition of its layers more internal and difficulty in burning process [2, 26].

For the different *in natura* biomasses, other elements, such as Na, Mg (magnesium), Cl, Ca, Mn (manganese), Al, P, Fe and S (sulfur), were found in inferior amounts ( $< 0.7\%$ ) and are known as trace elements, participating in several chemical reactions during combustion [30]. It is interesting note that *tucumã* seed residues at 80% N<sub>2</sub>

presented 8% Fe, *i.e.*, considerably above of the other biomasses, whose average value was  $\approx 0.25\%$ .

An important aspect to be evaluated in biomasses is Cl content, because when metallic materials are submitted to thermal processes containing such element in ambient, this can cause corrosion problems in metallic parts of the chamber combustion and air pollutant emissions [27]. Besides, the Cl can also react with alkaline metals, such as Na and K, forming chlorides, which are deposited in boiler surfaces and heat exchanger, leading to the corrosion and also affecting the heat transfer in these systems [23].

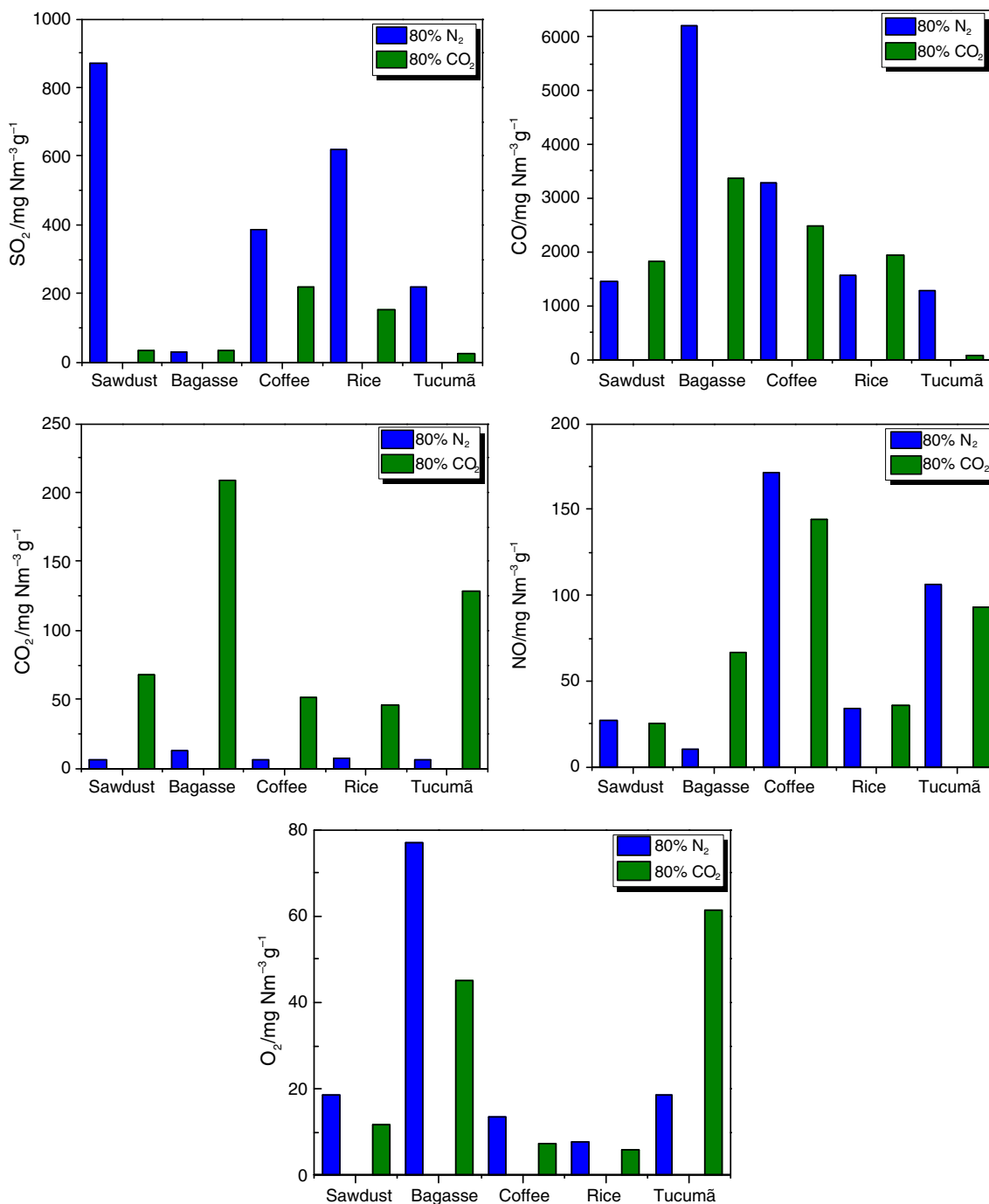
As regards the S content, these also should be quantified in biomasses, because in thermal processes it forms sulfates, causing incrustations and depositions, which compromise the combustors and gasifier performance. Moreover, this element forms undesirable pollutants such as sulfur oxides (SO<sub>2</sub>) in combustion processes and H<sub>2</sub>S (sulfuric acid) in the gasification. In this research, the S contents found *in natura* biomasses were in average 0.27%. Second according to Croiset and Thambimuthu [31], approximately 0.3% of S for the different biomasses keeps retained in the ashes. For this study, the S contents in residues of the different thermal processes were in average 0.25%, confirming such affirmation.

Other elements such as P, Ca and Na are also found in biomasses and its amount is lower than 0.5%, which interferes in low yield in the volatile compound combustion. Elements as Mg, Mn, Al and Fe also are commonly found in the biomasses for making part of its nature composition and can bring consequences undesirable to the thermal processes, for example, these elements also participate in the oxides formation reactions, affecting directly the corrosion process of the metallic parts and also decreasing the heat transfer in thermal power plants [23, 29].

Finally, it is understood that a more in-depth study is needed for obtaining more information about the possible biomass applications and/or residues that contain some inorganic elements environmentally undesirable. A possible suggestion to solve these problems would be the utilization of the ashes generated via different thermochemical processes by the concrete industries, composites, among others [2, 26, 27, 32].

### Emissions gaseous (air pollutants)

Figure 13 shows the average values of the main air pollutants (SO<sub>2</sub>, CO, CO<sub>2</sub> and NO) generated under conventional combustion (80% N<sub>2</sub>) and oxy-fuel combustion (80% CO<sub>2</sub>) atmospheres in DTF for the *in natura* samples. The O<sub>2</sub> concentration was used in this work as criteria for the verification of the evolution from respective thermal processes.



**Fig. 13** Main air pollutants generated by biomasses under conventional combustion (80% N<sub>2</sub>) and oxy-fuel combustion (80% CO<sub>2</sub>). Experimental conditions: furnace temperature: 1.000 °C, primary airflow rate: 1.5 L min<sup>-1</sup> and mass flow rate: 0.3 g min<sup>-1</sup>

Although pine sawdust and *tucumã* seed samples were not presented sulfur detectable limits in its composition, this exhibited the higher (873 mg Nm<sup>-3</sup> g<sup>-1</sup>) and lower (25 mg Nm<sup>-3</sup> g<sup>-1</sup>) SO<sub>2</sub> emission values under conventional combustion and oxy-fuel combustion, respectively.

The higher SO<sub>2</sub> emissions in thermal systems are an indicative of complete combustion or partially complete, because this gas participates effectively in the combustion

global reaction and is released totally in the volatile form in the char combustion [33, 34]. For explaining the lower SO<sub>2</sub> emissions under oxy-fuel combustion, Toftegaard et al. [35] and Normann et al. [36] also observed that this reduction is a common characteristic for this process type.

Croiset and Thambimuthu [31] revealed that variation in SO<sub>2</sub> concentration is mainly due to volume change in the combustion ambient. For instance, in higher oxygen



concentrations, other gases total flux inside of the thermal system is inferior, because less nitrogen and CO<sub>2</sub> are present, increasing SO<sub>2</sub> concentration.

For some pollutant species, for example, carbon monoxide (CO), the formation and destruction reactions are intimately coupled, and compression from the formation of these pollutants requires a perfect knowledge of the combustion chemical, which is very complex [37]. For oxy-fuel combustion (80% N<sub>2</sub>) atmosphere, the higher CO emissions were observed for sugarcane bagasse (6200 mg Nm<sup>-3</sup> g<sup>-1</sup>). Roy and Corscadden [38] found results similar for several wood species and briquettes burned in a domestic oven.

Probably, this increase in CO emission can be due to Boudouard's equation, which is presented in Eq. (1) [36, 39, 40].



According to Toftegaard et al. [35], in high partial pressures and temperatures the CO<sub>2</sub> can be dissociated in CO and O<sub>2</sub>, by means of strong endothermic reactions. For our specific case, in the reactor flame zone under oxy-fuel combustion process, only one condition can be observed, *i.e.*, high temperature ( $\approx 950$  °C), and such information was verified and confirmed in a previous study developed by our research group [26].

Sugarcane bagasse also presented the higher CO<sub>2</sub> emissions (210 mg Nm<sup>-3</sup> g<sup>-1</sup>) under 80% CO<sub>2</sub> atmosphere. According to Aghamohammadi et al. [41], differences in the formation rates of the combustion gases, for example, CO<sub>2</sub>, are due to the hemicelluloses, cellulose and lignin compositions. Oxygen excess and a better mixture can be useful in the organic emission control in this combustion stage. Finally, the unburned biomasses are naturally decomposed for CO<sub>2</sub> releasing.

According to Winter et al. [42], nitrogen (N) content is relatively low for the biomasses of agricultural residues and these produce low NO and N<sub>2</sub>O emissions. However, NO emitted during combustion process depends on other parameters, besides the compositional nitrogen, from low fixed carbon content and also takes into account operating mode, burner design and combustion chamber [43]. Consequently, agricultural residues can emit higher NO<sub>x</sub> concentrations, when compared to coal with same nitrogen content [44].

The *in natura* coffee husk samples presented a higher elemental nitrogen content (1.55%) and sugarcane bagasse the lower (0.25%) (see Table 1). The first sample exhibited the higher NO emissions under conventional combustion (172 mg Nm<sup>-3</sup> g<sup>-1</sup>) and 80% CO<sub>2</sub> (144 mg Nm<sup>-3</sup> g<sup>-1</sup>) probably by the total oxidation of its nitrogen content under oxidizing atmospheres. It is interesting to highlight also that the coffee husk and *tucumã* seed samples presented

under oxy-fuel combustion atmosphere a gradual decrease in their NO emissions in relation to the combustion atmosphere, while sugarcane bagasse samples showed a slight increase and pine sawdust and rice husk samples were unchanged.

Finally, by means O<sub>2</sub> concentration it was possible to observe the combustion process performance inside the DTF under different atmospheres and biomasses. It was observed a decreasing trend in the O<sub>2</sub> consumption: 80% CO<sub>2</sub> > 80% N<sub>2</sub>, where sugarcane bagasse presented the higher O<sub>2</sub> consumption rate for conventional combustion and *tucumã* seed for oxy-fuel combustion atmosphere.

The results obtained in this study by means of analytical techniques indicated that the thermochemical processes (direct combustion and oxy-fuel combustion) applied for the five biomasses presented a good performance, thermal efficiency and a satisfactory burning; however, when several lignocellulosic materials are employed, some trends can not always be achieved.

## Conclusions

In this study, gases were evaluated, such as CO, CO<sub>2</sub>, NO and SO<sub>2</sub> emitted from five *in natura* Brazilian biomasses: pine sawdust, sugarcane bagasse, coffee and rice husks, *tucumã* seed and the residues generated when these biomasses were applied to combustion atmospheres (N<sub>2</sub>/O<sub>2</sub>: 80/20%) and oxy-fuel combustion (CO<sub>2</sub>/O<sub>2</sub>: 80/20%) in a Drop Tube Furnace (DTF). The *in natura* samples and residues generated were evaluated by TG/DTG curves (thermogravimetry/derivative thermogravimetry), SEM images (scanning electron microscopy) and EDS analysis (energy-dispersive spectroscopy).

TG/DTG curves showed and confirmed that performance and combustion efficiency are functions of the biomass type, feeding system used and operating conditions of the DTF. By means of this technique, it was also possible to observe the quantities of moisture, volatile materials, fixed carbon and ashes remaining in the biomass samples after thermochemical processes in DTF.

The SEM images revealed some of the main morphological differences of the *in natura* materials, such as presence of tubes, medullas, lamellas, ordered structures and compacted, and porous structures. However, for the generated residues under conventional combustion and oxy-fuel combustion atmospheres, a large part of the lignocellulosic matrix was degraded, which indicates the good efficiency from thermal processes, although some biomasses still retained their original structures.

From EDS analysis, it was possible to observe that some inorganic elements, such as S, Si, Fe, Cl, Ca, Cu, K, P and Na, can damage the metallic parts of the thermal systems,

thermal changes during burning and the environment, when they are released into the atmosphere.

The gaseous emissions for both atmospheres (80% N<sub>2</sub> and 80% CO<sub>2</sub>) ranged between 90 and 6200 mg Nm<sup>-3</sup> g<sup>-1</sup> for CO, 5 and 210 mg Nm<sup>-3</sup> g<sup>-1</sup> for CO<sub>2</sub>, 10 and 170 mg Nm<sup>-3</sup> g<sup>-1</sup> for NO and 25 and 870 mg Nm<sup>-3</sup> g<sup>-1</sup> for SO<sub>2</sub> and are directly related to the chemical composition of the lignocellulosic materials, oxidizing atmospheres and furnace operating conditions. The O<sub>2</sub> consumption (6–77 mg Nm<sup>-3</sup> g<sup>-1</sup>) inside the furnace for the oxidizing atmospheres and different biomasses was also an indicative performance, and combustion efficiency exhibited an 80% CO<sub>2</sub> > 80% N<sub>2</sub> trend.

Finally, our findings have proved the perfect knowledge of some behavioral trends of lignocellulosic materials is mandatory, so that generalizations of proceedings cannot be applied when different biomasses and atmospheres are employed in thermochemical processes.

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